



Organic Materials for Sustainable Construction

Edited by Yves Mouton

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Introduction

In the building trade, for the majority of those involved, organic materials are still considered to be mere accessories, as products of secondary importance. However, they have proved to be omnipresent and therefore essential to the trade. This vision also explains why these organic materials have only been of interest to those authors of science and technology in the application's restricted framework, in the trade where each one of these materials is needed. Experience in the civil engineering domain has shown us that the "plastics", sometimes called *soft materials*, have many characteristics in common. All taken together, these characteristics may be interesting to compare, with the aim both to teach, and to stimulate research. Out of this aim, the 2003 work entitled *Matériaux organiques pour le génie civil – Approche physico-chimique* [MOU 03] was created and later translated into English as *Organic Materials in Civil Engineering* [MOU 06].

In this book we tried to define the field represented by these materials, which are characterized as:

- on the one hand, organic materials;
- on the other hand, construction materials.

In order to approach *organic materials*, we chose the physicochemical approach, meaning that we start by looking for what (in their molecular structure) characterizes these materials, and what exactly characterizes them as being part of the same category, regardless of their use. The intrinsic properties of these materials, namely their mechanical behavior, clearly depend on this structural data. Conversely, we were able to find all kinds of coherences between products with completely different uses, and we were then able to justify the *transversality* hypothesis which guides our work.

Introduction written by Yves MOUTON.

Here, we should be precise. Although they are largely in the majority, the compounds which chemists call polymers – which will be greatly discussed in this book – are not the only existing organic materials, particularly in construction. This is why bitumen¹ used for road engineering and sealing various types of constructions, has an “organic” structure but cannot be qualified as polymers. In the same way, lumber is not strictly a polymer. Therefore our subject exceeds the strict framework of polymer applications in construction.

The world of *construction materials* is so vast that we chose to limit ourselves to the civil engineering field, where we felt more at ease, taking into account our own professional experience. Works were carried out to the field of building construction, but primarily for extrapolation reasons.

This initial work could not be left in this condition. The interest it generated made us take up its cause again, and develop it on two points.

First of all, it was presented as a summary, an introduction to organic construction materials as seen by a generalist. To go a bit further, it seemed necessary to let various specialists in the field concerned have their say, the people of art and science, as well as practitioners, each one of them also having to worry about sustainable development. The transversality hypothesis expressed in the first work was then transposed to the level of the whole book and its organization.

Secondly, the initial work was limited to civil engineering; opening up the subject to the whole of the construction domain seemed essential.

The book we are now proposing is therefore a more in-depth extension of this initial work, presented by specialists in each field discussed. The authors were not asked to approach their subject in an exhaustive manner. Some did, whereas others developed parts of the subject which seemed the most important to them. This means that this book is not intended “to cancel and replace” the previous work but to recreate it in more depth, to show new aspects of it and to update it.

Let us finally add that, written by teachers, researchers, experts and French entrepreneurs, this book is presented, in a certain manner, as a reflection of the French technique of organic material construction.

¹ It may be noted that the French word “bitumen” is “bitumen” in English and “asphalt cement” in American English. We must note here that “bitumen” has a more accurate sense than “asphalt” which often appears as ambiguous. This is why we will use the European terminology concerning bitumen technology.

In addition the concept of sustainable development was already taken into account in 2003 [MOU 03], but it was only really explicit in the final chapter. The procedure which is proposed today appears as follows.

The book is presented in 8 parts.

Part 1. Problems Regarding Organic Materials and Sustainable Development: a successive approach to define the concerned field of materials, the requirements of sustainable development, the health and environmental impacts of these materials used in construction. Chapter 1 presents these materials and classifies them into three categories which are detailed in Parts 3 to 6 of this book. Chapter 2, the most detailed chapter of Part 1, establishes the problems concerned with organic materials in a sustainable development context. This will be taken up again in Chapters 3 and 4, which are intended to be used for reference purposes in future works. On this subject, it must be noted that referenced literature is relatively poor in these fields. It is not the same as “gray literature”, i.e. internal work in companies or research laboratories, but it is still difficult to bring it out into broad daylight. Asking this of the authors was still more difficult.

Part 2. Organic Polymers as Building Materials: starts with a thorough scientific presentation of these compounds.

As previously stated, *there is no identity between organic materials and polymers*, but road bitumens, for example, manifest properties which bring them closer to polymers and put them in this category of *soft materials*, which we mentioned at the beginning of the introduction.

With the concept of the polymer being defined, Part 2 follows by developing the way in which plastic manufacturers use polymer based products. Both the theorist’s (discussed in the first chapter) and the plastic manufacturer’s points of view respond to each other. Then, three phenomena which are at the core of many questions from users are discussed: first of all, the ageing and the durability of organic polymers, then, fire-proofing products containing organic polymers, and finally, processing the waste which is generated at the end of their life.

The first phenomenon is the subject of an important development, because it corresponds to a field where it is necessary to bypass the molecular scale if we want to understand these phenomena, and therefore be able to control the processes. The two others correspond to very widespread interrogations on the relevance of using organic materials when we speak about sustainable development. Here, there are ideas on eminently significant subjects ready to be put into place. Thus fire-proofing is the first response by producers to the anxious users of fire-sensitive organic materials, its balance being the definition of adequate constructive provisions. As for

the problem of waste management, it must be correctly replaced in its context to be dealt with, without *a priori*.

Part 3. Manufactured Products: meaning products which are to be implemented as they are.

First comes geosynthetics, which is used to carry out waterproofing or all kinds of work concerned with geosynthetics. “Waterproofing” is obviously the field of excellence for polymers which are, in their great majority, hydrophobic, and thus perfectly adapted to this use. This is initially dealt with thoroughly within a civil engineering framework. Then, as for plastic formulation, it is looked at in its daily use by the expert, within a general construction framework.

Their hydrophobic characteristic aside, certain polymers manifest particular elastic properties, more specifically elastomeric, which makes them very useful in several domains, particularly for manufacturing expansion or waterproof sealing, or expansion bearings or works of art. The study of these *elastomers* and *rubbers* also deserves to be widely developed.

Part 4. Composite Materials, Tensile Structures, Textile Architecture and Timber: is devoted to emblematic materials as particularly representing the original feature of organic materials: composites, architectural textiles and industrial wood.

Chapter 13 relates to organic matrix *composite materials*, some of which are real manufactured goods and others are implemented in situ. It is initially a question of presenting the pallet offered by these truly innovating products, while considering more particularly new constructions. Repair and strengthening structures will be discussed thoroughly in Part 7 as a specific application of binding.

Then materials for *tensile structures* arrived, which gave way to the practice now known as *textile architecture*, based on new mechanical concepts, particularly tensegrity.

Finally we should not forget *timber*, the oldest organic material, which has become an industrial material with masterful performances, and yet so unknown that it deserves to be developed further.

Part 5. Organic Binder-based Materials: concerns bitumen and other related products, paints and protective systems, products for repair and industrial mortars.

Bitumen, the first binder to appear in the field of construction and the most used organic binder today, is a complex product. Its colloidal structure expresses physical and mechanical properties, similar to polymers but more specific, which require

very interesting and considerable work on behalf of the researchers, to get closer to the work of polymerists. It must also be noted that significant results were obtained from this material with regard to research on the prevention of the industrial risks (see Chapter 3, Part 1).

For *paints* as well as *repair products and industrial mortars*, the last 20 years has seen spectacular transformations occurring in formulation concepts and implementation practices to fulfill the medical and environmental requirements which were to be part of the new standard. Those different domains had to take stock of the situation.

Part 6. Organic Compounds Built-in into Cement Matrices: particularly insists on hydraulic mortar and concrete admixtures. In the same spirit as for polymers in Part 2, the researcher is given a voice followed by the entrepreneur who lists the attributes of organic admixtures in construction processes. Chapter 21 takes stock of incorporating *organic fibers in cementitious materials* into the field of civil engineering.

Part 7. Problems Specific to Organic Materials: Adhesive Bonding: particularly illustrates the field opened by organic materials in the research domain, an essential assembly method for this type of material, and *characterization methods* which are also specific. These are two distinct domains. Bonding is a difficult phenomenon to pinpoint, which still opens the door to a lot of research, but which intervenes in a direct or indirect way as soon as an organic material is brought into play. *Strengthening of concrete structures* is the most important application of that technique in the field of civil engineering. Here the *durability of specimens under accelerated ageing* is used to qualify the materials.

Finally, for the *specific characterization methods of organic materials*, it is interesting to follow their evolution, both in terms of scientific knowledge and European and international norms. Bitumen, paints and concrete admixtures are particularly concerned.

Part 8. Organic Materials, Construction, Architecture, Creation and Sustainable Development: takes a step back. Firstly, the architect's point of view followed by that of the theoretical and applied mechanics' expert. This is then followed by setting up a perspective for the construction materials of tomorrow, when organic materials will play an important role but will not be exclusive. It will reflect the role of research and its pitfalls, before a conclusive article on the possible future of organic construction materials in a sustainable developmental perspective.

Hence, today we can say that organic construction materials are at the very heart of the awakening to the concept of sustainable development. Such an assertion

already passed for a pure provocation, five or ten years ago. Now it is becoming relevant, and today we turn our attention specifically to those who might have felt prompted yesterday.

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PART 1

Problems Regarding Organic Materials and Sustainable Development

Chapter 1

Organic Materials used in Construction at the Dawn of the Third Millennium

To the general public the most well-known available construction materials are stone, terra cotta (tiles and bricks), concrete, iron (or steel) and, with a little insistence, timber, or even tar or bitumen¹, for those thinking of road construction. The reality faced by builders on a daily basis is more complex; organic materials hold a strategically very important position, particularly in the technical uses of concrete and steel.

What exactly are organic materials?

First of all, these are materials whose physical-chemical structure falls within the category of organic chemistry, meaning that they are essentially made up of carbon and hydrogen. Putting timber aside, (and also bitumen, to a certain extent), here we are most often concerned with synthetic products manufactured using natural products: coal, oil, rocks, air, sea water, etc Their usage domains are very diverse, but can be categorized into three main roles which relate to cohesion, structure protection and achievement of structural, packing or design elements.

The first role relates to *cohesion auxiliaries*. Whether we are dealing with bitumen for road construction, binding agents of paint, polymers used in the

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¹ It may be noted that the French word “bitumen” is “bitumen” in English and “asphalt cement” in American English. We must note here that “bitumen” has a more accurate sense than “asphalt” which often appears as ambiguous. This is why we will use the European terminology concerning bitumen technology.

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formulation of repair or adhesive bonding products, or admixtures used to facilitate laying concrete, in all these examples we are looking to bind together units of granular minerals on different scales. Therefore, we can no longer talk about high performance concrete without mentioning the use of organic materials, either as a binding agent (asphalt concrete), or as an admixture (hydraulic concrete).

The second role concerns the *protection* of structures, firstly with respect to water (this is the general problem for waterproofing or caulking), then in relation to all kinds of pollutants, meaning the creation of a barrier effect, in the general sense.

The third role, *achievement of various elements*, concerns firstly the different uses of timber, which ranges from a building's structure to its trimmings. It also deals with a series of "plastic" applications, which range from the envelope, to interior house fittings.

Now if we take an interest in their use and function, we can then distinguish three uses:

- as they are, i.e. in the form of *manufactured goods*;
- as *binders*, i.e. used with granular components;
- as *being incorporated into* a cement mixture to modify its properties; they can then be considered as materials of the third degree, in relation to the first two.

This can all be presented in Table 1.1.

Organic materials	Cohesion auxiliaries	Protection	Main constructions using the produced pieces
Manufactured goods		Geosynthetics (geomembranes, geotextiles and related compounds) Extra-light alveolar structures Watertight complexes Isolating materials	Wooden frame and carpentry Wooden or "plastic" anti-noise wall elements, Elements for embankments Products for wrapping and covering Tubes, pipes, connections Profiled joinery and carpentry Floor coverings and walls Sanitary and electrical fittings
Binding agent	Road bitumen, paints, adhesives	Asphalts Seals	
Incorporated components	Concrete admixtures, organic fibers		

Table 1.1. Cross-classification of organic materials used in construction

These classifications give us a basic overview of these materials, but they do not provide anything about their properties. In particular, they do not tell us about their potential health and environmental impacts. It is essential to take an interest in their physico-chemical nature. Thus four categories can be distinguished:

- polymer-based products specifically;
- bitumens and related products;
- organic matrix composite materials;
- timber.

There are two ways to consider specifically organic polymers according to whether they are the base of manufactured goods – where they operate “finished”, as “plastics”, rubbers and geosynthetics – or they form on site, such as the resins used for adhesive bonding or repair of concrete structures, high performances paints, protection coatings, etc. – and are called “formulated”. Finally we should not forget the “incorporated”, the last generation of rheological admixtures whose active product is a polymer used for steric or electrostatic effects.

The composites used in construction also manifest these two different ways: elaborate products – panels, beams, connector pieces, etc. – or systems reacting at the moment when repairs are carried out on structures, or large buildings, antiseismic structures, etc.

1.1. Specifically polymer-based products

1.1.1. *Plastics, rubbers and geosynthetics*

Oil is the main origin of organic polymers. Figure 1.1 presents the diagram for the manufacturing of four main polymers used in the field of construction. It shows that two operators intervene successively: initially the refiner which insulates the basic commodities (monomeric or precursors of the monomers) and then the chemist, who prepares the monomers, formulates and manufactures the desired polymer (polymerization). In this diagram the paths are simple but it has already been seen, with PVC, that things can become complicated: here the chemist must synthesize the monomer (the vinyl chloride) starting with the precursor provided by the refiner (ethylene) and chlorine, itself taken from sodium chloride (marine salt or extract of mines). Here, we are still using simple processes, which it will be possible to follow during the material's lifecycle analysis.

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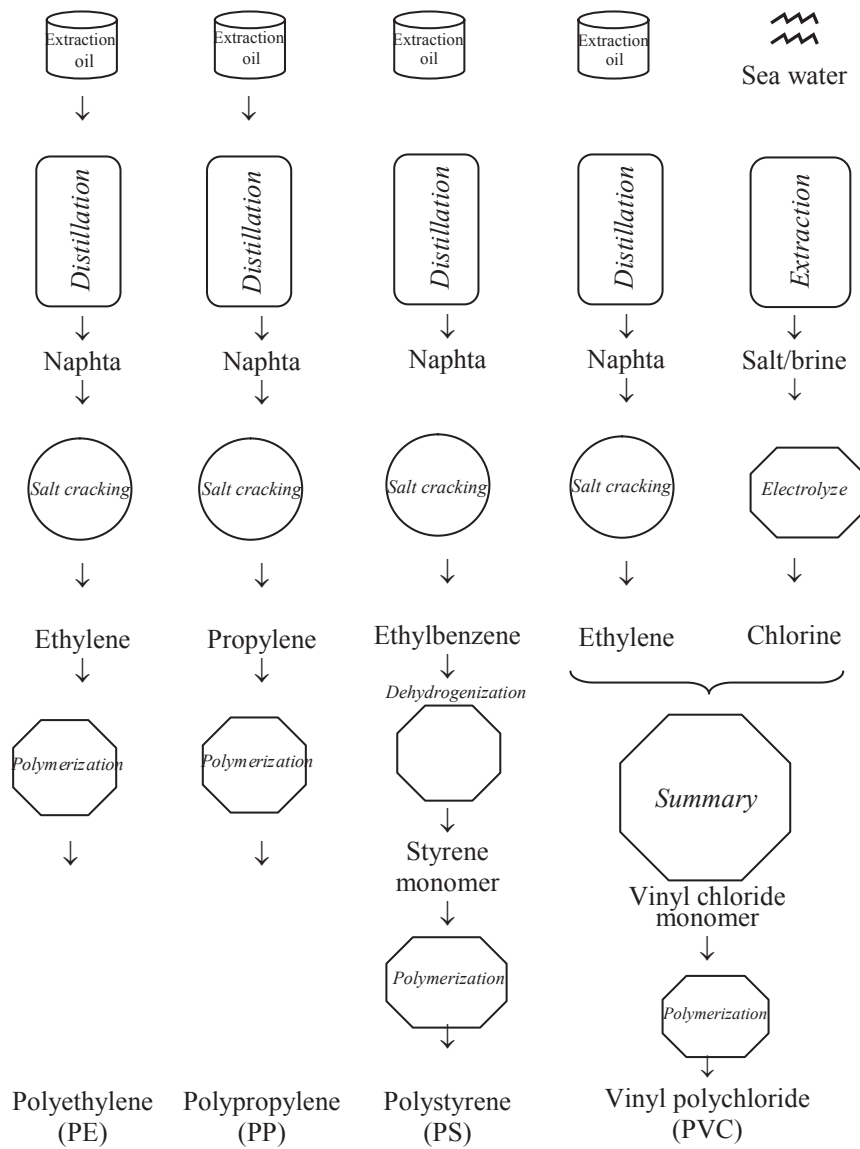


Figure 1.1. Origin of the main “plastics” used in construction

Chemical families	Polymers concerned	Applications
Polyolefins (or macromolecular paraffins)	high-density polyethylene (HDP)	Geomembranes, gas pipelines, hot and cold water pipelines under pressure (transport and distribution)
	Low density polyethylene (LDH)	Guy and pre-stress casing, networks pipelines (water supply in ships), sink sealings
	Polypropylene (PP)	Large diameter pipelines, geotextiles
Polyvinyl	Poly (vinyl chloride) or polyvinyl chloride (PVC)	Geomembranes, evacuation pipes, water supply pipelines (ship) various pieces of equipment, sink sealings Profiled joinery (window and closing) Industrial floor coverings Geotextile (PS matrix) Textile architectures, boardings
Styrenic and special styrene rubbers	Polystyrene	lighting accessories, thermal isolation of buildings, back fill (on compressible grounds) Boardings
polyvinylidene	(PVDF) polytetrafluoroethylene (PTFE)	<i>Coil-coating</i> for setting color and protection anti fouling, coextrusion for atmospheric protection of polyolefin polymers textile architecture (PTFE glass)
Acrylic derivatives	Polymethylmethacrylate (PMMA) and derivatives	Noise reducing walls, lighting accessories, industrial floor coverings, resin mortars
Diene polymers (special rubbers)	Polybutadiene and derivatives (EPDM)	Road junctions, bearing mechanisms of works of art, geomembranes
Polyesters - saturated - unsaturated	Copolymers (unsaturated polyesters - UPE), vinylesters	Geotextiles Art padding, composites (reinforced by glass fibers), building cladding, industrial grounds
Polycarbonates	PC	Noise reducing walls, lighting accessories, cladding
Polyamides	AP	Geotextiles
Polyurethanes	PUR	
Polysulfides	ethylene polysulfide of propylene	Reservoir waterproofing, pipelines

Table 1.2. *The presence of “plastics” in the construction industry*

For preparing other polymers, the process becomes increasingly complex, the role of the chemist becomes increasingly important but the reasoning remains the

same: use of an oil base, then preparing monomers from this base and other components, and finally formulating and then polymerization. We will see that the “other components” may be ammonia (NH_3 , itself prepared from nitrogen of the air) for synthesizing polyamides (textile), fluorine (drawn from a rock, fluorspar) for PVDF, and obviously oxygen in the air for various oxidations. We can even use the case of polyamide 11, as an example, which uses castor oil rather than petroleum.

Without going into too much detail, we can however show the various polymers used for manufacturing plastics, rubbers and geosynthetics in tabular form (Table 1.2 above) by categorizing the products into polymer families.

1.1.2. *Resins, coatings, paintings*

Here, we arrange products used for repair, maintenance, and building heritage conservation.

Products used for repairing concrete can be classified, from a physico-chemical point of view, into two families according to whether the formulation of the base binder is hydraulic, or synthetic resin-based.

In the first family, products containing polymer modified hydraulic binders which make it possible to combine the economic and mechanical performances of hydraulic materials, with the adherence and the flexibility of certain organic materials are widely used. The polymers used here are most often acrylic or vinyl.

In the second family, there are mainly two systems: epoxides (generally of epoxy-amine type) which are very resistant and very adhesive, and polyurethanes which are more flexible and often used for making floor coverings or for waterproofing.

Products used to conserve built surfaces are included in the category of paints and coatings. Let us recall that the researched functions primarily consist of preventing water (possibly charged with aggressive salts) from coming into contact with the structure that needs protecting, whether it is a matter of stone, steel or concrete and, in this latter, to also prevent carbon dioxide (CO_2) from penetrating the material's pores.

Paint is a film-forming product generally presented in liquid form and is made up of a complex mixture of powdery materials, binders, additives and generally a solvent also called a vehicle:

- the powdery materials include pigments which are responsible for the opacity (covering capacity), the color and possibly an anti-corrosive capacity, and the

charges, whose role relates to physical and rheological characteristics; they are generally inorganic;

– the binder is intended to make it possible to coat the powdery materials and to create a film during the drying process; thus here we are dealing with vinyl, glycerophthalic, acrylic, polyurethane, epoxide, silicone, etc. type polymers;

– the additives are used as, thixotropic, anti-skin, fungicide and wetting agents, used in very low doses;

– the vehicle can be an organic solvent (solvent phase paint) or water (water-soluble paints, water-based paint, water-dispersed paint). There may also be no vehicle and, therefore, we are talking about paint without solvent. This last case relates to two component paints, mostly epoxide.

Chemical families	Polymers concerned	Applications
Special styrene rubbers	SBR, SBS	PmB (polymer modified bitumen)
Polyvinylidene	Poly vinyl acetate and derivatives (PVA)	PmB (polymer modified bitumen)? additives for hydraulic mortars
Acrylic derivatives	Polyacrylamides	Water-swelling mortars
Diene polymers (special rubbers)	Polyisoprene	PmB (polymer modified bitumen)
Unsaturated polyesters	Copolymers (UPE), vinyl esters	Chemical anchoring
Polyurethanes	PUR	Paintings, pipe line repairs
Polyethers	Epoxy resins (EP)	Repair, protection (paints), coatings, adhesion, composites (reinforced by carbon fibers).
Phenolic and related derivatives	Phenoplasts, formophenolic or urea formaldehyde	Wood glues (glue-laminate, concrete scaffolding panels) Joining of timber
Polyorganosiloxanes	“Silicones”	Sealing, antifouling protection

Table 1.3. *Organic polymers used as binding agents or additives in the construction industry*

The range of the coatings is vast. Here we will find everything that we have discussed about paint and products used to repair objects. The difference lies, then, in the formulation and the size of the mineral powders used.

Table 1.3 groups together the most commonly used products.

1.1.3. *Incorporated components: organic fiber and concrete adjuvants*

The resistance and durability qualities of hydraulic concrete greatly depend strongly on its compactness, therefore on the conditions of its implementation. The objective is then to obtain optimal granular stacking. The pursued process brings into play the interfacial properties of fresh concrete's liquid phase. The progress made in the field of rheological admixtures, mainly superplasticizer, made the arrival of more powerful, easier to use, better quality concrete on the market possible. Generally today, admixtures (more specifically the family of plasticizers) are considered as a whole component of concrete.

The formulation of rheological admixtures has greatly evolved since their arrival on the construction market. The first plasticizers were by-products of the paper paste industry, called lignosulphonates. Then, without abandoning these last items, we have sought to use better defined molecules, like gluconates. Finally, when the admixture market showed that it could be lucrative, we planned to develop specific molecules. The poly-naphtalene sulphonates and poly-melamine sulphonates (PMS) initially were developed, and were then more recently followed by electrostatic or steric purpose polymers, with carboxylate, sulphonate or phosphonate termination. In addition, there are also organic admixtures used as retarders, water repellents, viscosity agents (water retentive agents used in the shotcrete technique), air-entraining agents intended to protect the concrete from the effects of freezing (see [MOU 06] and, to go a bit further, see [SPI 00], [AFN 02]). These products, however, have not acquired the inescapable role, which is that of the plasticizers and superplasticizers for the constructor.

1.2. Bitumen and related products

We call hydrocarbon binders the organic binding agents used in road engineering which include:

- bitumens themselves, coming from the distillation of certain crude oil, primarily of animal origin (transformation of marine sediments accumulated in lagoons, lakes and seas of the Mesozoic era;

- tar, made from coal or lignite by pyrogenation away from air, vegetable origin (decomposition of plants and forests located near shores and buried by movements of the Earth's crust);

- natural binders, i.e.:

- natural bitumens presented as a paste containing a strong proportion of heavy hydrocarbons (at least 40%) impregnated in schists or marl-limestones; the largest known deposit can be found in the Antilles, in the island of Trinidad,

- asphalt rocks or natural asphalts, made up of sand and fine limestone and siliceous fine particles, with 6-10% bitumen, the extracted ore following conventional mining techniques is then mixed to give asphalt powder.

Paving bitumen is presented (according to samples) as a very viscous fluid or a solid with the consistency of a soft to hard paste. It can be implemented in several ways:

- by plasticizing at high temperature (140 to 160°C), this is the technique of hot-mixing;

- by softening with the addition of a solvent, i.e. using thinners or fluxes for creating surface dressings for example;

- by emulsifying in water for making surface coatings, cold-mixes, treated gravel, repairs, etc.

These two last methods are collected under the term of cold techniques.

In addition, research on bitumen has led manufacturers to develop complex products called modified bitumens, special bitumens and bitumens with additives where the polymers mainly intervene.

Lastly, even if 90% of the bitumen production is intended to be used on roads, there are other uses: waterproofing, underground pipe protection, insulation and electrical equipment protection, pulverulent storage protection, etc.

1.3. Organic matrix composite

Composite materials consist of a matrix and a strengthening agent. The mechanical performances of the end product primarily depend on the choice and the geometry of the strengthening agent, the role of the matrix is to ensure continuity between the strains supported by the strengthening agents and their protection.

The current primary applications of organic matrix composites are presented in Table 1.4. The subject will be developed in detail in Part 3 (Chapter 13).

Fibers Matrices	Carbon	Polyesters	Aramides	Glass (Long or short fibers)
PVC		Textile architecture		Window frames
PTFE				Textile architecture
Polyester	Repairs, antiseismic structures,			Exterior wall panels, structure elements
Epoxides	Repairs, antiseismic structures		Repairs, antiseismic structures	Repairs, antiseismic structures
Vinyl esters	Repairs, antiseismic structures Exterior wall panels, structure elements			
Resorcinol				Exterior wall panels

Table 1.4. *Main composites with organic matrix used in construction*

1.4. Timber

The structure of the wood can be considered as that of a composite: a lignin matrix reinforced by cellulose fibers.

As with the plastics mentioned above, we can say that timber is used as “formulated”:

- to the extent where various processes are applied to the crude material to ensure its durability, and the continuity of its performances;
- to the extent where the present products on the market are generally made up of bonded structures allowing the optimal use of specific performances of crude wood.

The technology of timber has made great progress during the last few years and this has opened it up to markets where other materials were firmly established, in particular in construction. It should be noted that current products do not coincide with the traditional image of the wood as coming directly from the tree and therefore, when it is a question of analyzing their lifecycle, we should not forget the initial treatments and the products used for this situation.

That being said, timber remains a noble material, nice to look at, nice to feel, with multiple uses and increasingly needed in construction.

1.5. Conclusion

Organic materials are omnipresent in the construction, often invisible but especially essential. The pages which follow will endeavor to illustrate it from all angles, and to show how these “soft” materials, these “plastics” have transformed construction techniques in terms of ease, flexibility and comfort, without yielding to resistance and durability.

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Chapter 2

Sustainable Development Issues Regarding Organic Materials used in Civil Engineering

2.1. Introduction

Sustainable development is now part of our daily lives and occupations. In order to apprehend or establish the actions that favor sustainable development in the construction industry, it is necessary to define a common shared reference which describes the principles to be rejected. Accordingly, the general definitions and issues of sustainable development, such as they exist in a political sense, on a planetary scale are initially specified.

Problems which consist of analyzing these issues in the field of construction are exposed. Over centuries, man has gradually built up a heritage to try to meet his needs. Solving the problem in a technological way depends on localization, the wealth of the country, local construction material resources (even if some resources have to travel around the world). The nature of civil engineering works, as an indicator of society development and therefore of anthropic human activities, implies buildings as well as other infrastructures for mobility needs. Before the environmental approach towards the lifecycle of materials emerged, questions of maintenance had never been integrated into the initial construction evaluation.

Chapter written by Agnès JULLIEN.

However, applying the principles of sustainable development in organic material construction is progressively approached below. The scales to be taken into account are specified. The need for methods and evaluation and reference tools is then underlined, in order to write down the use of organic materials for both economic concerns and resource availability, particularly for future generations. In particular, the question of obtaining environmental data relevant to the application of lifecycle analysis for civil engineering works is raised. Examples of collected environmental data illustrate the information gathered in order to give it a practical sense.

2.2. Sustainable development: definitions, general issues and issues in construction

2.2.1. *The political concept*

The concept of sustainable development first emerged from the Bruntland report [BRU 87] but was then expressed as being a compromise between three fundamental contradictions [BRO 04]:

- compromise between the interests between present and future generations;
- north/south compromise between industrialized and developing countries;
- compromise between the needs of human beings and ecosystem conservation.

In any human activity framework, taking these three contradictions into account involves:

- being able to project what time actions undertaken either yesterday or today, as well as their consequences;
- taking into account the territories where activities are integrated or connected, and finally;
- being able to evaluate the economic and social consequences similar to the environmental consequences of the activity.

A sustainable development policy implies that human decisions are guided by these principles.

From the industrial revolution era, humanity has been involved in an enrichment process without precedent, resulting in the idea that a resource is that which is created, rather than that which we already have [MOR 08]. Thus, discussing sustainable development finally raises the question of the imbalances induced by man's activities, such as over-exploitation, destruction of natural resources, increase

in pollution, the increase of inequalities between areas, all due to globalization. As an example, we can see that in industrialized countries anthropy does increase and therefore, first the efforts can be applied to controlling the speed of this increase, or even act to slow it down. Globalization particularly favors free movement, of both goods and people. Next, in terms of imbalance, a simplistic vision of different world regions could lead to giving the following light: industrialized countries move because of the economy (economic sphere), other countries have to face a demographic explosion which needs to be managed (social sphere), finally the particular shortage of water resources, energy and cultivated areas (environmental sphere) create a major problem in a third-world country category. This means that the way of thinking in this very wide field of sustainable development, and the associated priorities, depends specifically on the country we live in, whereas most of the resources can circulate on a global scale.

2.2.2. Possible actions

Any activity carried out by man induces transformations of raw material, whether it is extracted, made artificially, transported, elaborated according to various processes and then used. The durability of the resources will be a major issue in the construction industry for years to come. Reducing the amount of waste to be stored, always in increasing quantities, is an expected response from the socio-economic agencies under pressure from public authorities. Recycling or valorization of alternative materials is not necessarily a lucrative economic activity; its application needs accompanying measures in order to overcome psychological boundaries, fears of inferior quality, environmental and health risks. The principle of these resources is recognized today as an important trigger for action, particularly in civil engineering.

The worldwide annual consumption of energy rose to 10,000 Mtep in 2004 (all sources together). In France, 2004, energy use was divided up on the basis of a final corrected consumption of 116.2 Mtep, in which 50.8 Mtep related to the transport sector [CDP 04]. The field of road construction and its production sites, material processing, as well as its need for transport, contributes to a significant amount of these consumptions. Taking into account the masses of resources used and transported, it seems relevant to seek favorable conditions to reduce such consumption.

The European objective is to reduce waste production by 20% from now until 2010, and 50% from now until 2050. The main actions to be implemented in particular consist of reducing resource consumption, recycling waste, developing environmental evaluation systems necessary to secure usage, to give the public access to environmental expertise. To achieve these goals, statutory European

constraints are likely to become increasingly severe, particularly in the case of waste landfills, release towards ecosystems and of the environmental quality of materials.

Rigorous planning is therefore necessary in order to ensure a balance between satisfying our needs for acceptable economic conditions and the need to protect the natural richness of our environment. In this respect, the current availability of resources, and the economic as well as environmental impacts of the materials' choice is declining, particularly in terms of transport.

2.2.3. Environmental considerations

2.2.3.1. Determiners of political and public action

Today, protecting the environment has become an international issue: in fact, the decisions and political commitment on the scale of one country are being projected on a worldwide scale. Namely, the recent creation of CO₂ rights for emissions for some economical sectors, although not concerning transport, is articulated with the Kyoto protocol and matches the aim of international environmental load mitigation by stressing industry at a European scale. These provisions are in agreement with the recent stance of climate change experts, the Intergovernmental Panel on Climate Change (IPCC) which specifies that “the essential element of climate change is probably due to greenhouse effect of human gas emissions” [GIE 07]. Therefore the European institutions, reflecting worldwide concerns, impose constraints on their Member States, with regard to different environmental aspects through statutory and normative means.

Regulation and legislation, constantly evolving since the 1970s, create important potential choices to various industrialists, project and work managers in order to integrate new environmental, economic and societal concerns beyond the only technical fields which, often in the field of construction, are widely covered by normalization. In March 2005, the French constitution introduced the environment to its laws, and since then, a meeting called *Grenelle de l'environnement* (a French environmental protection organization) has been organized to define potential actions for tomorrow's infrastructures. In addition to resource saving, one of the raised issues is biodiversity conservation.

Impact studies have been applied for many years in order to preserve the natural environment where an activity is established that is controlled by French regulation. Let us use the case of industrial material production sites (classified sites to be controlled in terms of emissions) which run under authorization in certain conditions and thresholds to make use of waste for the good of the environment. Also let us quote the studies of sites around the road projects which, essentially qualitatively, aim to consider mitigation measures to avoid environmental impacts. If all these

rules constitute a valuable source of data from industries in the associated sector and for the local territory area used, they are not useful to assess raw material fluxes, energy or releases that today have to be integrated in the way of thinking and evaluation of anthropic environmental load mitigation.

2.2.3.2. Analysis of targets to be preserved on very diverse scales

Any anthropic activity by man causes territory transformations by making it become artificial, particularly when infrastructures are built. Such transformations also act on other living species and on plants belonging to the impacted territory; here this particularly refers to habitat transformation. Biodiversity protection is an essential component in any anthropic activity, although protecting the presence of a species in the considered area is difficult to take into account in terms of “materials”, because the concerns in our daily lives are rather removed. Beyond spatial effects, construction activities produce short and long-term effects whose consequences must be apprehended.

The study of the environment relates to a wide extent of geographical scales. The consideration of the environment also covers a very significant number of substances. The consequence is that the number of targets impacted by man’s activities (including man himself) may also be important. Figure 2.1 shows an example of sources and targets subjected to potential effects; all the target entities to be evaluated link the list of environmental pressures generated by the sources inherent in construction or maintenance works, or even the deconstruction works and make the environmental evaluation of the associated industrial activities more complex.

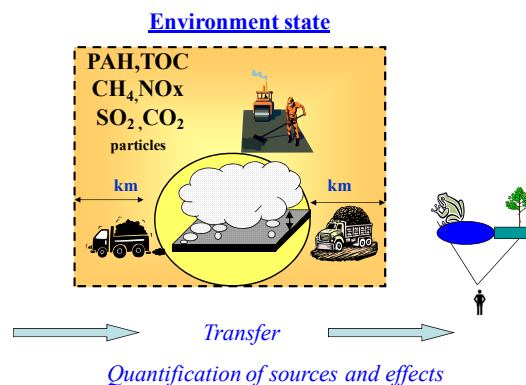


Figure 2.1. Example of construction activity representation with organic materials generated from pollution sources (here, towards air or water) and potentially affected targets

In particular, the concept of the site must be taken into account when evaluating potential human activity impacts. In the case of the natural environment which is to be protected, the spatial scales which must be considered extend from a planetary scale for greenhouse gases, and are to be restricted to smaller zones and elements which create them, such as rivers, park lands (with or without trees), or relief.

Concerning the environment, all man's activities have consequences, since the matter is transformed; we need to specify that the perimeters affected by these consequences are different according to the environments considered. The air circulates on a planetary scale, moving by dominant winds and currents, and cannot be confined. Therefore if there is an impact, it will be global. Water is distributed in a more restricted geographical way, where pollutant transportation occurs at shorter distances. The ground collects the waste material transported by the air (dust falls) or by water (pollutant filtration); it is not directly subjected to transport laws, but it is an integrating medium which, in time, gathers pollutant emissions from the other mediums transferred onto more or less long distances (air, water, waste). The ground can develop memory effects, according to the thermo-hydro-chemical mechanics it is subjected to. Studying these effects helps to interpret complex coupled effects.

2.2.3.3. *Concept of impact evaluation*

The impact concept tries to translate the consequences of man's activities in any of the spheres which illustrate sustainable development and which include the effects on different targets constituting the natural environment, as well as on territories and all kinds of resource reserves. Concerning the environment, we generally retain the following pressures deriving from human activities: natural energy resource consumption, water consumption, energy and matter recuperation. Then, regarding the emissions, we distinguish those pressures in the air, in the water, and on the ground. Finally, waste production is separated into reused or recycled, and eliminated waste. A collection of irritants associated with industrial matter transformation such as noise, vibrations, odors linked to the air environment who visual embarrassment may equally reinforce its perception [LAV 07].

Impact categories, fewer than the pressures exercised on the environment, make it possible to specify the kinds of potential effects on the environment in a more synthetic way. According to whether we refer to standards and or to scientific literature, the impact categories are indicated with some differences, in particular with regard to construction products [GOE 95], [AFN 04], [AFN 06]. To simplify, these categories mainly deal with the following aspects:

- natural resources (in terms of raw materials), energy resources, and water resources;

- climate change (greenhouse gases), destruction of the stratospheric ozone layer, photochemical ozone formation, atmospheric acidification;
- toxic and ecotoxic effects;
- generation of solid waste;
- discomfort generated by activities dependant on visual, aural, and olfactive perceptions.

With each impact category the evaluation issue consists of carrying out a quantified approach to the potential impact on the environment. According to the impact category, the form of the indicator may be different and the associated choice criterion also. According to the method of evaluation selected and the required level of precision, the calculation hypotheses of the indicators are crucial for an evaluation procedure. Transparency is necessary; in particular the data sources must be examined carefully to identify their obtaining method. A critical approach to the quality of the data used for the evaluation must be considered. It is important to remember at this stage that impact evaluation is a useful stage in a reflection.

2.2.4. Towards normative reference – certification of construction works

In civil engineering, a recent awakening has led to integrating environmental protection in the wide sense i.e. natural environment and health, into construction practices. The establishment of "clean" and "furtive" construction sites for the wellbeing of the residents and users of the built up areas, and constructions and town developments respecting principles of sustainable development have gradually been born. Different people in the construction industry are all implicated each with their own issues. The material suppliers and companies are centered today on material approaches, the construction and project managers are centered on works or project approaches. Finally, we are helping with the progressive establishment of new approaches related to conception. Certain approaches are "bottom-up" when they take into account the scales of reflection which go from the material to the work: they have resulted in setting up the standard NR FP 01010 [AFN 04] which aims to evaluate the lifecycle of materials in a construction. Other approaches are "top-down" and are based on the life of a work on the basis of considerations related to the development of the project itself. Thus, a label for high environmental quality was established in buildings constructions. This is the environmental high-quality (HQE in French) (<http://www.cstb.fr>) which was developed to guarantee that sustainable development would be taken into account at the design stage of construction works. Moreover, the label HQE-sustainable roads, is under development (<http://www.cg59.fr>) and tries to anticipate the consideration of the sustainable development upstream of road projects, at the stage where the infrastructure is introduced into a territory. Considering both materials and

infrastructures, good practice descriptions and their implementation, will be the key-elements of the field for years to come.

In fact, in environmental sciences it is useful to specify “raw material” and “product” to distinguish the development level of the material that can be used to add a number of transformation stages imposed by an industrial process, for commercial means and for a given use. The impact study, according to regulations, when it is implemented, aims to articulate the use of the construction work and the territory in which it is established. The manufactured objects or products are largely different from the built works. The object can be moved, the work is fixed; it is undoubtedly the essential difference between the two. The evaluation of either an object or construction work’s lifecycle deserves to be understood within the framework of a comprehensive approach, in the sustainable development sense. Indeed, we cannot apply the same usage approaches to a movable product and a product which is adaptable for the user, or to an infrastructure which is linked to a site and which is specially adapted case by case. Table 2.1 recapitulates the types of approach which can be considered in the field of products and construction works. This is linked to the realization of construction works, a production site or even still, the product itself. The unavailable methods or practices are displayed in italics, contrary to those which are available.

Finality	Approach type	
	Industrial production process	Insertion process to a natural site
Study of a construction work	– <i>No environmental method of evaluation of the site</i>	Impact study (Legislation/regulation)
Study of a product	– Inventory of lifecycle – Lifecycle analysis (Standardization)	– <i>No indicators of definite local impacts</i> – <i>No reference specific to the activity field</i>

Table 2.1. *Approaches and finalities in the studies of the impacts of products and construction works*

What, then, are *specificities of civil engineering*? It is a question of separating the approaches towards the “product” from the approaches towards the “construction works”, using evaluation tools, data and indicators adapted to each scale of study. Lastly, the exploitation phase of the work is often very different from the construction and maintenance phase; the evaluation hypotheses often need to be reconsidered, in particular the time scaling of anthropic actions that are counted.

2.3. Civil engineering materials in their environment

For each organic material, we are able to specify the properties: physical, mechanical, thermal, chemical, physicochemical. Among these properties, it is possible to separate those which are intrinsically connected to the matter and its cohesion – the first three properties – those which the environment has a direct effect on, either from the air, water, contact with a living target or an object of different nature. The material's contact with the environment, in a wide sense, is suitable in order to trigger its evolution over time which will or will not be transformed and then associated with impacts.

Must we also adopt an “environmental” classification for materials? For as long as we have studied the history of construction over different civilizations, we can easily underline that the heritage indeed displays characteristics of durability which particularly depend on the durability of the constitutive materials used. This explains the reference to stable natural materials on a geological scale, materials that are also available in great quantities. Artificial materials (or synthetic) have, however, been created by man to meet his needs. Must we envisage a difference between natural and artificial materials in a global approach which integrates sustainable development? Not if the construction's lifespan requirement prevails, because an artificial material can fill the requirements for good service life.

2.3.1. *Organic materials development practices*

The term “material” must be specified at each stage of an environmental approach, because it can be a source of confusion for the various interlocutors concerned. By the term “material”, the dictionary states that it is any matter used in civil engineering construction, road works, in architecture or in machine manufacturing. Finally, material science brings together the domains which study the matter which makes objects.

Materials in general are identified by family and are classified according to their chemical composition. A primary stage of material characterization consists of identifying the chemical composition and then the mineralogical composition. Then, according to civil engineering practice, it is a question of specifying physical and mechanical properties that they are supposed to reach in terms of usage. The transformation stages of the matter, of its elaboration and of the mixtures of the raw materials in order to obtain the products for construction are also studied and considered, based on known product properties. The elaboration temperature imposed by industrial furnaces so as to transform the raw materials plays a huge role. The mechanical action of all kinds of industrial equipment is also important in the global process of manufacturing the products. For each general material class,

the various physical and mechanical properties are measured on samples considering a standardized laboratory test framework. Thus, the organic materials are brought together owing to the fact that they show common chemical characteristics related to organic chemistry, whether they are of natural or artificial origin. This classification thus lies on the identification of very small chemical elements making up the objects and whose characterization is known according to material.

In addition, characterizing the waste materials release towards the environment consists of, for each substance assumed detectable or defined as non-desirable, initially determining the concentration of the waste materials over a relevant time period in relation to the construction work and external loads it is subjected to (climate, users, hydrological system, etc.).

2.3.2. From resources to construction: matter transformation

Man usually extracts the matter from a territory where there is a deposit of it, in order to guarantee that there is a substantial volume to supply his needs. The raw matter is in an ecological equilibrium because it is stored naturally in its geological, original environment. Once extracted, this matter possibly undergoes a first treatment or conditioning stage, and is then transported so as to be industrially manufactured. It then fully enters a production and product process. Contrary to construction works which are implicitly linked to the concept of usage, the materials remain attached to these base functions associated with the products.

Indeed it is always possible to distinguish organic materials for construction according to different categories:

- according to their source. Natural materials (wood for example) set against artificial materials. Natural material has a history related to the planet and possibly to the memory of its history, which man knows in a certain or statistical way. As for artificial material, it can be identified thanks to a given number of industrial transformation stages;
- according to the properties they bring to the construction material considered. Adjuvant or all sorts of fillers (powders, fibers, liquids) bring extra properties, with the idea that only a relatively low mass compared to the total mass will be used to achieve this goal (example of adjuvant).

But the environmentalist will prefer to separate non-renewable materials from renewable materials in order to transform the stock depletion with regard to available reserves and the possible reconstitution of these reserves (example of wood). Moreover, the environmentalist, within a lifecycle framework, recommends keeping the raw material mass as a key parameter in its environmental evaluations.

2.3.3. *Durability: the unquestionable effect of time*

With regard to civil engineering constructions, it is important to avoid confusion between sustainability and durability. Sustainable, as has already been specified, takes into account the parameters and indicators concerned with the three spheres: economy, environment and society. Durability relates to mechanical behavior and the physical properties of the materials which guarantee the lifetime of the construction in its environment.

Lastly, over time this stability of the materials' or products' properties is also invaluable. Here we are dealing with problems concerning durability, which comes under physicochemical interactions between the material and its environment. This type of interaction, likely to modify the microstructure of materials induces potential modifications of the microscopic and macroscopic properties, which in many cases reduce the required performance level, and even lead to premature replacement of the material in the work or will even ruin the work. The desired properties are initially intrinsic, to allow the initial design of the work and of its structural elements. Then, it is a question of obtaining temporal stability for its properties in the sense of durability, of controlling behavior with time (creep) until a state of equilibrium is reached (acceptable over short periods).

2.3.4. *About material lifecycle*

The position of materials in a construction process concerns (respectively):

- initial construction and final work;
- heritage maintenance, repairs, or consolidations which need to be demolished or undergo selective deconstruction in order to recover end of life materials to be able to convert them into alternative resources.

With regard to the work used, the effect of natural, chemical, physical, physicochemical and thermal loads can change the bulk properties of the materials and generate leaching when in contact with water.

In lifecycle approaches adapted to construction works, it is useful separate the cradle-to-product and product-to-grave approaches, where a material is manufactured for a specific purpose, and where a material is at the end of its life and it is then transformed into a potential resource, respectively [SET 93], [AFN 06]. Indeed the complete lifecycle approach is not always necessary from the outset for a “construction works” approach. As an example, for roads in France the end-of-life is not predicted *a priori* as opposed to the working life, which is. The following two

examples illustrate what must be seen in each of these cases before even approaching the evaluation methodology in the sense of lifecycle analysis (LCA).

2.3.4.1. “Cradle-to-product” approach

Example: bitumen production and laying.

The global system linked to hot mix plant emissions, in the sense of the definition given within the lifecycle analysis framework is presented in Figure 2.2. This system includes a group of successive transformation processes of the raw materials used. One of the important hypotheses when an environmental lifecycle evaluation is carried out consists of specifying the system’s limits and therefore the considered data. This systemic approach on which LCA is based has a completely general characteristic, which is applicable to other environmental evaluation methods.

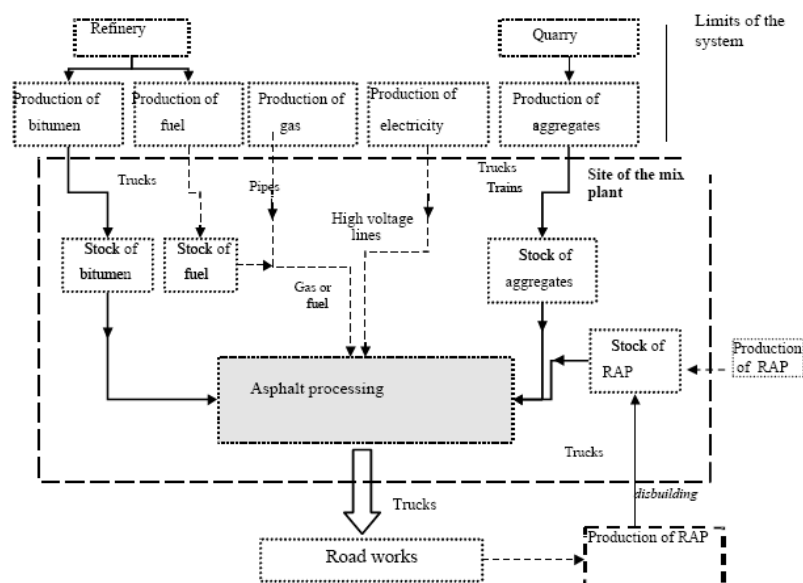


Figure 2.2. Environmental system associated with a mixing plant site

The supply of raw materials on the industrial transformation site must be counted. Transporting aggregates for the plant is usually by truck or more rarely by train; the aggregates (recycled) coming from road sites are just like the other components stored on the site. These materials are classified according to their granulometry before storage. The bitumen supply is performed by trucks, which bring

the hot binder ($\approx 170^\circ\text{C}$) from refineries. These bitumens are stored according to their class or type (origin), in permanently heated tanks; the standards specify the necessary conditions. The electricity and natural gas supply is delivered by the public network. The delivery of the hot manufactured bitumen is also performed by truck.

Then, beyond the perimeter of mixing plant, the bituminous mix is transported to the building site where it is laid and compacted. At this stage it is a question of identifying the civil work engines necessary and their working condition on the site, in particular to check consumption and to evaluate emissions.

2.3.4.2. “Product-to-grave” approach

Example: recycling asphalt concrete after milling a pavement at the end of its life

During deconstruction, several possibilities are offered to recover the reclaimed asphalt pavement. In the example presented in Figure 2.3 we are dealing with the recovery of homogeneous materials from the old pavement, that is, the second layer (binder course milled on a 4 cm thickness), to save non-renewable resources. The deconstruction scenario, in view of recovering targeted materials and to ensure their homogeneity, must therefore include a separate treatment of the higher layers. Bitumen saving will be obtained at the same time which is to be environmentally assessed by whoever recycles or re-uses these deconstructed materials.

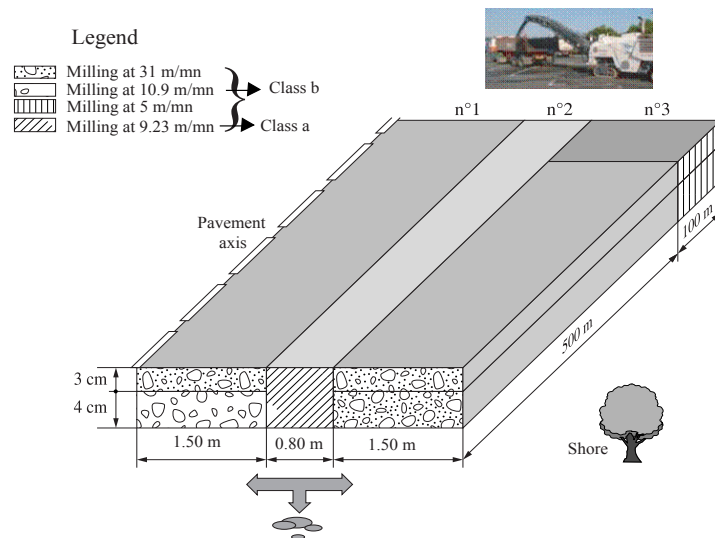


Figure 2.3. Milling scenario of an old pavement, possible milling speeds [JUL 05]

The environmental method consists of considering several deconstruction scenarios. The entire thickness is milled at one time, without instruction on the milling speed (three bands are done due to the available machines) and in this case, mixed waste is collected because many road layers are treated together. Therefore, milling is carried out by successive layering in order to select a homogenous composition of end of life materials. Moreover, the milling is done slowly so as to collect controlled granulometry of materials, which makes it possible to recycle them without having to recondition them on a roadbed. This field example also illustrates situations which exist in building construction, for materials at the end of their life. This particularly concerns the potential second life, which this alternative resource is intended for. The retained scenario must be put into perspective with the future use of the obtained waste. Often, at this stage, a physicochemical characterization of the waste after deconstruction must be carried out, particularly in terms of its leaching potential (<http://ofrir.lcpc.fr>). Sorting during deconstruction may turn out to be a preliminary, important stage.

2.4. Sustainable development and civil engineering

Typically, the idea of considering the act of construction to be over a long period of time, or planning to integrate repairs into it, comes under the aim of sustainable development, if it is linked to evaluating the associated industrial activities. Maintenance of constructed infrastructures or buildings or even their renovation by the integration of current objectives of energy and resources saving in a construction work lifecycle framework is one of today's top priority. It is a question of taking into account the rarefaction of certain resources, particularly natural and energy resources. Always being concerned with resources, recycling (consumption of waste developed into products) not only constitutes a direct source of financial savings, but rather an evolution in the history of construction, if we were to consider that recent decades have been dedicated to the development of higher performance materials. Thus, we must be assured of the stock of resources over a certain time period and of the traceability of used products, if the viewpoint consists of recycling over many phases.

2.4.1. *Links between study domains of material and construction work*

How should the question of sustainable development be approached regarding organic materials?

Multi-disciplinarity is essential. Such an approach, which covers concepts of territory, raw material circulation and civil engineering processes at the same time, calls upon a framework of reflection founded on systemics and evaluations using

indicators whose definition, meaning, relevance, feasibility (or representativity) and interest, must be controlled in a given framework.

Precepts of sustainable development applied to organic materials as presented below lie within this scope. Precise details relating to total environmental evaluation are developed a little further on.

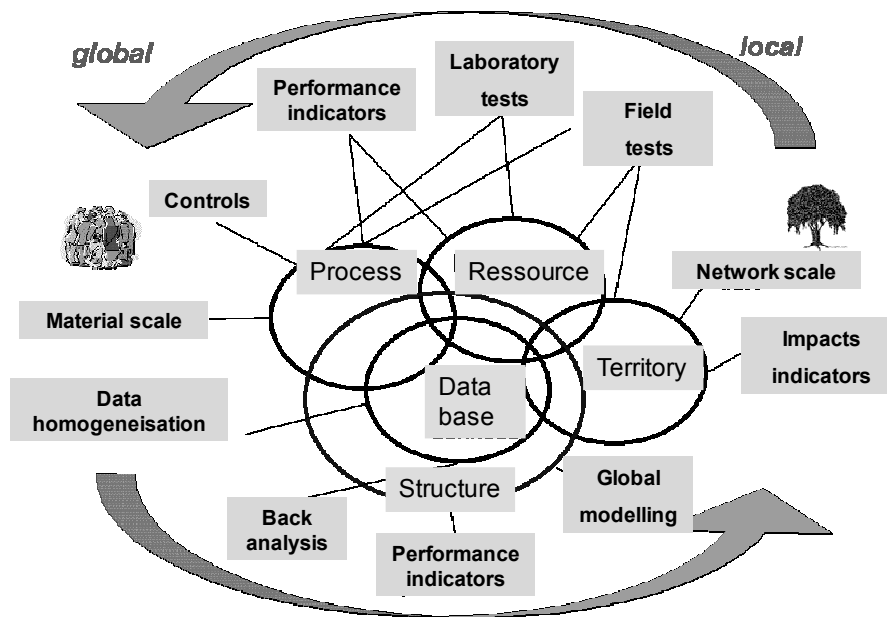


Figure 2.4. *Articulation of different research domains linked to evaluation of different organic materials for construction*

Figure 2.4 illustrates the articulation between the different domains relating to the consideration of sustainable development in the framework of civil engineering works with organic materials in a particular territory. The research application field is therefore mainly made up of civil engineering works such as roads, tunnels, bridges, large buildings, etc. With regard to these works, it is a more a question of considering the function of the work in its environment, which makes it possible to specify its use and therefore to define the resultant construction modalities, and the conception of the associated structural elements which use organic materials. Once the use is specified, logic leads us to define the construction and maintenance principles of the work considered so as to guarantee this use; in this framework, reflections are carried back onto the construction materials. Therefore, it is first a question of considering establishing the work in a territory and consequentially, in

an environment where its own constraints, and realization and usage modalities are imposed. In this phase, various engineers are motivated in order to find materials which respond better to the technological needs of the work to be constructed. The resources which are to be used, the processes needed to implement them, the characteristics of the soil where the work will be built are among many of the questions which need to be dealt with. Field tests, laboratory tests, are then carried out in order to gather the necessary data for the technical choices. During this stage, the integration of the environmental effects of the material chosen to carry out the work, the costs induced by these choices and their incidence on human beings can be integrated in the framework of a more global procedure. For this, creating an environmental method category is susceptible to partly concern materials and to allow for a quantified approach of the environmental impact of products; it is a question of finding the methods which aim to produce an environmental inventory. In order to widen the themes to be discussed, we need to specify that the approaches to be mobilized must be more global and therefore pass by the purely mono-disciplinary knowledge, particularly that involving mechanics, physics and chemistry.

2.4.2. Temporal and spatial scales to be taken into account for the environment

The environmental implications of the choice of materials are not only intrinsic to the material itself but are found throughout its lifecycle in the work. The environmental evaluation of the choice of materials for the works passes by both technical (feasibility, mechanical quality) and environmental knowledge, of all the transformation stages they undergo during use. In short that means:

- processes for extracting the raw materials and elaborating them upstream from their use to manufacture materials;
- processes for the transformation of these materials, and manufacturing stages of the mixtures (construction materials);
- conditioning stages for these materials to facilitate their transport to the civil engineering building site;
- the means of transport retained for these materials which must be adapted to the transported mass, to the type of conditioning selected, to the accessibility of the building site areas to be supplied;
- materials implementation processes including handling conditioned materials, their transformation work and implementation on the site (for example, geotextile positioning, polymerization of a glue, drying of a coating, etc.);

- their ageing during service time due to usual external loads such as thermal cycles, hydraulic cycles, exposure to UV, exposure to chemical substances;
- their behavior in the face of accidental conditions: fire, earthquakes, floods, etc.

With each one of these stages, it is possible to quantitatively assess the potential effects on the environment of all these transformations. Taking these effects into account when looking to reduce them is a procedure which comes under sustainable development principles.

In addition, only concerning the transformations of these materials so as to allow their usage in civil engineering, transformations which take place over rather short periods of time (a few years) in relation to the construction's working life (approximately a few decades), it is useful to consider the concerned time scales with regard to the environmental effects and the problems of threshold tolerances raised by some substances. The significant time scales to be integrated into global approaches, particularly environmental approaches, are in the order of 50-100 years, if we refer to the relevance of certain atmospheric pollutants: one year for release to water, and many years for a ground impact.

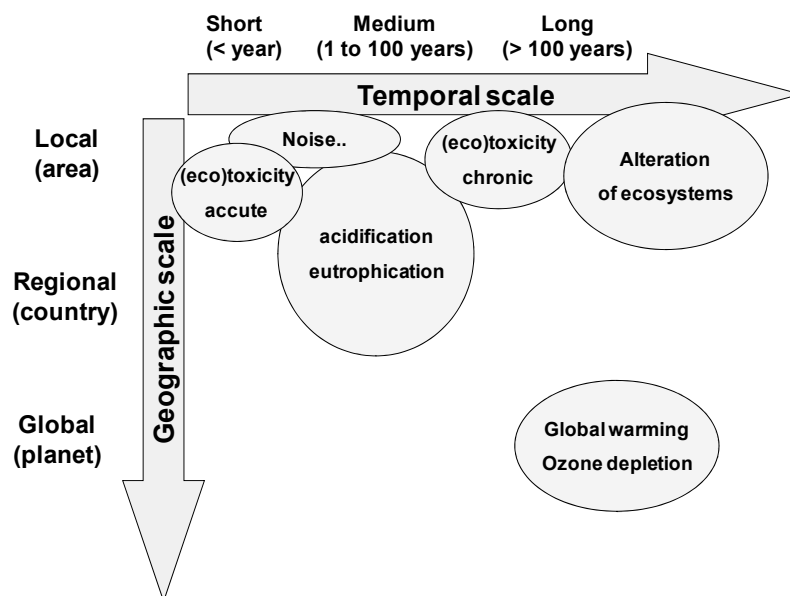


Figure 2.5. Significant scales to be taken into account in an environmental procedure

Then, with regard to the geographical scale, all the zones concerned are to be scanned (Figure 2.5) whether they are:

- local, i.e. close to the work itself or an industrial site used to develop the constitutive organic materials;
- regional, if considering the releases which are transported in the environment over relatively small distances and therefore impact rather limited territory;
- planetary, in the case of long pollution transfer distances (the case of air for example) or from resource stocks integrated into a globalized economy (case of bitumen residue in oil distillation).

What, then, are *the issues related to the choice of materials* used for constructions today? The choice of construction materials currently fits in with the issues previously described and is directed towards more economical practices in energy (and better for the environment), due to the rarefaction of oil and natural gas, and towards more and more systematic development of re-using schemes (recycling, regeneration) with the aim of reducing the volume of waste products in the construction sector, and spare resources.

2.4.3. Environmental assessment of materials lifecycle

2.4.3.1. History of LCA: principles

Developed over more than 30 years ago, the lifecycle analysis (LCA) is made up of successive stages [BLO 95] by first considering mass balance results used in the chemistry industry, then the energy reports used after the first 1973 oil crisis. The birth of the lifecycle concept was developed in the USA to be transformed into standard methodology with the support of the EPA (Environmental Protection Agency) which is the American agency for the protection of the environment, and a group of experts [EPA 04] known as the SETAC (Society of Environmental Toxicology and Chemistry) who bring together the skills and profiles of experts in the industry and business world, including public institutions and the world of research. There are certain companies who took over the LCA [BLO 99] to push their products, or to communicate in this domain. As an example, a LCA may make it possible for a company to compare products intended for the same use, to compare generic materials, to compare different processes to minimize environmental impacts, to help to identify product improvement methods but also to improve the competitiveness of their company.

The SETAC led to a scientific approach and then to a set of methodological detailed standards (série ISO 14040 [AFN 06]). Hence, the first works of the 1980s pointed out different standpoints and “battles” between different companies that did

not help LCA to develop as it has been understood as a “weapon” instead of a positive means. As for Europe, assessing the environment using LCA arose afterwards with general standards (i.e. NF X 30400) that, although describing LCA steps, remain a tool for experts.

The lifecycle analysis methodology, extending to the field of construction, continues to be a starting point for the today’s approaches. The LCA follows four steps (Figure 2.6) which are:

- defining the study objectives and the boundaries;
- realizing lifecycle inventory which consists of assessing flows-input/output balance;
- evaluating the potential environmental impacts;
- interpreting the results and its application.

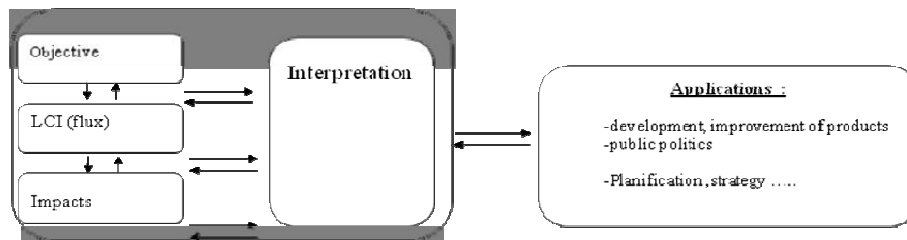


Figure 2.6. Lifecycle analysis phases (according to Standard ISO 14040 [AFN 06])

2.4.3.2. Example of LCI (lifecycle inventory) of an industrial mix plant

This inventory stage makes it possible, starting from the manufactured products, to draw up a complete assessment, substance by substance, of the consumption of renewable or nonrenewable resources, energy and emissions released into the water, the ground, the air as well as waste, all of which are associated with the lifecycle of a product. Figure 2.7 presents a flow diagram of an elementary mixing process, in terms of LCA. The input fluxes which enter the diagram are divided into resource consumption and energy consumption. For the resources, it is a question of binding agent and aggregates which are used to manufacture the bituminous mix. The considered energies are the fuel: natural gas or heavy fuel and the electricity necessary for the process to operate. The output fluxes are divided into bituminous mixes, air pollutants, water pollutants (and then soils), waste and harmful effects (noises and odors). Among these fluxes, only the manufactured bituminous mix, the air pollutants and fuel consumption belong to our analysis.

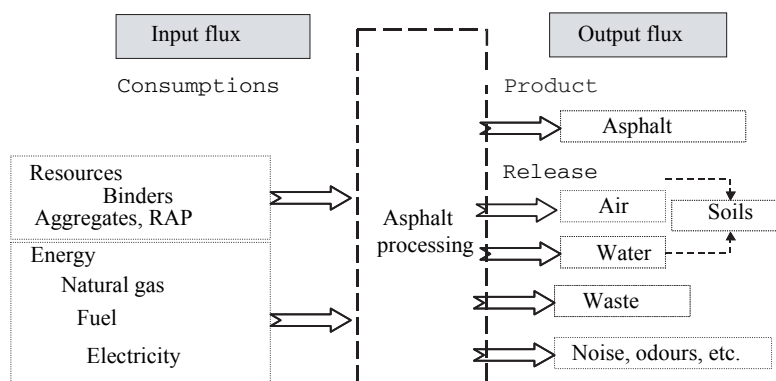


Figure 2.7. General outline of the mixing process in a mixing plant

2.5. Conclusion

By means of an assessment report, there is reason to notice today that there is a limited number of detailed data relating to emissions of the lifecycle of materials and their development process. Moreover, we suggest how to avoid the disparity in the limits of environmental studies performed in the LCA framework, and how it is useful to harmonize the LCIs for each resource. The data collection on consumption ranges and material emissions is in progress. In particular, it can only be definitely realized after a complete characterization of the processes, and undoubtedly of statistical approaches. At this stage, it is useful to question the origin of the data and the method of measurement used on industrial sites before carrying out a comparison of different substructure solutions for the construction works. Any comparison between new and recycled resources must also integrate this inhomogeneous nature, induced by the data before any conclusions are made.

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Chapter 3

Health Risks of Organic Materials used in Construction: What is the Situation Today?

3.1. Problems concerning the health risks, and available tools

The study of the health risks related to chemical agents benefits from structured processes. Epidemiology is the basic scientific method for studying the distributions of health effects in populations, and the relationship between exposure and effect in the population. The quantitative health risk assessment (QHRA) from now onwards constitutes a reference approach in the procedure of studying the health impact of chemical agents. This is the case for evaluations by one of the REACH (registration, evaluation, authorization and restriction of chemicals) procedures. These methods can be adopted for organic materials in civil engineering.

Epidemiology is a scientific method of observing health among populations. We can distinguish several types of epidemiological studies, among which can be found:

- cohort studies which deal with the occurrence of diseases in populations defined by their exposure and followed over a period of time. For example, this is the case of the European study of cancer mortality in workers exposed to bitumen fumes [BOF 03] and its partial analysis in various countries, including France [STU 03]. In these studies, which are carried out in significant number, it is often difficult to analyze the relationships between the level of exposure and its effects, and to separate this influence from various risk factors (other professional or environmental exposures, smoking habits, etc.);

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- case-control (or case-referent) studies which compare the exposure of subjects carrying the studied disease, and the paired referents (subjects without the disease) As an example, a case-control study nested in the European cohort study mentioned previously has been performed. The case-control studies, which are carried out on a limited number of subjects, make it possible to specify exposures better, and to take other risk factors into account.

By comparing exposed and non-exposed subject groups, epidemiology makes it possible to define several types of risk factors [DAB 07]:

- the basic risk (BR), i.e. the probability of a health issue occurring in the general population;
- the relative risk (RR) which is the relationship between the risks of the two groups exposed and studied. For instance, an RR of 5, means that the exposed group presents a risk 5 times greater than the non-exposed group. The relationship, here, is multiplicative;
- the excess risk (ER) which is the risk difference in between the exposed and non-exposed subjects, and represents the proportion of the risk due to exposure. It is obtained by withdrawing from the risk in the exposed group the basic risk (BR), which would have occurred in any case;
- the attributable risk which is the excess risk related to the exposed group's risk. It is expressed as a percentage and thus represents the proportion of the risk amongst the exposed group, which is related to a particular exposure;
- the etiologic fraction of the risk in the general population (EFRp) which is the excess risk in the entire population, and which is due to the exposure studied. It expresses the number of theoretically avoidable cases if the exposure were removed. It is linked to the relative risk but also to the exposure frequency in the population.

Thus, a low risk in the population could correspond to a higher RR agent, if the exposure frequency is low. Conversely, and this is a current challenge for public health, an important excess risk could correspond to a weak relative risk in the case where the exposure frequency is large.

The quality of epidemiological studies particularly resides in acquiring suitable knowledge on professional or environmental exposures. A new discipline, called *exposure assessment*, is being developed, which relates to:

- exposure determinants, i.e. the factors which will influence the exposure: various elements of the process, becoming a pollutant in the various environmental mediums, ways and scenarios of exposing different populations, prevention, etc.;

- the exposure parameters which are in particular the level of exposure (often expressed in pollutant concentration in exposure environments), exposure time expressed by different scales;
- the exposure indicators which constitute synthetic tools usable in studies or following up exposures.

RESEARCH	RISK ASSESSMENT		RISK MANAGEMENT
<i>Epidemiology;</i> <i>Experiment:</i> Harmful health effects of an agent's exposure	<i>Identification of danger</i> (is the agent likely to be the cause of a harmful effect?)	<i>Risk characterization</i> (what is the current or foreseeable incidence of the studied affection in a given population?)	<i>Development of statutory or compensation choices</i>
Knowledge on the <i>extrapolation methods</i> from high to low dose and on the <i>transposition</i> from animal to man	<i>Estimate of the dose-response relationship</i> (what is the relationship between the dose and the response?)		<i>Evaluation of the medical, economic and social consequences of protection choices</i>
Ground measurements; <i>Exposure estimate</i> Populations definition	<i>Exposure evaluation</i> (what are the current or foreseeable exposures in varied circumstances?)		<i>Decision and action of companies' health authorities</i>

Figure 3.1. *Four steps of a quantitative health risk assessment (from [BAR 95] and [NRC 83])*

The quantitative health risk assessment (QHRA) is a structured procedure which is integrated between the scientific procedure for knowledge production, and risk management, similar to a predictive approach. It is conventionally structured in four steps (Figure 3.1):

- Identification of the danger (or the dangerous potential) of a chemical agent (for example), being defined as an intrinsic property of this agent likely to cause harm to health (or the environment within another framework). For instance, the carcinogenicity of a chemical agent is one of its properties which relates to the possibility of causing cancer. With regard to the mechanism of producing harmful effects, the danger is related to the physicochemical properties of the agent which

will influence its interaction with targets within the human organism. Identifying this danger relies on a scientific procedure of the likelihood of the causality. Therefore, as an example, the International Agency for Research on Cancer (IARC) proposes a classification of carcinogenic agents according to four levels of proof, and the European Union according to three levels [CIR 06], [JOC 67].

– Estimation of the dose-response relationship. According to available scientific knowledge and a codified scientific procedure, this stage makes it possible, for the various types of effects, to develop toxicological reference values (TRV) by national and international bodies. According to whether the action mechanism is considered as presenting an effect threshold or not (i.e. a level of exposure from which an effect appears), the toxicity references values will be different. In the case where toxicological reference values may exist, the TRV will be of a daily tolerable dose (DTD) type, expressed in mg of pollutant per kg of body weight per day (mg/kg.j) or of tolerable concentration (TC) type, expressed in mg/m³, in the event of exposure through respiratory tract. The DTD and TC correspond to a maximum theoretical dose (or concentration) which can be administered without effect, even in the sensitive groups. One of the first descriptions of the method as it is used in France, concerns reprotoxic agents [AFS 07]. In the case of an absence of threshold, the TRV is expressed as a unit risk (UR), i.e. the slope of the gradient connecting the level of exposure at very low doses to the probability of an effect occurrence. It is expressed in (mg/kg.j)⁻¹ [MUL 03].

– Population exposure assessment. On the basis of analysis of the exposure's different determinants and parameters, the procedure consists of constructing exposure scenarios which are made on truthful representations. Using measurements which are possible (we cannot measure everything, especially in projects) and modeling the scenarios, it is possible to gain quantitative exposure evaluations, for example as “daily exposure dose” (DED) expressed in mg of pollutant per kg of body weight per day (mg/kg.j).

– Risk characterization, which is a combination of the preceding stages. It consists of calculating a risk or an excess risk by putting in the amount daily exposure dose (DED) and the various toxicological reference values (DTD or TC, UR). It also consists of specifying the uncertainty around this risk estimate and locating it, compared to the risk which is considered acceptable.

This quantitative risk assessment procedure is at the heart of the health security policy defined and implemented in France (and Europe) several years ago with the creation of a network of French public health agencies (in particular AFSSET, French Agency for Environmental and Occupational Health Safety) and the public health plans, including the national security environment strategy, and health-work strategy. The public health strategies propose public health objectives, developed from a public health procedure.

3.2. Available data in organic construction materials

With the exception of bitumens which are researched in epidemiologic or toxicological domains, organic materials are not usually studied as such in international scientific literature. It is possible to find work on their components but which are outside their application, like materials and particularly construction materials. To illustrate the problems surrounding the evaluation and management of health risks related to organic construction materials, two problems will be presented: the current state of knowledge on risks related to bitumens, and the management of the health quality of construction materials.

3.2.1. *State of knowledge on the risks related to bitumens*

Amongst organic construction materials, bitumen is probably the most studied material with regard to health risks. A conference held in Dresden in 2006 made it possible to combine the available data [JOE 07].

Today, everyone recognizes that the bitumen used as binder in road coating (95% of its current use in France) or in waterproofing works, is not made from coal tar, which is a recognized carcinogen [IAR 87]. However, due to their physical relationship and common use over a certain time, the question was raised several years ago regarding its risk of causing cancer.

Many epidemiological cohort studies relating to the cancer risks in bitumen workers were published. They mainly deal with the risk of lung cancer and cancer of the upper aerodigestive tract. In 1994, Partanen and Boffetta published a meta-analysis of studies which were then available [BY 94]. Meta-analysis is a statistical procedure, strictly defined, combining the results of a series of independent studies on a given problem. This combination of results related to seven studies of workers in the waterproofing domain, and four studies concerning the workers of road bitumen mixes. In the first case, the relative risk between exposed and non-exposed was of 1.8 with a confidence interval of 95%, ranging between 1.5 and 2.1. This means that, by associating all these studies, the risk of cancer was almost twice as high (1.8) in the construction workers with experience of working in the waterproofing domain (exposed) than in the non-exposed. The hypothesis of an identical risk in the two groups was not in the confidence interval. In this meta-analysis the relative risk was not statistically significantly different from 1 for those spreading the road bitumen mix (RR = 0.9; CI 95% 0.8-1.0). In their summary, the authors noted that those working in the waterproofing domain had been exposed to coal tar smoke over history during their work, and this constituted a possible confusion factor. They also noted that possible exposures to asbestos and smoking cigarettes could provide partial explanations for this excess risk.

Since then, many epidemiological studies have been carried out, which the European studies referred to above are a part of [BOF 03, STU 03]. In Dresden, Fayerweather [FAY 07] presented a new meta-analysis of forty studies, presenting an important variation in the results. This synthesis, at the same time qualitative and quantitative, related in particular adjusting the data with regard to the exposure to tar smoke, and the statistical study of heterogeneity. After this adjustment, the relative risk is close for the two uses (waterproofing and bitumen road mixes) and close to 1: the combined RR is 1.01 (CI 95% = 0.88-1.17).

Other epidemiological studies are in the process, including a case-witnesses type analysis of the cancer cases studied in the populations of the European cohort.

Apart from the problems surrounding cancer, some studies also show the irritating effects of bitumen smoke, highlighted by respiratory function tests as well as by biological indicators of inflammation [HEI 07].

The development of molecular biology allows the study of the bitumen smoke effect mechanisms on experimental animal models or cell cultures. The current results are difficult to interpret. For example, in a recent study of rats exposed to bitumen smoke, Halter *et al.* [HALL 07] were not able to highlight genetic abnormalities in blood cells of the exposed animals. On the other hand, they were able to identify DNA adducts in the pulmonary and nasal epithelium, increasing with the time and the exposure dose. In a study of those working in the waterproofing domain, Marczyński *et al.* [MAR 07] found that the workers exposed to bitumen smoke expressed a higher level of damage in the DNA (adducts and breakage of DNA strands) compared to the controls. They, however, could not highlight exposure/effects relationships and this does not exclude that other factors could take a part.

Assessment of workers exposure to bitumen smoke is a current field of research. It relates to:

- studying the chemical agents present in bitumen smokes and their analysis, smoke emitted in laboratory conditions and used in experimental models as well as those which the workers are professionally exposed to;
- studying the biological indicators. Among them, the urine tests make it possible to realize, in a way which integrates all the professional exposure methods and the transformation of the chemical agents in the organism;
- studying the respective parts of respiratory and cutaneous exposure made up of bitumen smoke. Studying cutaneous exposure has been carried out for a few years by measuring the pollutants either by patches stuck to the skin, or collected by washing the skin. It is therefore possible to study the relationship between this cutaneous measurement and the urinary metabolites, integrating all the exposures.

McClean [MCC 07] studied the cutaneous and respiratory exposure in workers of the waterproofing industry, using biological indicators and showed that the cutaneous exposure was a significant determinant of the total absorbed dose. Van Rooij and Jongeneelen [VAN 07] summarized their knowledge on this subject. Animal experiments showed that compounds of the bitumen can penetrate through skin, causing genotoxic effects on the skin and other tissues and causing skin cancers. Within humans, genotoxic effects on the skin are not clearly confirmed in the exposed workers. An experimental study of humans in an exposure chamber showed that approximately 50% of the PAH (polycyclic aromatic hydrocarbons) of 3 and 4 cycles can be absorbed through the skin. The collection of available ground data does not currently allow for a conclusion with regard to the proportion of cutaneous exposure;

– studying the determinants of the exposure to bitumen smoke. Deygout [DEY 08] therefore collated the principal determinants in scientific literature for the exposures during road bitumen spreading:

1. *conditions relating to the work station and the tasks to be carried out*: the work function (drivers, operators, etc.); the type of applications (road, waterproofing); the type of direct tasks (bitumen mix application) or annexes (cleaning, maintenance, displacements) and their relative duration in a day's work; the distance between the exposure source and the exposed worker which can be normalized (1, 5, 10 m),

2. *conditions relating to the process, the material and the equipment*: the type of process and the conditions (manual or mechanized applications); the tools and the type of machines used; the existence technical means of prevention (exhaust ventilation); the level of production (pavement surface); material application temperatures; the type of relative material (standard and characteristic of the bitumen); the type of bitumen (mixture) and its bitumen and adjuvant content (polymeric modified bitumens); the use of tack coat (emulsions) and the type used; additional sources contamination agents nearby (current use of gas oil for cleaning and fuel in the machinery),

3. *conditions relating to place*: localization of the building site and particularly the containment level (field, narrow street); the presence of road traffic or similar,

4. *conditions relating to the weather conditions, climate and season*: the temperature, the presence of wind, its force and its direction (upstream/downstream across), relative humidity and rains, atmospheric pressure,

5. *conditions relating to the worker*: professional practice (habits, productivity, age), dress code and respecting work uniform, wearing individual protective gear, personal hygiene (hand washing),

6. with these determinants related to work, the *conditions relating to the exposure measurement* are added: sampling strategy and analytical methods used, type of samplers used (individual, portable or static).

It is not possible to go into detail here for all of these determinants. Deygout [DEY 08] highlights, for example, that the particulate and volatile fractions of the pollutants measured near the respiratory tracts of the workers in building sites where bitumen mix spreading is produced, represent two different kinds of chemical agents, and their predictors are also different: the process and the bitumen temperature have a large effect on the PHA particulate fraction while the noticeable effects on the soluble fraction are the external conditions.

In conclusion, studying exposures and the effects of bitumen smoke on health remain as a field of interest and study, at the same time on the scientific and public health front. Regardless of the advances in knowledge, risk prevention remains a priority.

3.2.2. *Quality of inside air and health qualification of construction materials*

The problems concerning health risks of organic construction materials are a component of the inside air quality.

The quality of inside air is a question which is both complex and important to the current public health. First of all, this is because it relates to the entire population – on average, we spend 22 out of 24 hours inside, on average 16 hours 10 minutes in our accommodation [ZEG 08] – and because the air that we breathe can have effects on our health from annoyances to aggravation, or the development of pathologies such as respiratory allergies, for example.

Interior pollution comes from three primary sources: combustion apparatus (carbon monoxide, nitrogen dioxide), building components, including equipment and furniture (formaldehydes, organic volatile compounds, fibers) and human activity (use of domestic products, DIY, gardening, mites, mould, tobacco, etc.).

The volatile organic compounds (VOCs) found in the inside air are numerous (several hundreds), some of which of a very weak amount. Their sources are also very numerous. The VOCs are more numerous are more concentrated inside than outside, taking into account the multiplicity of sources.

In 2004 and 2005, the French indoor air quality observatory (OQAI) carried out a national campaign to study the quality of indoor air, representing the situation of the 24,000,000 main homes in continental Metropolitan France. It became possible

to measure the air of 567 main homes and to question 1,612 residents in 74 towns in of 55 *départements* (boroughs). Therefore, approximately 30 parameters were followed over one week. The VOCs are detected in 2.3% (2-butoxyethyl acetate) to 100% (acetaldehyde, formaldehyde, hexaldehyde, toluene, xylene) of the accommodations according to the compounds. The aldehydes are among the most frequent and most concentrated molecules found [KIR 07].

The aldehydes, whose most well-known compound is formaldehyde, belong partly to the family of VOCs. With low molecular weight, this substance (resulting in particular from the reaction between ozone and certain VOCs present in the air) has the property of being a gas at room temperature. The main sources of aldehyde emission are construction and decoration products: insulating foams, lacquers, adhesives, varnishes, coatings, but also majority of agglomerate and laminated wood. Many every day use products (maintenance products, papers, etc.) and certain textiles contain aldehydes. Lastly, aldehydes are also present in certain pesticides.

Formaldehyde has a double topicality. On the one hand, this molecule was classified by the international research center on cancer as being carcinogenic to humans (group 1) and these problems primarily affect exposed workers, some of which who are in the production of agglomerate wood panels. In addition, the exposure to formaldehyde in moderate concentrations may cause a great number of symptoms of irritation, including a sensation of temporary burning in the eyes and nose, as well as a sore throat. In a domestic environment, sensitization to common pneumallergens and the development of asthma would be favored, and the bronchial response to allergens would increase, in subjects with asthma. The mechanisms of these responses are complex [DAL 04], [PON 07]. Exposure frequency, on the one hand, and the growing increase of asthmas particularly children on the other, suffice to make it a major issue of public health.

The French national health environment strategy 2004-2008 [SAN 09] comprised 45 actions, including 12 priority actions. Within this framework, the third objective aimed at protecting the general population from the pollution inside the buildings. The purpose of action 14 was to improve knowledge of the interior air quality determiners and to reinforce the regulation. Action 15 (priority) was to label the health and environmental related characteristics of construction materials. The mid-term objective (2010) was to strive for 50% of construction products put on the market being labeled. This objective follows the orientation of the European construction products directive (CPD) which provide this ECC regulation on construction products aimed at the French market as in the ECC.

For several years the evaluation protocols of the emissions have been proposed on a European level. In 2006, AFSSET (in partnership with the CSTB, a French research organization for building construction), released a notice similar to a health

risk evaluation procedure, concerning the volatile organic compounds and formaldehyde emitted by the products of construction [AFS 06].

The national reference database INIES [INI 09] on the environmental and health related characteristics of construction materials and products gradually recorded the environmental and health declaration forms for construction products provided by manufacturers or trade unions.

The PNSE2 (French second national health and environment strategy) under preparation and which integrates the *Grenelle de l'environnement* solutions, seeks to reconcile energy conservation and interior air quality. For this, it seeks to:

- limit the inside air pollution sources. This forbids CMR1 and 2 and implements obligatory labeling with regard to the emissions (in particular VOCs and formaldehyde) from construction and decoration products;
- air, ventilate and use air-conditioning healthily;
- manage and monitor the inside air quality better.

It should simply be recalled that “the interior air quality is managed by the combination of three determining factors: occupants, sources (of contamination) and air movements. It is advisable to act simultaneously on each one of these axes; were we to neglect one of them, the strains on the two others would be destroyed; it is a question of putting a real collection of coordinated measurements into place” [COC 08].

3.3. Conclusion

The evaluation and management of the health risks of organic construction materials still remains an under-explored field. The examples presented show that they can be approached as they are (bitumens) or as an element of vaster health problems (material position in interior air quality). According to whether they concern the exposed workers or the general population, they will have different repercussions.

A new era could well arrive with the implementation of the European regulation REACH, which will enforce the evaluation of the risks of chemical agents such as substances, preparations or articles. Construction materials are also concerned. Beyond information on the materials, which are not always specific to their use in the construction industry, we can expect that the evaluations to relate to exposure scenarios.

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Chapter 4

Ecological Impacts of Organic Construction Materials: What is the Situation Today?

4.1. Problems and available tools

Using organic materials in the field of civil engineering requires us, as for other potentially pollutant materials, us to preliminarily check their non-impact on ecosystems. On the international front, we are currently lacking in methodologies for evaluating ecological risks which are adapted to such materials and their usages. In addition, the existing material test processes to date primarily relate to characterizing materials themselves, and only slightly reflect their behavior and impact when they are in their environment. Therefore, it is necessary to develop methodologies which make it possible to study the environmental behavior of organic materials “in context” or “in a scenario”.

To do so, two types of approaches are possible:

- The first is based on observations and studies in situ. It is a vital stage in order to understand the response of ecosystems subjected to anthropic disturbances. However, due to the complexity of natural environments, it only provides one global response and only leads to one official report (upstream-downstream, before and after disturbance, etc.). This makes it possible, with some difficulty, to identify the different mechanisms involved and, consequently, to predict future impacts of using such a material on our ecosystems.

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– The second approach, which aims to make these predictions, corresponds to the methodologies used for evaluating ecological risks (or ecotoxicological risks, if we are only referring to the impact of pollutants). These methodologies, which have been more developed in other fields, require a joint study of the term “source” of pollution (characterization of the intrinsic ecotoxicity of materials used, quantification and study of the spatial-temporal variability of pollutant flows given off by the construction, etc.), of what becomes of these pollutants in the environment (identification and quantification of the transfer, dispersion, retention and transformation mechanisms of the pollutants), as well as studying the response of the communities living with these pollutants under specific exposure conditions of the studied scenario. Figure 4.1 represents the main “type” of stages of an ecological risk assessment; stages which are based on the results of these studies.

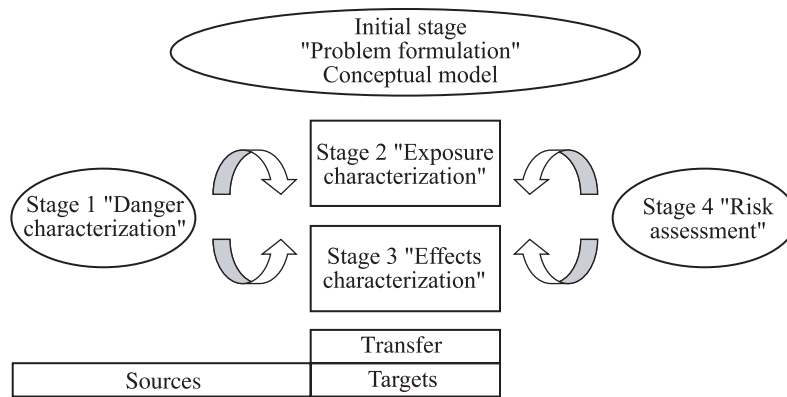


Figure 4.1. Four stages of ecological risk assessment (ERA) methodology

Developing a procedure adapted to organic materials used in construction is to be further developed in an interdisciplinary framework (chemists, geotechnicians, hydrogeologists, biologists, etc.), and can benefit from recent works carried out to study the environmental behavior of other potentially polluting materials. Among them here we can particularly use the example of the US-EPA (US Environmental Protection Agency) methodology for ecological risks assessments related to polluted sites, the ADEME (French Agency for the Environment and Energy Management) methodology for studying the eco-compatibility of mineral waste transformed into materials, the CETMEF (French Institute for Maritime and Waterways Studies) methodology of ecotoxicological risk assessment related to sediment dredging, and the SETRA (French Technical Department for Transport, Roads and Bridges Engineering and Road Safety) methodology of ecotoxicological risk assessment related to road infrastructures.

A synthesis of these four methodologies is presented in Table 4.1.

	ERA polluted sites	Eco-compatibility scenarios of waste development	ERA dredging sediment discharge	ERA road infrastructures
Organism/s carrier/s	EPA (US)	ADEME (France)	CETMEF (France)	SETRA (France)
Conception	EPA (US)	INSA-POLDEN + 9 French teams	ENTPE + CEMAGREF (France)	ENTPE/SETRA/CETE (Northern France)
Year	1998	2000	2001	Planned for 2011
Status/Role	Methodology to assist with managing contaminated sites	Methodology to assist with waste management	Methodology to assist with managing contaminated sediments	Methodology to assist with managing run-off water and the conception of retention works
Assessment of pollution emissions	Modeling and/or experimental measurements. Integration of available field data	Idem ENV 12-920 (Long-term waste behavior norm)	Column percolation tests, sediment age tests	National bibliographical data and/or measures on similar sites
Assessment of pollutant transfers	Modeling and/or experimental measurements. Integration of available field data	Parametric tests + integral test	Column percolation test	Theoretical calculations
Assessment of impact of pollutants on our ecosystems	Use of toxicity or reference values and/or experimental measurements (bio-tests) Integration of available field data	Tests on microcosms and mesocosms	Tests for ecotoxicity + microcosms	PNEC (Predicted No Effect Concentration) from international databases and/or ecotoxicity tests
Final risk characterization	Risk quotient calculation or comparison exposure/relation profiles between dose and effect	Comparison of pollutant flows emitted or convoluted with acceptable flows + expertise	Quotient calculation (PEC/PNEC) + expertise	Quotient calculation (PEC/PNEC) + expertise
Nature of the matrices	Grounds polluted with various pollutants	Mineral waste	Sediments with mineral and organic pollutants	Run-off water with metals, particularly PAH

Table 4.1. *Summary of the four Ecological Risk Assessment methodologies presented*

4.2. Works available in the field of organic construction materials

We saw in the introduction that there are currently no ecological risk assessment methodologies dedicated to the use of organic materials in construction. In international scientific literature however, we can find a certain number of works which partially deal with this problem. These works can be classified into two main categories:

- works which characterize the intrinsic ecotoxicity of organic materials;
- works relating to coupling water behavior tests (leaching tests, for example) and ecotoxicity tests.

A summary of this work is presented in Tables 4.2 to 4.5.

Study carried out	Behavior tests performed	Ecotoxicity tests performed	Main results	Authors
Bitumen leaching behavior	- Leaching tests in lab - PAHs emitted in leachates	None	PAH concentrations in leachates lower than the fixed boundary conditions for drinking water by the European Union	Brandt A.C. and De Groot P. [BRA 01]
Leaching behavior of nine bitumens and one asphalt	- Dynamic and static leaching tests, based on existing Dutch tests for construction materials - PAHs emitted in leachates	None	- Static Tests: weak PAH salting-out, stabilization after five days of leaching, and up to thirty days of leaching - Dynamic Tests: weak salting-out after 30 hours of contact	Bowen C., De Groot P. and Brandt A.C. [BOW 00]
Behavior with the leaching of a bitumen (<i>pure vacuum residue has</i>) and of an asphalt (<i>year oxidized bitumen/asphalt</i>)	Three tests of Dutch and British leaching - Follow-up of the PAH, the BTEX and the metals emitted in the leachates	Nothing	Non-detectable PAHs and metals in two bitumen leachates Ethylbenzene and toluene traces in the oxidized bitumen leachates	Eurobitume Report - [EURO 05]

Table 4.2. *Synthesis of work completed on bitumens*

Study performed	Behavior test performed	Ecotoxicity test performed	Main results	Authors
Behavior of concrete coating leachates produced during the construction of a tunnel in Norway (cement projection containing acrylamide)	Collection in situ of leaching water and calculation of the exposure concentration of the organisms in the river	- PNEC research in literature - Calculation of the ecological risks generated for the local river	Significant risk reached for one of the exposure scenarios	Vik E.A. <i>et al.</i> [VIK 00]
Behavior of coating leachates containing acrylamide and methyl acrylamide produced during tunnel construction	In situ follow-up of leachates concentration, according to time	Ecotoxicity tests	Real ecotoxicological risks in the event of "catastrophic" scenarios	Weideborg, Kallqvist <i>et al.</i> , [WEI 01]

Table 4.3. *Synthesis of the work completed on concrete coating*

Study performed	Behavior tests performed	Ecotoxicity test performed	Main results	Authors
Behavior of water with mortars and superplasticizer adjuvants	Bibliographical study on the migration of molecules during contact with water	None	Decomposition and possible migration of the molecules during contact with very alkaline water from the mortars	Rossini D. and Moulin I., [ROS 03]
Risk assessment related to the use of some superplasticizers (thiocyanates and acid resins)	Leaching tests on several materials	Use of acute theoretical toxicity and chronic values for fish	Ecological risks proven in certain exposure scenarios	Andersson and Stromvall, [AND 01]
Environmental impact of superplasticizer (naphthalene sulfonate condensates)	Leaching tests on several finished products + theoretical emission model	Use of theoretical toxicity values		Galli and Kiayias, [GAL 96]

Table 4.4. *Synthesis of the work completed on mortar and concrete adjuvants*

Study performed	Behavior tests performed	Ecotoxicity tests performed	Main results	Authors
Environmental assessment of pillars containing plastic materials recycled on river water quality	Nothing (in situ follow-up of organic and mineral pollutants salting)	None	- Weak salting-out to be linked with impurities integrated into recycled plastic - Limited pollution in water compared to wooden pillars (pesticides)	Xie <i>et al.</i> , [XIE 97]
Study of emissions from stabilizer Chimassorb 944, from low density polyethylene membranes used in bed deposits	- Leaching tests simulating burial - Follow-up of the molecule in the leachates	None	- Emissions according to desorption/diffusion, but also biological decomposition - Concentrations lower than the toxicity thresholds in literature	Haider and Karlsson, [HAI 99]
Use by US Navy of five biodegradable polymers rejected into the environment	Incubation of polymers with 45°C during 90 days: - in distilled water - in sea water	Tests of ecotoxicity (acute and chronic) on: - seven species watery (shellfish, fish, micro algae, etc - two plants (emergence and growth of the stems and roots)	- Observation of an ecotoxicity moderated with certain polymers and on certain aquatic and land species	Arfsten <i>et al.</i> , [ARF 04]

Table 4.5. Synthesis of the work completed on the plastics

4.3. Prospects for organic materials used in construction

Evaluation risk assessment methodologies currently at work are primarily concerned with mineral materials and/or materials other than organic used in construction.

For these latter materials, we can benefit from the existing tools:

- by referring back the general methodological approach of the methods presented (definition of a scenario, study in line with the words “source”, “transport” and “impact”, etc.) as well as articulating the experimental tests and modeling stages that they propose;

- then by adapting the methods concerned to organic materials by taking account of their specific properties.

One of specific properties of these materials lies in their more or less biodegradable nature (or biodeteriorable), which may influence the term “source” of pollution to a significant degree, as well as becoming environmental pollutants. This biological decomposition is thus a fundamental parameter to take into account for the global ecological risk assessment of organic materials. For this study, we can also use existing tools, such as the many standardized procedures which exist on the international front (see section 4.6), intended to assess the resistance of various types of organic materials (mainly plastics and paints) to biological agents. These procedures can, with a certain number of modifications, be adapted to the study of microbial alteration for the majority of other organic materials used in construction.

Among the tests recommended for these procedures, we can distinguish three main categories:

- tests in artificial solid culture environment;
- tests in artificial liquid culture environment;
- simulation tests (more or less complex, implementing a real environment or simulating reality).

The classic approach consists of, as with characterizing biological decomposition of chemical substances [OCD 92], putting a material into contact with a microbial agent over several weeks (generally a pure strain or a mixture of micro-organism pure strains) under laboratory conditions favorable to microbial development. Then, after the incubation period, the parameters of material description are measured and compared to the initial parameters. The biodeterioration is therefore measured by the alteration of the material’s essential characteristics.

These tests provide partial information to correctly envisage this evolution in real conditions. Indeed, the influence of the exterior environment can be considerable in the biological evolution of a material, particularly indirect biodeterioration mechanisms which can turn out to be significant. Therefore, it is often necessary to try to reproduce or simulate real environmental conditions which will reflect those of the material during use. We are then directed towards the “simulation tests”, which are generally longer and more complex than the accelerated tests.

The transposition of the procedures developed for a type of material (generally plastics or paints in standardized procedures) to another type of organic material is only possible after adapting the experimental conditions. The main factors which must be reconsidered are the nature of the inoculum, the mode of inoculation, the incubation conditions, and the composition of the incubation environment.

Another characteristic of organic compounds is their sensitivity to the substances with an organic solvent character. Therefore, when organic materials are used in

civil engineering, we will have to take into account the fact that whether or not they are subjected to run-off water rich in hydrocarbons (urban run-off, for example), which can play the part of a co-solvent and to support the dissolution of potentially polluting organic substances.

4.4. Conclusion

The use of organic materials in construction probably has only a little impact on ecosystems in many cases. On the contrary, in certain situations, this usage could disturb aquatic or terrestrial ecosystems significantly, as well as adding to the degradation of drinkable water resources.

The parameters which can lead to one or another of these situations are a function of the material itself, but moreover, of the context of their use. This is why the ecological risk assessments that they generate requires as preliminary, just like for other potentially polluting materials, to precisely define the scenarios in which they will be implemented. With these scenarios being defined, we will be able to develop ecological risk assessment methodologies adapted to their specific properties, by using existing methodologies. This will particularly account for the more or less biodegradable character of organic materials, as well as their sensitivity to substances displaying organic solvent characteristics.

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PART 2

Organic Polymers as Building Materials

Chapter 5

Organic Polymers

5.1. Introduction

5.1.1. *Brief history*

Natural organic materials (wood, horn, skin, etc.) have been used since the dawn of humanity. Textile fabrication from vegetal fibers (linen, cotton, etc.) or from animals (silk, wool, etc.) reached an “industrial” stage from the Middle Ages onwards. The idea of changing raw matter by specific physical or chemical treatment (dyeing fibers, leather tanning, etc.) is practically as ancient as the applications themselves. In the 19th century, however, a new idea emerged: chemically modifying natural substances (fibers, skins, etc.) so as to make them completely different from the natural forms. The two main processes are:

- *rubber vulcanization* (Goodyear 1839) which is open to a large variety of applications, such as air chambers (Dunlop 1888) and pneumatics (Michelin 1891);
- *cellulose nitration* (Parker 1862), which quickly led to the creation of celluloid (Hyatt 1869). At the time, it is believed that this was developed to replace the ivory used for making snooker balls.

Synthetic materials such as Bakelite (1909), which owe nothing to natural materials, would not appear before the 20th century. The great thermoplastics (polyethylene, poly (vinyl chloride), polyamides, etc.) came about between the 1930s and 40s. It was not until the 1950s and the boom of the consumer society that the real explosion in the polymer industry took place. This transition coincided with

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a new formation process: injection molding, which made it possible to make all sorts of objects at a quicker rate.

Is it possible to imagine consumer society without plastics, and the explosive development of plastics without injection? We will let historians answer these questions.

Scientific developments specific to polymeric materials have approximately a century of prehistory (1830-1930), a century in which researchers collected observations. For example, Joule, in 1857, reported on the specific character of the thermoelastic behavior of rubbers. However, it was not before the 1920s and 1930s that the macromolecular structure in polymeric chains was firmly established (Straudinger, Nobel Prize). In the 1940s and 1950s, P. Flory (Nobel Prize) built the physical foundations for polymer science by carrying out a harmonious fusion between structural chemistry, mechanical statistics and thermodynamics. At the beginning of the 1970s, P.G. de Gennes (Nobel Prize) introduced scaling laws, which gave a new impulsion to polymer physics.

Great synthesizing methods (ionic and radical polymerization, copolymerization, polycondensation) were already discovered before the end of WWII. In the 1950s and 1960s, Ziegler and Natta (Nobel Prize) invented the stereospecific catalysis which quickly led to high density polyethylene and isotactic polypropylene, two of the most important industrial polymers in terms of tonnage. In recent decades, new synthesizing methods have emerged: group transfer polymerization, controlled radical polymerization, metallocene catalysis, etc. But the classic methods never stopped being perfected at the same time. This is what is meant when we speak of the 5th, 6th or even 7th generation, in the case of polyethylenes for pipes or polypropylenes for injection molded parts. Each stage in this progression constitutes a significant level of progress in relation to the previous stage.

5.1.2. *Polymers among materials*

Where should we place industrial organic polymers in the category of materials? Here we are dealing with a sub-category with diffuse boundaries. It essentially contains organic substances, meaning those based on carbon chemistry, but we are also including semi-organic substances such as organo-silicic polymers, or even inorganic substances such as polyphosphazenes. In this sub-category, only types with high molecular mass (typically higher than 10 kg mol⁻¹) carry the status of material (usable in solid state), hence the denomination of high polymer or macromolecule. However carbons (diamond, graphite) are excluded from this category. By their structure (non-deformable networks) and their processing method,

carbons belong to the ceramic family. Finally, high polymers consist only of linear chain macromolecules (eventually branched) and deformable networks.

We can see that it is not easy to outline the precise contours of industrial organic polymers. However, three general characteristics allow us to distinguish them from other materials quite clearly.

5.1.2.1. *Organic characteristic*

This presents both great advantages and disadvantages. The advantage is the low density ($\rho \leq 2.5$) linked to the low atomic mass of constitutive atoms (C, H, O and N, essentially). We know that density plays an important role in dimensioning mechanical parts [ASH 01]. The disadvantage is that only a few organic structures can survive a short exposure to 400°C, and a long exposure (10 years) to 250°C. From this point of view, compared to ceramics and metals, polymers are “the bottom of the class”. However, for an immense variety of applications, a ceiling temperature slightly above room temperature is sufficient. Thermal instability is not, then, an unacceptable defect.

5.1.2.2. *Polymers have a chain structure or an easily deformable mesh network*

Such a structure is characterized by the existence of strong covalent bonds in line with the chain (typical energy density: 2 to $10 \cdot 10^{10} \text{ J.m}^{-3}$) and weak interchain (Van der Waals) bonds (typical energy density: 4 to $8 \cdot 10^8 \text{ J.m}^{-3}$). In every inorganic material, however, each atom is linked to neighboring atoms by strong bonds (covalent, ionic, or metallic) in the three directions of space. We see, then, that it is relatively easy to deform a polymer by modifying the chain conformation without breaking the strong bonds of the macromolecular skeleton. In contrast, in an inorganic material, every deformation must overcome the strong bonds. As a result, polymers are the least rigid materials (Young’s modulus $E < 5 \text{ GPa}$ for the majority of isotropic polymers against $E \geq 10 \text{ GPa}$ for the majority of industrial inorganic materials). The “one-directional” character of the strong bonds in polymers is clearly demonstrated in the case of linear polyethylene: its Young’s modulus is generally smaller than 1 GPa, and its ultimate stress is smaller than 40 MPa in the injection molded or quasi-isotropic extruded parts. Yet, as ultra-oriented fibers, (bullet-proof vests, for example) the modulus exceeds 100 GPa and the ultimate stress increases to higher than 1 GPa; properties which are similar to many metals. In the case of fibers, tensile loading directly strains the covalent bonds of the macromolecular skeleton, hence the observed properties.

Another important consequence of the low rigidity of polymers: their low thermal conductivity, which is primarily related to the propagation speed of the elastic waves in non-metallic materials. The polymers are, then, thermal insulators, generally with a conductivity value in the order of 0.1 to $1 \text{ W.m}^{-2}.\text{K}^{-1}$ whereas it is

approximately ten times higher in porous ceramics (concrete, brick, rock, glass, etc.) and one hundred to a thousand times higher in metals.

The characteristics of low rigidity and thermal insulation may constitute advantages or disadvantages, depending on the application considered. But, the advantage of polymers is that fillers can be incorporated into them (strengtheners or conductors) or they can be used as foams, so as to vary the considered properties in very wide proportions.

5.1.2.3. Role of temperature and strain rate

All materials are characterized by a major transition (glass transition for amorphous, melting for crystallines) which marks out the route of the solid state to the liquid state. Far from this transition, their mechanical properties are only lightly dependent on temperature (T) and strain rate ($\dot{\epsilon}$). On the other hand, the behavior is greatly influenced by these parameters around the transition. What clearly distinguishes polymers from other industrial materials is the fact that their glass transition (T_g) and melting (T_f) temperatures are relatively close to room temperature, typically $-100^\circ\text{C} \leq T_g$ and $T_f \leq 400^\circ\text{C}$. We therefore expect the mechanical behavior to be more or less greatly affected by variations in temperature and loading rate (or loading times, in the case of static strains).

For all materials, let us summarize that:

$$0.5 \leq \frac{T_g}{T_f} \leq 0.8$$

In addition, we note that the melting enthalpy ΔH_f of polymers is not so different from that of metals. If we consider the equilibrium free energy of melting ΔG_f at constant pressure:

$$\Delta G_f = \Delta H_f - T_f \cdot \Delta S_f = 0$$

$$\text{hence: } T_f = \frac{\Delta H_f}{\Delta S_f}$$

If the melting point of polymers is lower compared to inorganic materials, it is because the entropic term ΔS_f of the thermodynamic balance of melting is higher for polymers than for other materials. The relative importance of the entropic term (linked to the diversity of conformations that can be adopted by a chain) is one of the most characteristic traits of polymer physics.

5.2. Polymer structures

Let us remember that by a polymer, we refer to a substance which is made of macromolecules, whose structure is characterized by the repetition of a large number of a group of atoms, called structural unit, repetition unit, monomer unit or constitutive repeat unit.

5.2.1. Three structure scales

Generally, we distinguish three main structure levels, all three capable of having a major influence on the usage properties of the material. Each level concerns specific conceptual and experimental tools. The study of the properties of polymers is therefore nearly always a multi-scale problem, and the analysis of the structure is a multidisciplinary problem. The characteristics of these three structure levels are summarized in Table 5.1.

Structure level	Entity	Main characteristics	Experimental tools	Conceptual tools
Molecular	Monomer unit	Chemical reactivity Polarity/cohesion Flexibility dynamics	IR NMR	Organic chemistry
Macromolecular	Chain Network	Chain size Cross-link density	SEC Viscosimetry, sol-gel	Physico-chemistry of polymers
Supramolecular	Crystalline lamella Spherulite Various heterogeneities	Size Rigidity Anisotropy	Microscopy Thermal analysis Radiation scattering	Material science

Table 5.1. Three large structure levels (IR: infra-red spectrophotometry; NMR: nuclear magnetic resonance; SEC: steric exclusion chromatography
Only the main analytical tools are quoted)

If polyamides have a higher melting point than polyethylenes, it is above all because the monomer unit of polyamides is much more cohesive than that of

polyethylenes. The differences in polymer melting points are primarily linked to differences in structure on a molecular level. The other structure levels (molecular mass, lamella size, etc.) can indeed play a role, but to a second order.

If polyethylenes are much stronger than paraffins with the same molecular structure, it is because they have a higher molar mass. Here, the difference is found on a macromolecular level. The strength in solid state and the viscosity in molten state are both properties which are greatly influenced by the size of macromolecules.

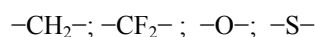
If branched polyethylenes have a Young's modulus of 200-300 MPa, whereas linear polyethylenes have a modulus of 800-1,000 MPa, it is because the linear polyethylenes are clearly more crystalline than the branched polyethylenes. Here, rigidity is essentially linked to crystallinity, meaning, to an ordered arrangement of chains, one in relation to another, on the supramolecular structure level.

5.2.2. Molecular structure

Organic synthesis can generate a quasi-infinity of macromolecular structures. However, we can observe that the large majority of industrial polymers have been made from a relatively limited number of groups which seem to be the structure's building blocks. These groups can be classified according to their main function in the monomer unit. We distinguish the following functions.

5.2.2.1. Ball joints

These groups allow for easy rotation, they allow the chain to be flexible:

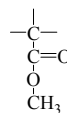


Substituted aliphatic carbons are equally ball joints, but their flexibility tends to decrease with the size and mass of lateral groups.

For example:



Polystyrene

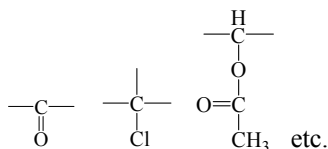


Polyacrylates

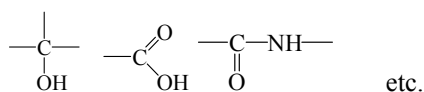
5.2.2.2. Dipoles

These groups display electric dissymmetry, therefore they will be able to more or less strongly contribute to cohesion (interchain interaction). We distinguish:

– moderately cohesive groups:

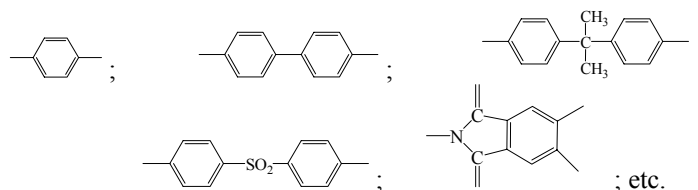


– strongly cohesive groups (hydrogen donors in hydrogen bonds):



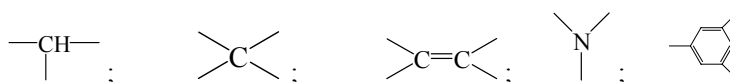
5.2.2.3. Rigid elements

These non-deformable groups will reduce the flexibility of the chains so much that they are bigger:



5.2.2.4. 3D junctions

The functionality group strictly higher than 2 is the basis for branching or cross-linking:



The two large physical properties which essentially depend on the molecular structure scale are *cohesion* and *chain flexibility*.

Cohesion is related to interactions (secondary bonds) between the chains. We characterize this by the cohesive energy density d_c defined by:

$$d_c = \frac{E_{\text{coh}}}{V}$$

where E_{coh} is the sum of all the intermolecular interaction energies in volume V of the material. d_c is an energy density, which can be expressed in pressure units.

For the majority of industrial polymers:

$$250 \text{ MPa} < d_e < 800 \text{ MPa}$$

At the low end of the interval, we find apolar polymers, such as polytetrafluoroethylene (PTFE), polyethylene (PE), polypropylene (PP), etc. At the top end of the scale, we find the most polar polymers, such as poly vinyl alcohol (PVAL), poly acrylic acid (PAA), etc.

We note that PTFE, PE and PP appear amongst the most hydrophobic polymers, while PVAL and PAA are soluble in water. Interactions between polymers and solvents are, in effect, controlled by the following rule (Hildebrand 1949): the closer the cohesive energy densities, the more the polymer interacts with the solvent.

We can define the solubility parameter by: $\delta = d_e^{1/2}$.

The solubility parameters of industrial polymers schematically vary between $13 \text{ MPa}^{1/2}$ (PTFE) and $27 \text{ MPa}^{1/2}$ (PVAL).

NOTE.— The Hildebrand rule (maximum interaction for $\delta_{\text{polymer}} = \delta_{\text{solvent}}$) is only approximate. It is only used to indicate general tendencies.

Dynamic flexibility is defined as the chain's aptitude to deform under thermal agitation. The strain results from elementary rotations of the groups around the macromolecular skeleton bonds.

The glass transition temperature (T_g) which marks out the passage from low amplitude localized mobility to high amplitude cooperative mobility (see further down), is a good criterion for chain dynamic flexibility. Three main factors affect chain flexibility by hindering rotations:

- interchain interaction (meaning cohesion). We have seen that cohesion was considerably stronger in PVAL ($T_g = 120^\circ\text{C}$) than in PP ($T_g = 0^\circ\text{C}$) – two polymers whose monomer units have the same geometry;

- the size of lateral groups. This is why polystyrene (PS) has a T_g (105°C) higher than that of polyvinyl chloride (PVC, $T_g = 80^\circ\text{C}$), whilst the latter is more cohesive;

- the mass of non-deformable groups which increases the inertia of corresponding segments and makes their rotation more difficult. This factor tends to prevail in the high temperature domain where the interchain interactions tend to be negligible. We can observe this effect in the sequence in Table 5.2. The effect of the groups' mass is represented by the rigidity parameter F , defined by:

$$F = \text{molar mass/number of bonds capable of rotation}$$

Acronym	Structure	T _g (°C)	F (g.mol ⁻¹)
PBT		60	24.4
PET		80	27.4
PEEK		140	48
PC		150	63.5
PSU		190	110.5
PESU		210	116
PPMI		350	191

Table 5.2. Characteristics of some polymers containing aromatic rings in the chain

In Table 5.2, we consider that the isopropylidene ($-\text{C}(\text{CH}_3)_2-$) and sulfone ($-\text{SO}_2-$) groups are not ball joints because they block rotations of aromatic nuclei on each side.

We see in Figure 5.1 that T_g tends to increase in a quasi-linear way with F .

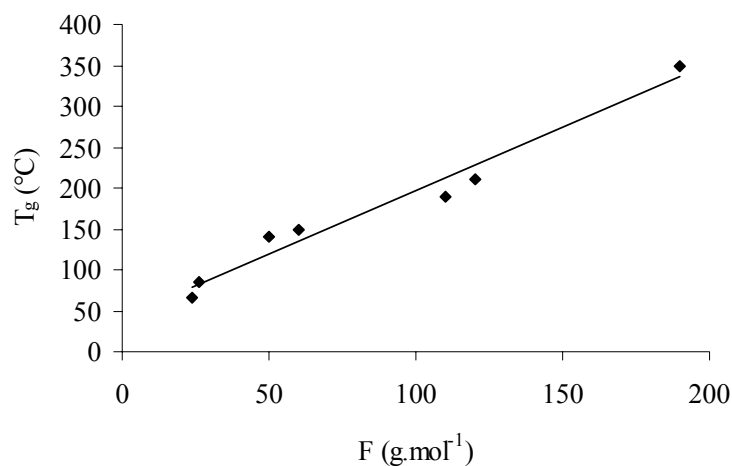


Figure 5.1. Variation of vitreous transition temperature (T_g) with the rigidity parameter (F) (see text)

In addition to the physical properties above, *the molecular structure determines important aspects of the chemical properties*, particularly the reactivity to oxidation and hydrolysis. In the case of oxidation (thermally or photochemically initiated), the weakest structures are aliphatic CH bonds. In the case of hydrolysis, the reactivity is linked to the presence of hydrolysable groups, for instance esters, in the chains. We will return to these aspects in the chapter on aging.

5.2.3. Order in the chain – copolymers, stereoisomers, conformations

5.2.3.1. Copolymerization

A polymer based on a single type of monomer $-(A)_n-$ is called a homopolymer. The combination of two monomers A and B may result in a large variety of structures. The following can be distinguished:

- statistical copolymers: - A-A-B-A-B-B-B-A-A-A-B-A-A-B-B;
- alternate copolymers: - A-B-A-B-A-B-;
- block copolymers: - A-A-A-A-A-B-B-B-B-;
- grafted copolymers: -A-A-A-A'-A-A-A-A-A-
B-B-B-B-B-B-B-B-

Combinations of three (or more) monomers also exist, for example: ABS = acrylonitrile – butadiene – styrene. Very schematically:

– alternate copolymers are equivalent to a homopolymer $[-(AB)-]_n$;

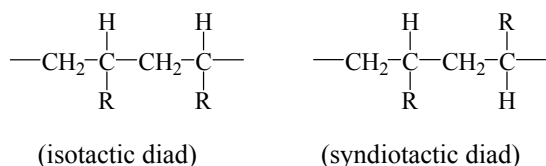
– statistical copolymerization creates a material with intermediate physical properties between those belonging to the homopolymer $[-(A)-]_n$ and $[-(B)-]_n$. Therefore, one can use this to more or less tightly control the properties. We can also use statistical copolymerization to create a certain disorder in the chain, and thus limit crystallization;

– block copolymerization may produce new properties: the sequences $[-(A)-]_n$ and $[-(B)-]_n$ are generally non-miscible. There is, then, a phase separation, but both phases are linked together by covalent bonds, which will ensure a good interfacial adhesion. This type of morphology is used in abundance to improve polymer impact strength (ABS, copolymers, ethylene-propylene, etc.);

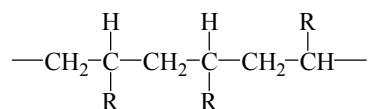
– grafted copolymerization is particularly used to modify surface properties: printing, wetting, adhesion etc., when the polymer “trunk” is apolar, polyethylene and the grafted polymer is highly polar, for instance polyacrylic acid.

5.2.3.2. Stereoisomery

When the monomer is dissymmetric (for example, vinyl monomer $\text{CH}_2=\text{CHR}$) it can give way to two types of sequence which are optical isomers:



A given polymer can be regarded as a “copolymer” of isotactic and syndiotactic diads, and the triad at the junction of these two is “heterotactic”:



When stereoregular sequences (iso, or syndiotactic) are short (lots of heterotactic junctions), the polymer is known as *atactic*.

Atactic polymers (for example polystyrene “crystal”, poly (methyl methacrylate)) are completely amorphous.

Highly stereoregular polymers, predominantly iso or syndiotactic, can crystallize and reach high crystallinity ratios, eventually above 50%. Polymers with low iso or syndiotactic predominance may lead to microcrystal formation in weak concentration, for example, 55% syndiotactic PVC having a crystallinity ration of 2 to 5 %.

5.2.3.3. Conformations

In liquid state, the chain is animated by ample movements which come from elementary rotations of the groups around the skeleton's aliphatic bonds. This can be seen, for example, in the case of a vinyl polymer (Figure 5.2).

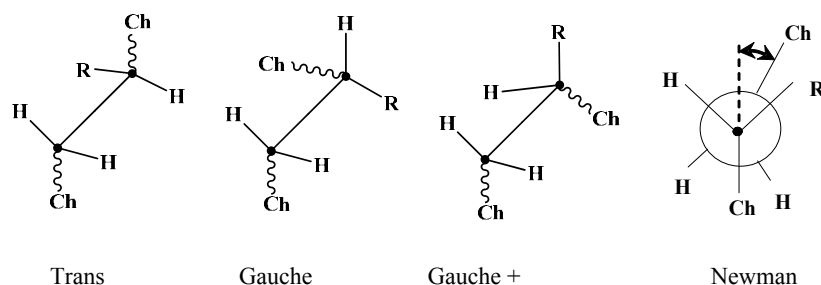


Figure 5.2. Shifted representation of the trans conformation and two gauche conformations of a vinyl polymer. (Right): Newman representation. Ch = chain, R = lateral group. The carbon in front is used as a reference. We are actually studying the carbon at the back

The potential energy varies with the rotation angle θ according to a curve with the shape of Figure 5.3.

Conformations can be experimentally observed by NMR.

Two quantities play a crucial role in a large number of physical properties:

– The height of the deepest potential well (E_T in Figure 5.3). This height determines the system's capacity to produce rotations around the considered bond. This capacity is expressed by the term:

$$R_D = \exp - \frac{E_T}{RT}$$

The deeper the potential well, (meaning a large E_T), the higher the rotation starting temperature. R_D can be called dynamic rigidity;

– The difference in height of trans and gauche potential wells:

$$R_s = \exp \frac{-(E_T - E_G)}{RT}$$

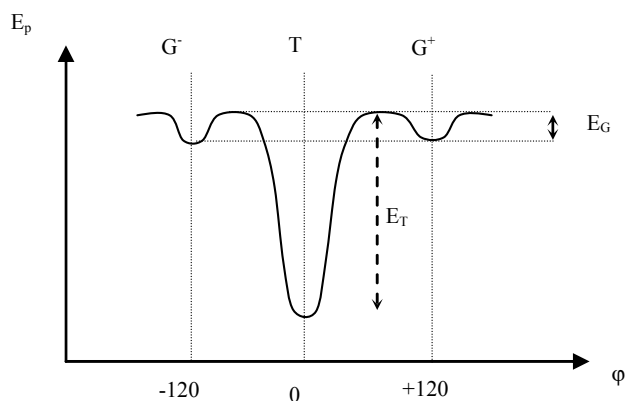


Figure 5.3. Variation shape of potential energy with the rotation angle. Note: the potential well of gauche conformations in some cases can be deeper than for the case of trans conformation

If this difference is high, the most stable conformation will prevail. If this difference is low, the trans and gauche populations will be close. We can see that the trans conformation leads to a plane zig-zag. We have diagrammatized the case by Figure 5.4.

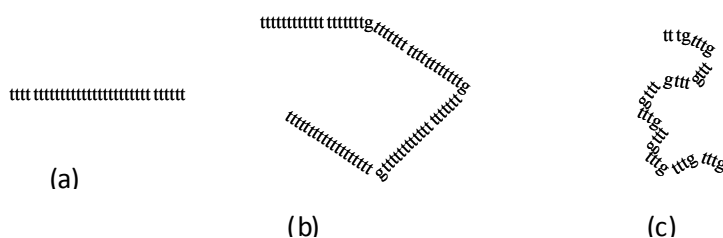


Figure 5.4. Diagram of three chain conformations: (a) all trans: the chain is a rigid rod; (b) widely predominant trans: the chain is weakly tortuous; (c) weakly predominant trans: the chain is very tortuous

What we call the *persistence length* is the length of the trans-trans sequence. If the chain length is large in relation to the persistence length, it appears as a “random

coil”, which has an important characteristic: the end to end distance r . For a chain containing N segments of length l , one can define the chain characteristic ratio C_∞ , for a large N :

$$r^2 = C_\infty N l^2$$

In the majority of industrial polymers, C_∞ varies between 2 and 10. C_∞ is linked to R_S , which we can call the chain’s static rigidity. If R_S is high, meaning that the chain is rigid, C_∞ is also high (polystyrene, poly(methyl methacrylate, etc.). If the trans and gauche conformations have close potential energies, C_∞ is low (polycarbonate, polysulfones). As we will see, static rigidity plays an important role in rheological properties and fracture behavior.

5.2.4. Macromolecular architectures: thermoplastics and thermosets

We know a large variety of macromolecular architectures. The main ones are represented in Figure 5.5.

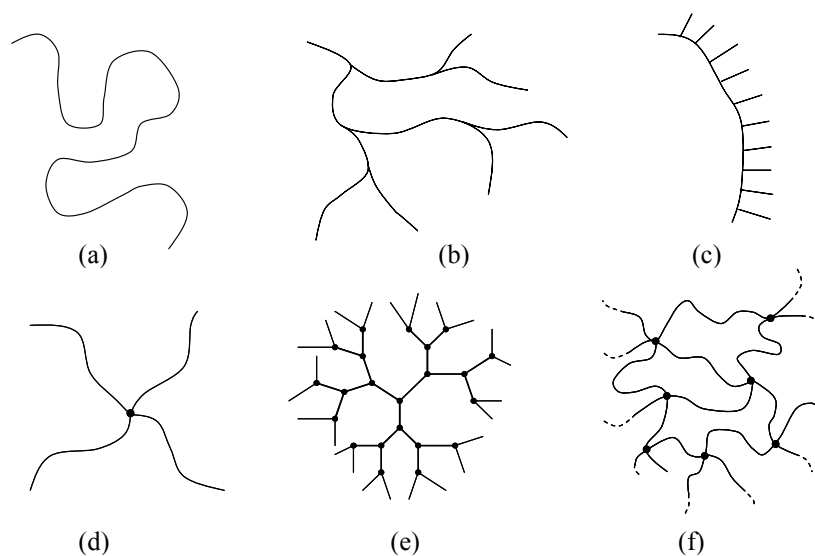


Figure 5.5. Different types of macromolecular architecture: (a) linear chain, (b) chain with long branches, (c) chain with short comb-like branches, (d) star, (e) dendrimer, (f) network

It is important to distinguish the species (a), (b), (c), (d) and (e), of finite size (molar mass generally between 10 and 10^4 kg.mol⁻¹) from species (f), of quasi-

infinite size, since its boundaries are those of the considered object. For example, the epoxy matrix of an aeronautical part (20 kg matrix) is made of a single macromolecule with a molar mass of: $M = 20 \times 6.02 \times 10^{23} = 12 \times 10^{24} \text{ kg.mol}^{-1}$. Here, the mole would be a quantity which is more relevant to astrophysics than physicochemistry.

For the processing expert, the boundary between material families is not topological, but simply linked to the size of the macromolecules. Schematically, for any polymer, there is a maximum size, which often corresponds to a molar mass M_L between 100 and 1,000 kg.mol^{-1} , such as:

- if $M < M_L$, a liquid state may be reached by raising the temperature, and the forming can be achieved by flow (injection, extrusion, calendering, rotomolding, welding, etc.). We, then, have to deal with a *thermoplastic*;

- if $M > M_L$, then the liquid state cannot be reached, the material undergoes a thermal degradation before reaching this stage. In this case, flow forming can only be carried out on monomers, prepolymers or species which have not completely reacted, which are able to be taken to liquid state. Once forming is complete, the material can be “cured” in order to reach its definitive chemical form. Now, we are dealing with a *thermosetting polymer*. The synthesis-processing channels are therefore represented in Figure 5.6.

Thermoplastics:

Monomer(s) → Polymerization → Polymer → Formed or processed → Object finished or work achieved

Thermosetting polymers:

Monomer(s) → Mixing → Liquid object or workable mix → Formed or processed
→ Polymerization → Finished object or work achieved

Figure 5.6. Representation of the elaboration ways in the case of thermoplastics and thermosetting polymers.

5.2.4.1. Monocomponents and bicomponents

Applied to the construction domain, Figure 5.6 demonstrates the differentiation between two modes of presenting the material [MOU 06]:

- when it is enough to fluidify, soften through heating, or apply as an emulsion or solution, we use the product as proposed by the manufacturer directly, without chemical modification, and therefore we can speak of a *monocomponent* product;

- on the other hand, when it is necessary to mix two reactive components during use to achieve polymer synthesis, we are then talking about a *bicomponent*. This

term occasionally includes more complex mixes, for example when the product is loaded and the load is partly released, or when the reactional system contains a base, a catalyst and an accelerator which are to be mixed at the last moment and in the right order. Then, we can speak of a *tricomponent*.

That being said, we must not conclude from this that all monocomponents lead to thermoplastic materials, and bicomponents to thermosetting materials. Thus, the chemistry of polyurethanes allows a formulation of monocomponents which react with air humidity. These are actually bicomponents, to the extent where atmospheric water plays the secondary role of the monomer, or even “blocked isocyanate” based monocomponents which use the thermoreversability of the polyurethane formation reaction in order to release one of the polycondensation reactants. These two types of “monocomponents” may also lead to thermoplastics as well as thermosetting materials.

As can be seen, things are not as simple as we would like to think. At all costs, we must avoid turning the user into a “little chemist”, meaning, letting him take the initiative in the preparation of the mix which is to be applied. This is why formulators have developed mixing guns, screw mixers, etc., which mean that we can obtain the desired product directly.

Additionally, there is no absolute identity between linear and thermoplastic polymers on one hand, and between tridimensional and thermosetting polymers on the other hand. Transparent semi-products made of cast PMMA, used in buildings, have molar masses higher than $1,000 \text{ kg}\cdot\text{mol}^{-1}$ and cannot be formed by thermoplastic processing method. The monomer is cast in a mold, and polymerization takes place there within. This is then a matter of a thermosetting process. However, PMMA with a molar mass of $\sim 50 \text{ kg}\cdot\text{mol}^{-1}$ can be injection molded, for example, for the rear lights of a car. This is a thermoplastic. For some polymers such as polyamides or polyurethanes, both processing types can coexist for the same molar mass (thermoplastic and reaction injection molding RIM varieties). Here, the choice is made according the number of parts to be made, the RIM molds being noticeably lower in cost than the injection molds.

5.2.5. Structure on a macromolecular scale

5.2.5.1. Linear and branched macromolecules

For all types of architecture except networks, the size of the macromolecules is a fundamental characteristic. An industrial polymer is always a mix of different sized macromolecules, characterized by the molar mass distribution. $N_i = f(M_i)$. N_i is the number of i type macromolecules with a molar mass M_i .

There are experimental methods (SEC, MALTI-TOF *matrix-assisted laser desorption/ionisation-time of flight*), which allow for a distribution of molar masses. From this, we can define averages, particularly the average in number:

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

and the average in weight:

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

It is easy to check that we still have $M_w \geq M_n$ and that the ratio $\frac{M_w}{M_n}$, known as the polydispersity index, is a measure of the broadness of the distribution.

In practice, the average molar masses are often determined by simpler and cheaper experimental methods than SEC or MALDI, for example:

- the chemical or spectrochemical titration of terminal groups; in principle:

$$[b] = 2 M_n^{-1}$$

where $[b]$ is the concentration of chains ends in the polymer;

- viscometry:

$$\eta = k M_w^\alpha$$

where k does not depend on the molar mass and α is a scaling parameter which is not strongly dependent on the polymer's nature.

In the case of viscometry in solution, η is the intrinsic viscosity and $\alpha \sim 0.7$.

In the case of rheometry in molten state, η is the Newtonian viscosity and $\alpha = 3.4$.

In amorphous state, the chains are overlapped, entangled. The entanglements constitute nodes of a physical network which is responsible for the existence of a rubbery state above T_g and a ductile behavior in glassy state, below T_g (Figure 5.7).

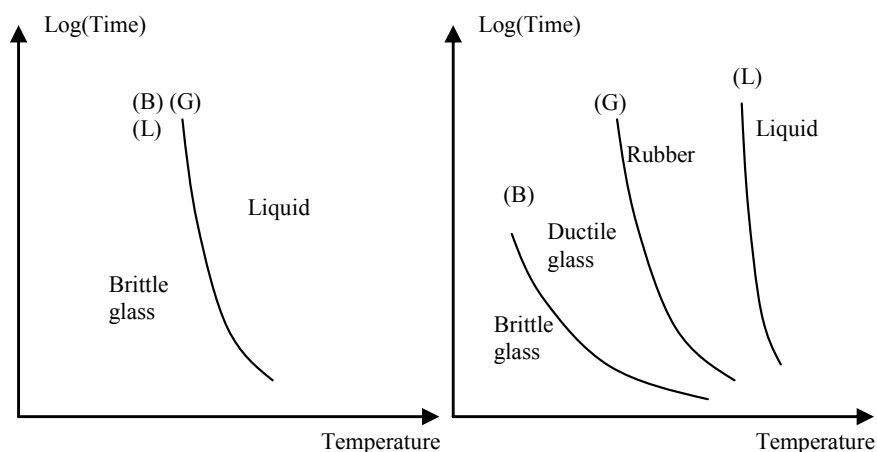


Figure 5.7. Behavior domains in the time-temperature space. (G) is the glass transition (B) is the ductile-brittle transition (L) is the (pseudo-) rubber-liquid transition. Left: unspecified amorphous material (polymer with low molecular mass included). Right: high polymer (typically $M > M_c$; M_c of the order of 10 to 100 kg.mol⁻¹).

The entanglements only appear when the molar mass is higher than a certain critical value (Figure 5.8).

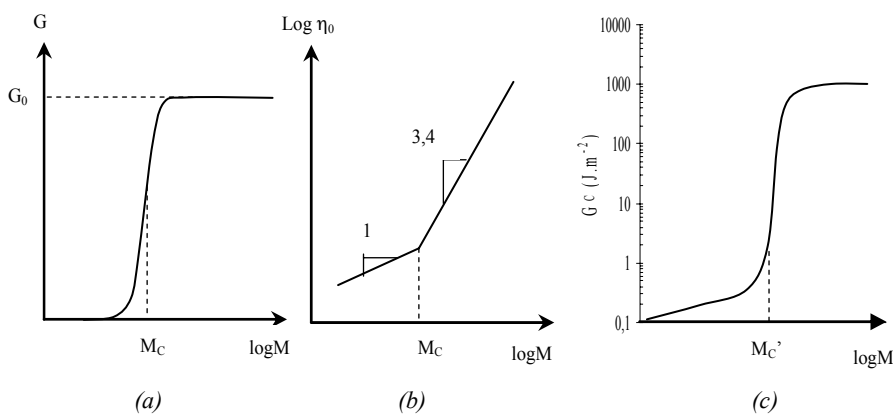


Figure 5.8. Shape of the variation with molar mass: (a) rubber modulus, (b) Newtonian viscosity in molten state, (c) toughness in glassy state for a linear amorphous polymer. Note – $M_c' \sim 2$ to $5 M_c$

The shear modulus of rubber (G) tends towards an asymptotic value (G_0) when the molar mass tends towards infinity. G_0 is linked to the chain length between entanglements (molar mass M_e) by the Flory theory [FLO 53].

$$G_0 = \frac{RT\rho}{M_e}$$

where R is the gas constant and ρ is the volumic mass.

M_e ranges approximately between 1.5 and 10 kg.mol⁻¹ for the majority of industrial polymers.

The relationship between M_e and structure on the molecular scale is now well known [FET 99]. M_e increases and chain tortuosity decreases when the chain transversal diameter increases.

5.2.5.2. Networks

A network is characterized by:

- the molar mass M_e of its elastically active chains (EAC), e.g. chains linked to network nodes at both ends;
- node functionality (the number of chains leading to a node).

An ideal network is one in which all the chains are elastically active.

We can then link concentration x in nodes with the EAC length:

$$x = \frac{2}{f.M_e}$$

There are only a few experimental methods which allow a determination of x or M_e :

- the rubbery state elastic modulus in tension (E) or shearing (G) which lead to M_e thanks to the Flory theory mentioned above. However, in the case of elastomers, there are some corrections which must be made (see further on). These corrections can be minimized or even canceled out altogether when the modulus measurements are carried out on samples swelled by solvents;
- the equilibrium swelling ratio in a solvent which can be used to determine M_e , on the condition that the χ coefficient of polymer-solvent interaction is known [FLO 43];

– the glass transition temperature which is an increasing function of the cross-link density.

For ideal networks, we can use Di Marzio's law [DIM 64]:

$$T_g = \frac{T_{gl}}{1 - K_{OM} \cdot F \cdot x}$$

where T_{gl} is the T_g of the copolymer (hypothetical) which contains all the structural elements of the network except the nodes; K_{OM} is a universal constant ($K_{OM} = 3$ for trifunctional nodes). F is the rigidity parameter defined in section 5.1.2.

For incompletely cured networks, we can use the Di Benedetto equation [PAS 02]:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda y}{1 - (1 - \lambda)y}$$

where:

- y is the conversion ratio (varying between 0 and 1);
- T_{g0} , T_g and $T_{g\infty}$ are T_g values for $y = 0$, $y = y$ and $y = 1$ respectively;
- $\lambda = \Delta C_{p\infty} / \Delta C_{p0}$ where ΔC_p is the heat capacity jump at T_g , measurable by differential scanning calorimetry (DSC).

Contrary to what it usually claimed, networks are neither systematically more rigid nor more brittle than linear polymers. The only major difference lies in the fact that linear polymers can be brought to liquid state (if their molar mass is not too high), while the tridimensional polymers do not have a liquid state, whatever their cross-link density. Not all linear polymers are thermoplastics, but all three-dimensional polymers are thermosets (although some can be hardened by irradiation, without raising the temperature).

5.2.5.3. Cross-linking, gelation

We can schematically distinguish two types of cross-linking processes:

- a) Those which come from a linear high polymer. Cross-linking, then, consists of “welding chains by points” at their ends if they have a particular reactivity, or on randomly distributed sites along the macromolecules (Figure 5.9).

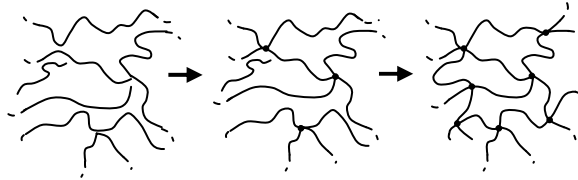


Figure 5.9. Diagram representing linear macromolecular cross-linkage

b) Those which come from small molecules where at least one of them has a functionality which is strictly higher than 2 (Figure 5.10).

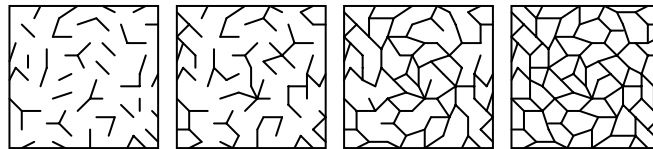


Figure 5.10. Diagram representing cross-linking process from small molecules

In both cases, cross-linking represents the formation of macromolecules with a progressively high size and branching. The properties, particularly rheological properties, do not vary in a monotonic way with the chemical conversion (Figure 5.11).

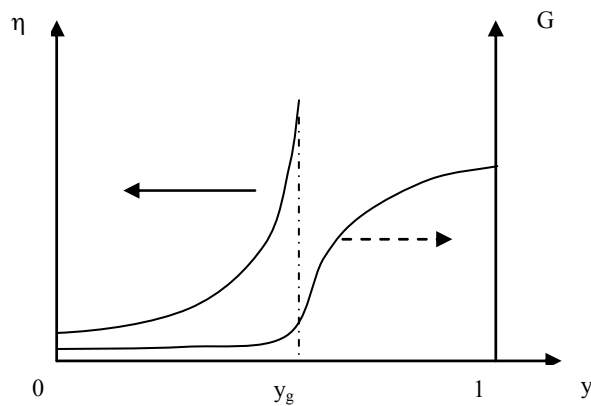


Figure 5.11. (Left) Viscosity and (right) shear modulus of the reactional medium during cross-linking

Gelation point ($y = y_g$) relates to the moment when a quasi-infinite macromolecule (i.e. size in the order of the reactor size) appears in the medium. It is a percolation threshold. In the case of processing by flow, the gelation point is the “point of no return”. On this side, forming or processing is possible. Beyond this point, it is impossible.

The value of y_g depends on the size and functionality of the reactive molecules. In the case of cross-linking linear macromolecules of initial molar mass M_{w0} (Figure 5.8), we have:

$$y_g = \frac{1}{M_{w0}}$$

We can see that the system gels at low conversion ratio.

In the case of a bicomponent (A+B) system where the reactant functionalities are respectively f_A and f_B and where A and B are in stoichiometric ratio, it can be written [FLO 53]:

$$y_g^2 = \frac{1}{(f_A - 1)(f_B - 1)}$$

For example, in the case of diepoxide cross-linking ($f_A = 2$) by a diamine ($f_B = 4$), then $y_g = 0.58$.

5.2.6. Structure on a supramolecular scale

5.2.6.1. Amorphous phases and glass transition

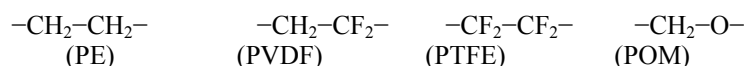
Let us consider an unspecified polymer. Brought to a sufficiently high temperature, it will be found in a liquid or rubber state, meaning in a state of maximum disorder where the chains, in configuration of random coils, are largely overlapped/entangled. When it is cooled, for example at a constant speed $\dot{T}$ of temperature decrease, it tends to crystallize in order to minimize its potential energy, as with all substances. However, this tendency can be contradicted, or even completely stopped. This leads us to distinguish the following four polymer families:

- *Family A_I* : the chemical structure which is too irregular, is incapable of being in order, whatever the cooling conditions. All atactic polymers, many statistical copolymers, and nearly all the thermosetting polymers belong to this family.

– *Family A₂*: with the cooling rate $\dot{T}$ being too high in relation to the crystallization rate, the material does not crystallize but, with a slower cooling process, crystallization then becomes possible. PET (poly(ethylene terephthalate)) is part of the polymers which can be easily obtained in an amorphous or semi-crystalline state. Polycarbonate (PC) is always formed in an amorphous state, but if it is maintained at a temperature higher than its glass transition temperature for long time enough, it is susceptible to crystallization (which has no practical interest).

– *Family C₁*: in the range of normal cooling rates, the polymer crystallizes. We can vary the crystallization rate by playing with $\dot{T}$. Polypropylene (PP) and polyamides (PA) both belong to this family which differs from family A₂ only because it is difficult to acquire 100% amorphous samples.

– *Family C₂*: the polymer will crystallize whatever the cooling rate (though this is limited anyway by the weak thermal conductivity of the material). Polymers with a symmetric monomer unit belong to this family.



The symmetry of the monomer unit favors quick crystallization.

Let us now consider the A₁ type amorphous polymers, and return to the cooling experiment (at $\dot{T}$) from a liquid state. There are two main approaches for its behavior: one based on free volume considerations, and another based on chain configuration entropy considerations.

5.2.6.1.1. Free volume theory

According to this theory, the mobility (cooperative mobility, i.e. motions of relatively large amplitude) of the chain segments is only permitted because a fraction f of the volume is free. This fraction can be defined by using dilatometric data (Figure 5.12).

The dilatometric behavior of the material is represented, as a first approximation, by two half-straight lines coming from the point of glass transition. In glassy state, the expansion coefficient α_g is generally between 1 and $4 \cdot 10^{-4} \text{K}^{-1}$. Expansion is essentially linked to atom vibrations around their equilibrium positions. There are no (or few) rotations.

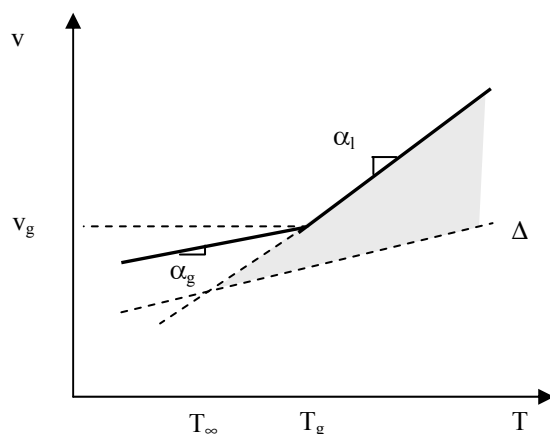


Figure 5.12. Definition of the free volume fraction (shaded area)

The expansion coefficient in liquid/rubber state α_l is generally between 5 and $10 \cdot 10^{-4} \text{K}^{-1}$. As a first approach, we could say that the excess free volume allowing motions of cooperative rotations in liquid/rubber state is equal to the excess volume created by the expansion $f = \alpha \cdot (T - T_g)$ at $T > T_g$ with $\alpha = \alpha_l - \alpha_g$. However, detailed studies show that a significant mobility stays at T_g , which leads us to propose:

$$f = f_g + \alpha \cdot (T - T_g) \text{ (the order of quantity } \alpha \text{ is } \sim 5 \cdot 10^{-4} \text{ K}^{-1})$$

f_g has a quasi-universal value of 0.025 (in other words, the free volume constitutes 2.5% of the total volume at T_g).

The free volume is canceled at T_∞ as:

$$C_2 = T_g - T_\infty = \frac{f_g}{\alpha} \sim 50 \text{ K}$$

Vitrification (transition from liquid to glassy state) can be explained by the fact that during the cooling process, the material contracts until the fraction of free volume becomes lower than an (f_g) volume where cooperative motions become impossible. Thus, the chains become fixed, and only localized motions with low amplitude remain.

5.2.6.1.2. Entropy theory

Let us consider the population of a kind of conformation, gauche for example, whose molar fraction is $[G]$. An equilibrium value $[G]$ corresponds to any

temperature, depending on the static flexibility of the chain. During the cooling process from T to $T - \Delta T$, the conformation fraction moves from $[G]$ to $[G] - \Delta[G]$. In other words, a section of the gauche conformation transforms into a trans conformation. However, the corresponding rotation is not instantaneous and its rate decreases when the temperature decreases.

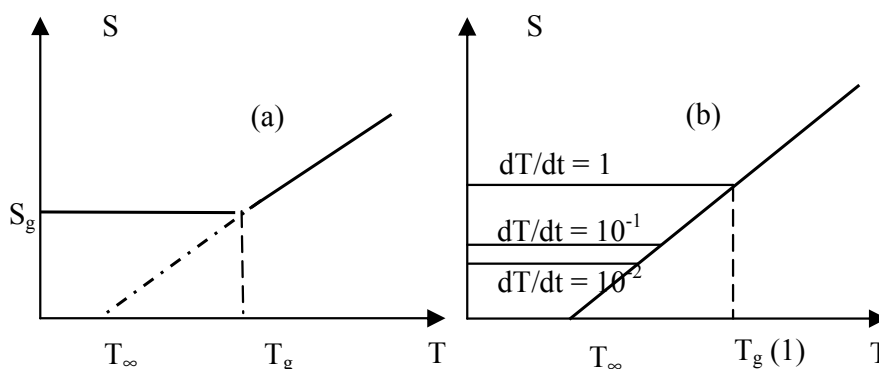


Figure 5.13. (a) Shape of variations in entropic chains around T_g ; (b) influence of the cooling speed

We can make the following observations:

- The glass phase is out of thermodynamic equilibrium (it is therefore likely to evolve slowly by moving towards this equilibrium, a process which is called “physical ageing” or “structural relaxation”).

- Since vitrification is a dynamic phenomenon, a weaker $\dot{T}$, means it will take longer (at a lower T_g) for the vitrification to occur (Figure 5.13b).

- By extrapolating the equilibrium line (in liquid state) we are cutting the temperature axis at $T_\infty = T_g - C_2$ with $C_2 = 50$ K. In theory, T_∞ is the T_g that we would expect with an infinitely weak cooling speed. Actually, it is difficult to observe T_g variations more than 20 K in an experiment, taking into account the excessive duration of tests and the difficulties of controlling extremely low cooling rates.

5.2.6.1.3. Other physical approaches

The theory of quasi-punctual defects [PER 01] is an interesting alternative to the aforementioned theories. At this current time, molecular modeling is rapidly developing and is starting to give us results for glass transition.

5.2.6.1.4. Glass transition temperature in practice

T_g depends on the time scale where it is determined, it hardly varies in the range of temperature variation rates which are accessible to the normal approaches of thermal analyzes (typically 10^{-2} to 100 K.min^{-1}). The data found in literature on the subject generally refers to measurements done between 1 and 20 K.min^{-1} . The three most commonly used methods to determine T_g are shown diagrammatically in Figure 5.14.

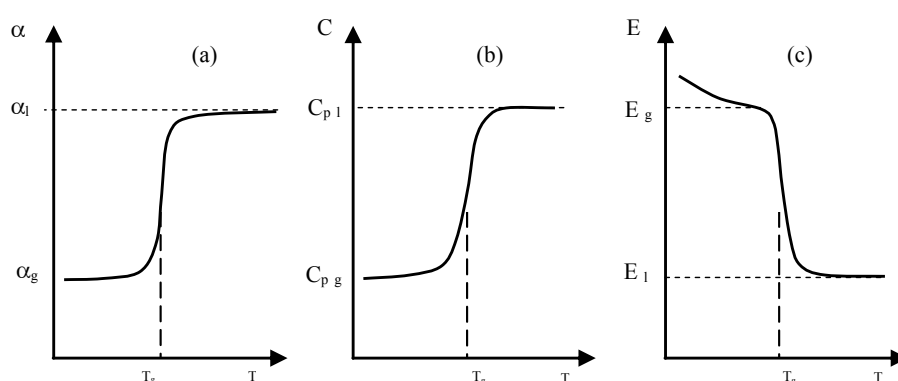


Figure 5.14. Shape of volumic expansion ratio variations (a) of heat capacity (b) and of Young's modulus (c) around T_g . NOTE: In the case of the modulus (c), we observe that transition α associated with glass transition T_∞ increases when the measurement frequency (dynamic modulus) increases

The order of magnitude of boundary values found in Figure 5.3 is given in Table 5.3.

Characteristic	Glassy state	Rubbery state
α	$(1 \text{ to } 5) \cdot 10^{-4} \text{ K}^{-1}$	$(5 \text{ to } 10) \cdot 10^{-4} \text{ K}^{-1}$
C_p	$(1.6 \pm 0.1) \text{ kJ.kg}^{-1} \cdot \text{K}^{-1}$ (a)	$(1.9 \pm 0.4) \text{ kJ.kg}^{-1} \cdot \text{K}^{-1}$
E	$\sim 1 \text{ GPa}$	0.1 to 10 MPa

Table 5.3. Physical characteristics on both sides of T_g
 Notes: (a) for halogen polymers $C_{pg} \sim (1.0 \pm 0.1) \text{ kJ.kg}^{-1} \cdot \text{K}^{-1}$;
 (b) for structure relationships $-T_g$ see section 5.2.2

5.2.6.1.5. Morphology of amorphous polymers

Some types of amorphous polymers (“crystal” PS, “crystal” PVC, PMMA, poly(dimethylsiloxane)) are transparent and, in some cases (PMMA), are limpid even at such great thicknesses. These materials appear as “fixed” liquids.

Other amorphous polymers (vulcanized rubbers, thermosetting polymers, thermostable polymers, etc.) are opaque in strong thicknesses, and translucent in weak thicknesses. The fact that they diffuse light may be linked to fluctuations in the refractive index, revealing heterogeneities which are typically higher than 100 nm. However, even in these materials, only very sophisticated methods of analysis allow for precise characterization of these heterogeneities which have been the subject of much controversy for a long time, in the case of epoxy networks, for example [PAS 02].

In the case of diphasic systems (polymer blends, copolymers, block copolymers), a more clearly contrasted morphology can be observed by electron microscopy or atomic force microscopy. One of the most beneficial morphologies, in terms of mechanical properties, is a morphology where nodules with low dimensions are dispersed in the matrix (Figure 5.15).

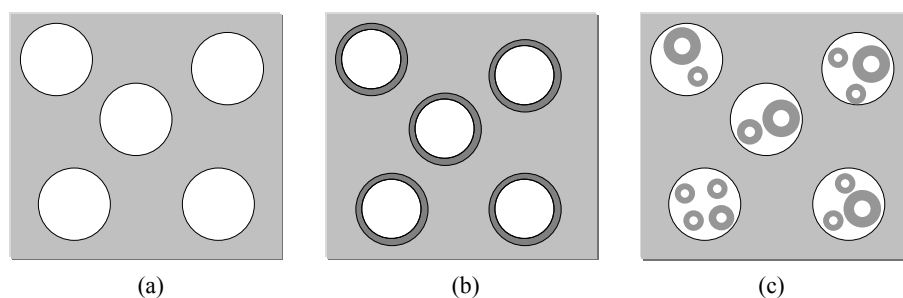


Figure 5.15. Diagram showing three current types of nodular morphology.
(a) Simple nodules; (b) core-shell nodules; (c) inversion phase nodules.
The nodule sizes in the 100 nm – 10 μ m interval are relatively common

Other morphologies (in labyrinths, onions, etc.) can also be observed.

5.2.6.2. Crystallization and melting processes

Crystalline phases are characterized by the existence of a melting point T_f and a higher packing density than the corresponding amorphous phases, with the volumic mass ratios ρ_c/ρ_a ranging between 1.05 and 1.25. When a polymer can easily be

acquired in amorphous or crystalline form (PET or PEEK, for example) it is possible to demonstrate through experiments the difference in behavior between the amorphous and crystalline phases (Figure 5.16).

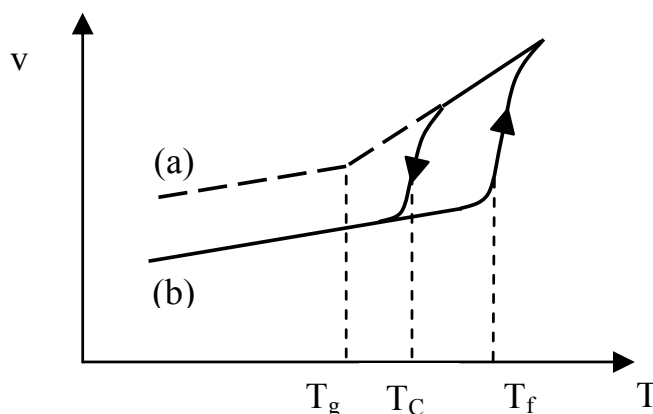


Figure 5.16. Diagram showing volumetric behavior of a polymer in amorphous state (dashed lines), in 100% crystalline state (continuous lines). The arrow indicates the direction of the temperature variation

The graph displays an important hysteresis: crystallization occurs at a temperature which is clearly lower than the melting temperature. The melting temperature is an instantaneous phenomena, whilst crystallization is a kinetic phenomenon.

Thermal behavior is similar to dilatometric behavior (Figure 5.17a). Regarding elastic properties, the crystalline phase modulus is slightly higher than that for glassy amorphous phases and around 1,000 times higher than for rubbery amorphous phases (Figure 5.17b).

The crystallinity ratio χ_c can be determined from density measurement:

$$\chi_c = \frac{\rho_c}{\rho} \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

It can be also determined by differential scanning calorimetry (DSC) (Figure 5.16a), by X ray scattering and, in some cases, by a spectrochemical method (IR, RMN).

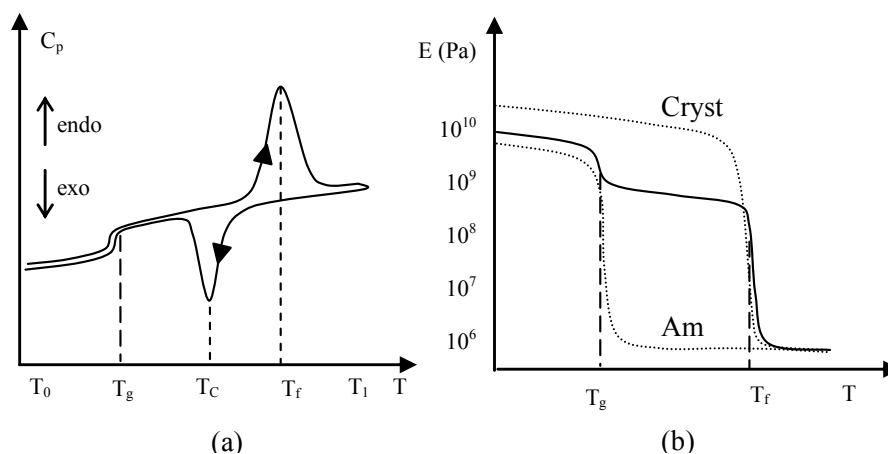


Figure 5.17. Semicrystalline polymers: (a) specific heat variation with temperature during a $T_0T_1T_0$ cycle. The melting peak is endothermic, the crystallization peak is exothermic. The melting peak surface can be used in certain cases to determine the crystallinity ratio. When the crystallinity ratio is high, the jump of C_p at T_g (linked to the amorphous fraction) can be quite undetectable; (b) modulus variation with temperature for a semicrystalline polymer (full line) for the same polymer which is 100% crystalline (Cryst) and 100% amorphous (Am). The scale is only indicated to give the order of magnitude

Crystalline morphology can take various forms, with the elementary structure being either the fringed micelle or plate-like lamellae (Figure 5.18).

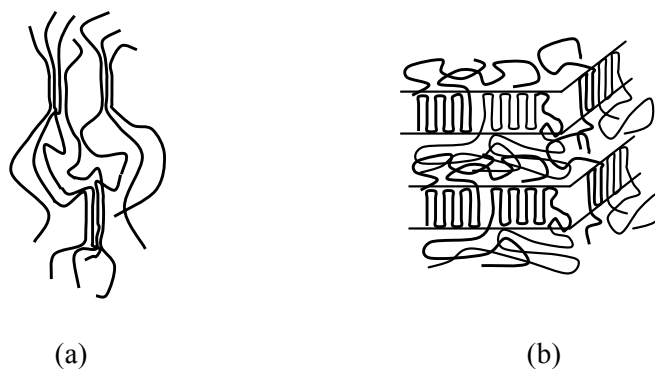


Figure 5.18. Diagram of crystalline morphology. (Left) fringed micelles (samples generally in small crystalline amounts). (Right) lamella resulting from the crystallized chain folded on itself

The long period l_p can be determined by small angle X-ray scattering (SAXS). The lamellae thickness can be determined from the melting point (Thomson relation).

$$T_f = T_{f0} \left(1 - \frac{2\sigma}{\Delta H_f \cdot l_c} \right)$$

where T_f is the melting temperature of a crystal with infinite thickness, σ is the surface energy and ΔH_f the melting heat. l_c generally varies between a few nanometers and a few tens of nanometers.

When the crystallinity ratio is raised, the lamellae form ribbons and are radially organized into spherulites growing from a nucleation center.

5.3. Additives and fillers

Organic polymers are rarely used pure, with the exception of a few organic glasses. Additives and fillers are incorporated into the polymers to adjust their properties so they can be adapted for specific usage. In principle, additives are dissolved in the polymer, whereas fillers are insoluble and thus form a diphasic system (composite) with the polymer.

5.3.1. Additives

5.3.1.1. Processing aids

The most commonly used additives are lubricants, such as fatty esters, amides or acid salts. They are used in weak concentrations, just like anti-static or anti-blocking agents which are particularly used in films.

5.3.1.2. Stabilizers

Some (thermal) stabilizers are essentially used so as to protect the polymer at higher temperatures, when it is being processed. Anti-oxidants (phenols, amines, sulfides, phosphites, etc.) are used in virtually all aliphatic polymers, with the exception of fluorides which are intrinsically stable. Certain polymers, particularly PVC, involve specific stabilizing methods based on the principle of substituting labile chlorine atoms (soaps containing Ca/Zn^{++} , organostannics, etc.).

Anti-UV stabilizers are used in external exposure applications. 2 hydroxy benzophenones, hydroxyphenyl benzotriazoles, substituted acrylonitriles, and benzylidene malonates are the most frequently used UV absorbers, in concentrations higher than 1%.

5.3.1.3. *Plasticizers*

Plasticizers are generally used to soften organic glass (dioctyl phthalate type esters in PVC, aromatic chlorides in polycarbonate, etc.). 30% of dioctyl phthalate transforms the initially rigid PVC ($T_g = 80^\circ\text{C}$) into an elastomer ($T_g \sim -50^\circ\text{C}$) which can be used to create textile coatings, flexible tubes, soft toys, etc.

5.3.1.4. *Anti-flammable agents*

These agents are used to improve the fire resistance of polymers which are considered flammable in their natural state. These are a mixture of species, such as aryl phosphates, halogen molecules and inorganic fillers such as antimony trioxide, aluminum trihydrate, etc. (see the Chapter 8).

5.3.1.5. *Various additives*

Plastosoluble dyes, anti-static agents (quaternary ammoniums, for example), bleaching agents, etc., can be seen in certain particular applications.

5.3.2. *Fillers*

5.3.2.1. *Micrometric granular fillers*

Some fillers are used as white pigments, (TiO_2 , ZnO), black pigments (carbon black), etc. Pigments are generally used in low concentrations.

Other fillers with weak aspect ratios (talc, calcium carbonates, etc.) are often used as “dilutants” in the polymer matrix due to their low cost. Generally, they have a tendency to increase the rigidity and softening temperatures under mechanical loads. But on the other hand, they are disadvantageous in terms of ductility and resilience.

Fillers with higher aspect ratios, such as mica plates or acicular fillers (wollastonite) sometimes greatly increase the modulus and resistance to fracture.

Some fillers play a particular role, such as making a polymer which was initially an insulator into a conductor of electricity (carbon black, metallic powder), making it opaque to X-rays (Ba sulfate), to neutrons (borates), etc.

5.3.2.2. *Nanometric fillers*

At the current time, research on nanometric sized fillers (montmorillonite, etc.) is developing quickly. In weak concentrations, these fillers can act as strengtheners (carbon nanotubes), greatly decreasing gas permeability, etc.

5.3.2.3. Fibrous fillers

Glass, carbon or aramide fibers (Kevlar, for example), either long (impregnation process) or short (injection, extrusion, etc.) have a heightened strengthening effect which is linked to their particularly beneficial aspect ratio, and are widely used as much in thermosetting matrices as in thermoplastic matrices.

5.4. Processing properties

5.4.1. Thermoplastics

First of all, let us remember the shape of variations in the shear modulus G with temperature, G being determined in a fixed time scale, for example by dynamic measurements at a frequency of 1Hz (Figure 5.19).

Curves $G=f(T)$ allow us to define two transitions:

– *Glass transition* (T_g) drawing out the passage from a glassy state to a liquid or rubbery state, with a drop in the modulus by a factor of 100 or more. T_g depends on the molar mass according to the Fox-Flory equation:

$$T_g = T_{g\infty} - \frac{k_{FF}}{M_n} \quad \text{with } k_{FF} \text{ in the order of } 10 \text{ to } 100 \text{ K.mol.kg}^{-1}$$

k_{FF} tends to increase with the dynamic rigidity of the chains, like $T_{g\infty}$.

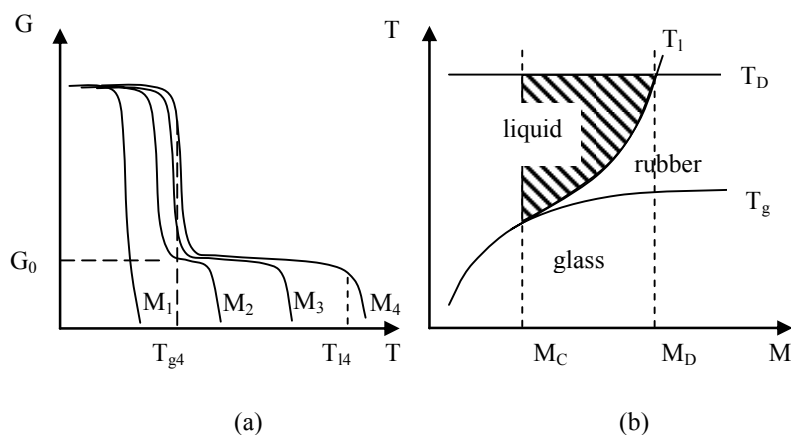


Figure 5.19. (a) Modulus-temperature curves for different molar masses: $M_1 < M_c$ $M_2 > M_c$ $M_3 > M_2$ $M_4 > M_3$. (b) Phase diagram coming from figure (a)'s curve beam, where the thermal degradation temperature T_D has been added

– “*Liquid-liquid*” transition (T_L) draws out the path from a rubber to a liquid state. This is a diffuse transition, without discontinuity of thermodynamic quantities. We can, then, consider this as an isoviscosity point. For $M < M_c$, T_L is equal to T_g . For $M > M_c$, $T_L - T_g$ (the rubber plateau length) rapidly increases with M .

The degradation temperature T_D must also be arbitrarily defined. Beyond this temperature, the polymer’s thermal degradation (in the considered time scale) then becomes unacceptable with regard to the user.

The intersection between curves T_L and T_D relates to a molar mass M_D which has the following meaning: M_D is the highest molar mass which can be brought to a liquid state, which allows for material processing by flow. For $M > M_D$, this material degrades before reaching the liquid state. Let us not forget that for $M < M_c$ the material is extremely brittle and cannot be used for a mechanical application.

There are many polymers for which $M_D < M_c$, in other words, for which there is no usable molar mass interval (PVC, PP, etc.) Fortunately, additives such as thermal stabilizers (acting on T_D) allow boundaries of different physical states, as shown in Figure 5.19b, to be displaced, and for “processability windows” to be opened, as represented by the curvilinear triangle cross-hatched on the figure.

Let us recall that liquid state viscosity depends on the molar mass according to the scaling law $\eta_0 = K.M^{3.4}$ where K depended on temperature and material chemical structure, and η_0 is the Newtonian viscosity. Curves $\eta = f(\dot{\gamma})$ have the shape of Figure 5.20.

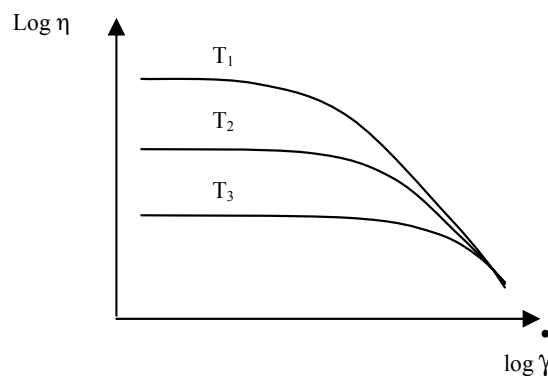


Figure 5.20. Shapes of curves $\text{Log}(\text{viscosity}) = f[\text{log}(\text{shear rate})]$ at different temperatures $T_1 < T_2 < T_3$. At a given temperature, the Newtonian plateau is as long as the molar mass is low

In branched samples, the Newtonian plateau tends to decrease and even disappear. In the liquid state, injection, extrusion, rotomoulding and calendaring are performed, as seen in the cross-hatched window of Figure 5.19b. These methods differ by the imposed shear rate, and require adapted viscosity ranges. For example, injection, which is characterized by particularly high shearing rates, requires viscosities (molar masses) which are lower than extrusion. Plastic manufacturers commercialize grades which are adapted to specific processing methods.

Thermoforming is the only processing method where the material is in a rubbery state and can be subjected to large strains without rupture.

5.4.2. Thermosetting polymers

As we have already seen, we can characterize the evolution of a material during its cross-linking process on the one hand by the conversion ratio y of the reaction, and by the glass transition temperature T_g on the other. By plotting T_g versus y , we obtain Figure 5.21.

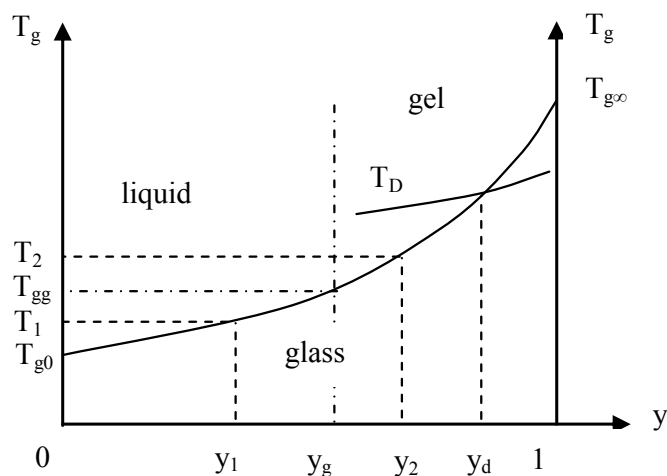


Figure 5.21. Diagram temperature – conversion ratio relative to thermosetting hardener

The T_g of the starting mixture is T_{g0} . The T_g of a totally cross-linked material is $T_{g\infty}$. During the reaction, T_g increases according to a hyperbolic law (see above, section 5.2.5.3), which is represented by the full line on the figure. The material is characterized by its gelation point at conversion ratio y_g .

Let us consider various cases of isothermal treatment:

- if $T \leq T_{g0}$, the reactive mixture is in a glassy state. With the molecular mobility extremely reduced, the reaction does not occur. The reactive mixture can (and must) be preserved at $T < T_{g0}$;
- if $T_{g0} < T_i < T_{gg}$, and the reactive mixture is initially in liquid state, it will react; however, at the conversion ratio y_1 , if T_g is equal to the imposed temperature, it will go to the glassy state (vitrification) and the reaction will stop;
- if $T_{gg} < T_2 < T_{g\infty}$, the reactive mixture reacts, gels for $y = y_g$ but keeps enough mobility, in the rubbery state, so the reaction can continue. It will vitrify for $y=y_2$ and the reaction will stop;
- if $T > T_{g\infty}$, cross-linking can be completed, since the material stays in its rubbery state from the beginning to the end.

However, in certain cases, particularly for materials having $T_g > 250^\circ\text{C}$, it is possible for the degradation temperature T_D to be lower than $T_{g\infty}$. Thus, there is an optimal conversion ratio y_D which must not be exceeded so as to avoid degrading the material to the point of being unacceptable.

Experts use temperature, time, and transformation graphs (TTT), which add the time variable to the two variables of the graph in Figure 5.21. It must be simply recalled that the reaction is as slow as the temperature is low [PAS 02].

5.5. Mechanical properties

5.5.1. Elastomers

Elastomers are materials which are rubbery at room temperature. As we have already seen, for the T_g values to be low enough, the chains must be flexible and almost apolar, which is achieved in the case of polydienes, (natural rubber, polybutadiene) amorphous or slightly crystalline hydrocarbons polymers or copolymers such as polyisobutylene, ethylene-propylene copolymers and more generally nonpolar or slightly polar polymers such as poly(dimethylsiloxane) e.g. silicone rubber, and certain halogen polymers: polychloroprene, fluorinated polymers and copolymers (Viton), etc.

To ensure that the materials do not creep, they are cross-linked (the term used in the profession is *vulcanized*). The vulcanized elastomer is, then, characterized by its cross-link density, expressed in terms of node concentration in the network or in the

average molar mass of elastically active chains M_e . Let us recall that $x = \frac{2}{fM_e}$ where f , node functionality, is often equal to 4.

If the starting polymer is linear and characterized by a molar mass M_n , its shear modulus is given by:

$$G = G_0 \left(1 - \frac{2M_e}{M_n}\right)$$

The term $\frac{2M_e}{M_n}$ can be considered as the effect of dangling chains. G_0 is the modulus of a network based on a linear polymer of infinite length, with the same node concentration.

Rubber elasticity, also known as entropic elasticity or hyperelasticity, displays the following characteristics.

1) *Nonlinear elasticity*. The behavior law, in the basic theory, takes the following form at equilibrium e.g. for a low strain rate:

$$\sigma = \frac{RT\rho}{M_e}(\Lambda^2 - \Lambda^{-1})$$

where Λ is the draw ratio defined by $\Lambda = \frac{l}{l_0}$.

Experts often use force f on the initial section s_0 of the test-piece:

$$\frac{f}{s_0} = \frac{RT\rho}{M_e}(\Lambda - \Lambda^{-2})$$

These relationships characterize an ideal network. In the case of a real network, we use the Mooney-Rivlin equation:

$$\frac{f}{s_0} = (C_1 + C_2\Lambda^{-1})(\Lambda - \Lambda^{-2})$$

where $C_1 = \frac{RT\rho}{M_e}$ and $C_2\Lambda^{-1}$ is the corrective term. Some theories predict that $C_1 \sim C_2$. However, C_2/C_1 tends to decrease when the cross-link density increases, or when the elastomer is swelled by a solvent.

2) *The modulus is proportional to the absolute temperature*, which shows that, in a thermodynamic balance of deformation, the entropic term widely dominates the internal energy term, hence the name of entropic elasticity and the interest taken by thermodynamicists in this original kind of behavior.

3) *Strains occur at constant volume*, Poisson's ratio is very close to 0.5.

4) Strain is reversible, even on very large strains (Figure 5.22).

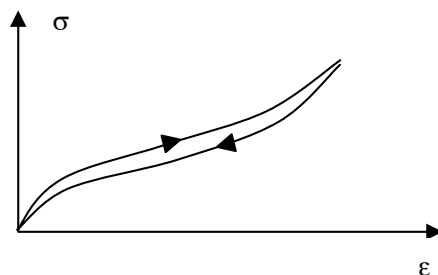


Figure 5.22. Shape of the stress curve – strain during a loading/unloading cycle of an elastomer. The hysteresis is linked to the material's viscoelasticity

The stress/strain curves often demonstrate the existence of a final hardening not taken into account by the equations shown above. Crystallization induced by chain stretching is one of the possible causes for this phenomenon (Figure 5.2).

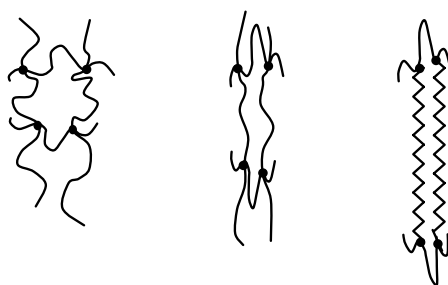


Figure 5.23. Diagram of crystallization by stretching. This orientates the chains and creates an order which promotes crystallization

Pure elastomers are sometimes relatively brittle, but adding fillers such as carbon or silica greatly increases their resilience. The theory predicts that the critical rate of elastic energy release in mode I, G_{Ic} , characterizing the resistance to crack propagation, should vary (as with the draw ratio at break Λ_R) proportionally to the square root of molar mass M_e of elastically active chains:

$$G_{Ic} \propto \Lambda_R \propto M_e^{1/2}$$

In truth, although these equations accurately predict these trends, real elastomers can divert significantly from these relationships.

The mechanical behavior of elastomers at low strains obeys a *principle of time/temperature equivalence*, which is expressed as follows:

$$\mathbf{P}(t, T) = \mathbf{P}(t/a_T, T_R)$$

where $\mathbf{P}$ is the considered property, T_R is an arbitrary reference temperature, and a_T is a shift factor which only depends on temperature.

Williams, Landel and Ferry showed in the 1950s [WIL 53] that a_T varied with the temperature according to the law known as WLF:

$$\text{Log } a_T = \frac{-C_1(T - T_R)}{C_2 + (T - T_R)}$$

On the other hand, these authors showed that if T_R was taken to be equal to T_g , then C_1 and C_2 would take a quasi-universal values: $C_{1g} \sim 17.4$ and $C_{2g} \sim 51.6$ K. In fact, we find that in scientific literature, there are some C_{1g} and C_{2g} values which significantly move away from these values. However, their ratio does not seem to move away from $C_{2g}/C_{1g} \sim 3$ K. Let us note the identity of C_{2g} with the values of C_2 which are specific to the free volume theory, or the theory of entropy (section 5.2.5). This result is not a coincidence. The WLF law can easily be established from free volume or entropy considerations.

Note that by calling $T_\infty = T_g - C_{2g}$, the WLF law then becomes:

$$\text{Log } a_T = A \exp \frac{B}{T - T_\infty}$$

with $A = \exp(-C_1)$ and $B = C_1 C_2$. This equation is thus known as Vogel's law.

The WLF law can also be written:

$$\ln a_T = \frac{-2.3 C_1 (1 - \frac{T_g}{T})}{1 - \frac{T_g - C_2}{T}}$$

meaning:

$$\frac{d(\ln a_T)}{d(\frac{1}{T})} = \frac{2.3 C_1 C_2}{(1 - \frac{T_g - C_2}{T})^2}$$

In a narrow temperature interval around T , we may consider that a_T obeys the Arrhenius law, with the apparent activation energy E_a , such as:

$$\frac{d(\ln a_T)}{d(\frac{1}{T})} = \frac{E_a}{R} \quad \text{either: } E_a = \frac{2.3 R C_1 C_2}{(1 - \frac{T_g - C_2}{T})^2} \quad \text{or,}$$

$$\text{at } T = T_g: E_a(T_g) = 2.3 R \frac{C_1}{C_2} T_g^2 \approx 6 T_g^2$$

Effectively, we observe that $E_a(T_g)$ is of the order of several hundreds of kilojoules/mole and that it tends to increase with T_g .

5.5.2. Mechanical properties of glassy amorphous polymers

5.5.2.1. Elastic properties

Elastic behavior is characterized by four measurable quantities: compressibility modulus K , shear modulus G , Young's modulus E and Poisson's ratio ν .

The continuum mechanics allows us to establish relationships between these quantities:

$$E = 3 K(1 - 2\nu) \quad G = \frac{3(1 - 2\nu)}{2(1 + \nu)} K \quad G = \frac{E}{2(1 + \nu)}$$

Knowing two of these quantities is sufficient for the other two to also be known. K and G can be considered as fundamental quantities which determine the values of

E and ν . The variation of moduli with temperature is set out in a diagram in Figure 5.24a. Poisson's ratio is shown in Figure 5.24b.

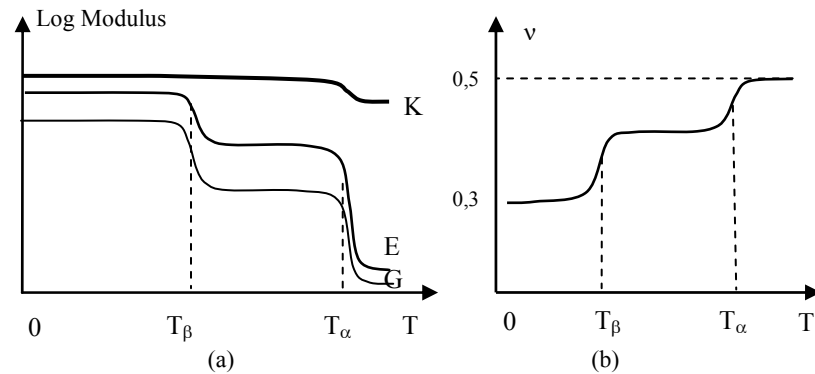


Figure 5.24. Diagram of modulus variation (a) and of Poisson's ratio (b) with temperature

The modulus M at an unspecified temperature T in a glassy state can be expressed as:

$$M = M_{00}(1 - \alpha T) - \sum_0^T \Delta M_i$$

where:

- M_{00} is the modulus at 0 K;
- α is in the order of $1/(2T_g)$, in other words the extrapolated glassy modulus at T_g is approximately half of modulus 0 K;
- ΔM_i is the modulus jump corresponding to the i^{th} secondary transition below the test temperature.

The compressibility modulus K is not influenced by secondary transitions. Essentially it depends on the cohesive energy density:

$$K = K_{00}(1 - \alpha T) \quad \text{with} \quad K_{00} \sim 20 \text{ d}_e$$

K decreases by a factor of approximately 2 across T_g .

The shear modulus G_{00} at 0 K also exclusively depends on cohesion. However, with the difference of K, it is affected by localized molecular movements, which are responsible for secondary transitions. These movements are characterized by the frequency f which increases with thermal agitation according to Arrhenius' law:

$$f_i = f_{i0} \exp\left(-\frac{E_i}{RT}\right)$$

where: f_{i0} and E_i characterize the i^{th} transition.

To study secondary transitions, we generally use dynamic mechanic analysis (DMA), or dynamic mechanical thermal analysis (DMTA) methods, which consist of the following principles: the transition is observed at temperature T_i such as the strain frequency f_{si} equal to the frequency of the considered molecular movement. It is either:

$$f_i = f_{si} = f_{i0} \exp\left(-\frac{E_i}{RT_i}\right)$$

or, for two different frequencies f_{si1} and f_{si2} :

$$\frac{1}{T_{i1}} - \frac{1}{T_{i2}} = \frac{R}{E_i} \ln\left(\frac{f_{si1}}{f_{si2}}\right)$$

We see that the transition temperature T_i displacement linked to a given frequency variation is as big as the activation energy is small.

For example, let us consider the case of transition γ for a polyethersulfone (PES) type aromatic polymer: $T_\gamma = 160$ K for $f = 1$ Hz. If the same transition is measured by ultrasound at $f = 10^7$ Hz, the application of the above equation gives $T_\gamma = 289$ K because for this type of material $E_\gamma = 48$ kJ.mol⁻¹.

The main transition T_α associated with the glass transition is characterized by an apparent activation energy of several hundred kilojoules/mole (Figure 5.25):

- If, at low frequency (full curve), $T_\beta < T_{\text{amb}}$ (room temperature), then relaxation β is total at T_{amb} : the corresponding modulus G_l is the “relaxed” modulus.
- If the frequency is sufficiently raised (dotted curve), T_β will be higher than T_{amb} . The corresponding modulus will then be the “unrelaxed” modulus G_u .

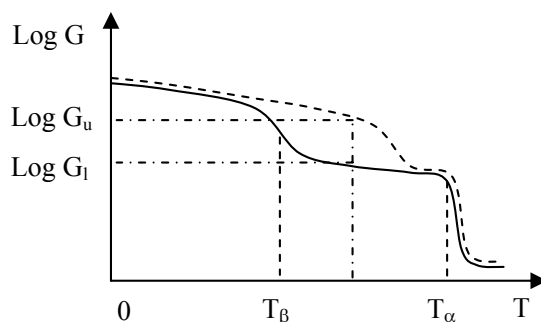


Figure 5.25. Shape of the shear modulus variation with the temperature for two different frequencies

Secondary transitions differ from one to another by their temperature at a given frequency, by their activation energy, and by the corresponding modulus jump $\Delta G = G_u - G_l$.

Some relaxations are very important mechanically (ΔG important). For example, this is the case for polymers with aromatic cycles in the chain, such as polycarbonate and polysulfones, whose most important secondary transition is found at -100°C at 1 Hz.

Other relaxations are not very mechanically active (ΔG weak). This is the case for polystyrene, for example, which also has a secondary transition towards -100°C , but with a low modulus jump.

Localized chain motions responsible for secondary relaxation can affect strongly the modulus at ambient temperature. For instance polycarbonate or aromatic polysulfone, which have a strong β transition, have a modulus $E \sim 2.4\text{--}2.6$ GPa. Polystyrene is stiffer ($E \sim 3$ GPa) despite its lower cohesive energy density, because it displays a very low local mobility.

These same relationships make Poisson's ratio vary more or less strongly around the secondary transitions, as indicated in Figure 5.24. Typical values are in the order of 0.35–0.37 in an unrelaxed state and 0.40–0.42 at room temperature for polycarbonate-polysulfone type polymers which display a relatively intense sub-glass relaxation.

All the above observations are valid for thermoplastics as well as for thermosetting materials.

5.5.2.2. Yield and fracture properties

The yield stress corresponding to the onset of plasticity σ_y (Figure 5.26) is essentially linked to the polymer's rigidity. At weak strain speeds, typically:

$$\sigma_y \approx \frac{E}{40}.$$

σ_y depends on the strain rate $\dot{\epsilon}$ and on the temperature according to Eyring's law:

$$\frac{\sigma_y}{T} = \frac{R}{V} \left(\ln \dot{\epsilon} - \ln \dot{\epsilon}_0 + \frac{E_y}{RT} \right)$$

where $\dot{\epsilon}_0$, E_y and V are characteristics of the material. V (activation volume) is generally of the order of 1 L.mol^{-1} .

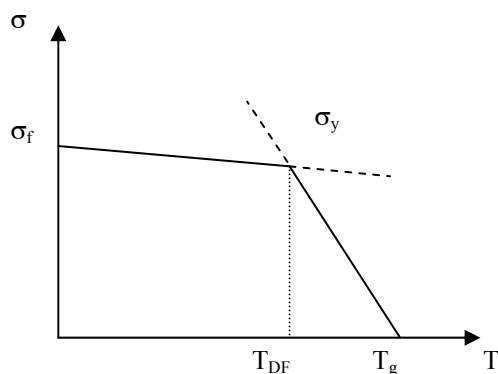


Figure 5.26. Diagram of the competition between fragile and ductile processes

It must be pointed out that σ_y also depends on the history of the material, and tends to increase according to the physical aging time (thermal aging between T_β and T_g).

Fracture behavior can be described as resulting from a competition between a brittle process (characterized by a stress σ_f which is hardly dependent on the temperature) and a ductile process (characterized by the yield stress σ_y decreasing in a quasi-linear fashion with temperature (Figure 5.26)).

This leads us to define a ductile-brittle transition temperature T_{DF} and an interval of ductility temperature: $\Delta T = T_g - T_{DF}$.

We can observe that certain polymers like polycarbonate or polysulfones have a very wide interval of ductility ($> 200^\circ\text{C}$). Others such as polystyrene or PMMA have a very narrow ($\sim 10^\circ\text{C}$) and practically unusable ductility interval.

We notice that polymers with a wide ductility interval are characterized by an intense β transition, well separate from the glass transition. Additionally, these polymers are characterized by highly tortuous chains (C_∞ low). On the other hand, polymers with ductility interval are characterized by a weak β transition, close to the T_g . These polymers, whose prototype is polystyrene, have in common a higher chain characteristic ratio (C_∞).

Wu [WU 90] proposes the following empirical equation:

$$\frac{T_{DF}}{T_g} = (0.135 \pm 0.027) + (0.082 \pm 0.004)C_\infty$$

In organic glass, brittle rupture is generally preceded by crazing: the lips of microcracks are put back together by fibrillae where the polymer has been subjected to an important localized plastic strain. Crazing is disadvantaged by a weak C_∞ , by cross-linking, by chain orientation.

With regard to fracture mechanics properties, we can distinguish fragile polymers (F) and ductile polymers (D).

For family F:

$$\text{Log } K_{Ic} \sim 0.5 \text{ Log } \sigma_R - (0.9 \pm 0.4)$$

σ_R is the fracture stress under tension.

For family D:

$$\text{Log } K_{Ic} \sim (1.0 \pm 0.3) \text{ Log } \sigma_y - 1$$

σ_y is the yield stress, K_{Ic} is expressed in $\text{MPa}\cdot\text{m}^{1/2}$ and σ in MPa.

For family F, K_{Ic} generally varies between 0.6 and 1.2 $\text{MPa}\cdot\text{m}^{1/2}$. For family D, K_{Ic} varies between 0.8 and 10 $\text{MPa}\cdot\text{m}^{1/2}$.

We should remember that $G_{Ic} = \frac{K_{Ic}^2}{E}$ in a state of plane strain and that $G_{Ic} = \frac{(1-\nu^2)K_{Ic}^2}{E}$ in a state of plane stress. For ductile polymers ($\nu > 0.4$), the two values differ slightly. G_{Ic} values generally vary between 100 and 10^4 J.m^{-2} for most industrial (unreinforced) polymers.

5.5.2.2.1. Behavior under fatigue

To our knowledge, there is no synthesis on the relationships between structure and properties under fatigue. However, we do know that, for glassy amorphous polymers, crazing is often responsible for a relatively weak endurance limit, often smaller than half the yield tensile stress. Cross-linking which disfavors crazing, generally allows for an improvement to fatigue resistance. Let us remember in addition that, in the case where materials have a T_g which is close to the test temperature, we can observe failure due to self-heating, particularly under high strain frequencies.

5.5.3. Mechanical properties of semi-crystalline polymers

5.5.3.1. Elastic properties

In section 5.2.5 we saw the shapes of temperature variation of a 100% crystalline elastic modulus, 100% amorphous or $x_c\%$ crystalline fictive polymer. In every solid state, the modulus is an increasing function of crystallinity ratio. However, this dependence is moderate in glassy state, whereas it is very strong in the rubbery state.

In the glassy state of amorphous phase, we often consider that the increase of the modulus is connected to the excess cohesion brought by the crystalline phase. The excess cohesion is similar to H_f melting enthalpy.

$$K = b(d_e + x_c \frac{H_{f0}}{V})$$

where:

b is a parameter to the order of 10 at room temperature;

d_e is the cohesive energy density;

x_c is the crystallinity ratio;

H_{f0} is the polymer's enthalpy of melting, expressed in J.mol^{-1} ;

V is the molar volume of a structural unit whose molar enthalpy of fusion is H_{f0} .

Generally:

$$0.1d_e \leq \frac{H_{f0}}{V} \leq 0.9d_e$$

In other words, crystallization increases the modulus by a factor smaller than 2, with regard to the amorphous glassy phase.

If the amorphous state in rubbery state ($T > T_g$), the crystalline phase is around 1,000 times more rigid than the rubber phase. As a first approximation, we can say that the modulus (shear or tensile mode) tends to be proportional to the crystallinity ratio. For example, the Young modulus at room temperature of polyolefins in rubber amorphous phase is in the order of:

0.15 to 0.30 GPa	for PEbd
0.40 to 1.20 GPa	for PEhd
1.1 to 1.6 GPa	for PP

against 2 to 4 GPa for current glassy amorphous polymers, and a few MPa for the corresponding rubber phases.

Semi-crystalline polymers are different from glassy amorphous polymers essentially by their softening temperatures (HDT = *Heat Deflection Temperature*).

In the case of amorphous polymers, the HDT is close to the glass transition, typically:

$$\text{HDT} \sim T_g - \Delta T \quad \text{with} \quad \Delta T = 5 \text{ to } 10^\circ\text{C}$$

We will note that HDT may vary in some degrees according to the measuring conditions, particularly the applied load.

In the case of semi-crystalline polymers, HDT is generally higher than T_g (Table 5.4).

The example of PE shows that HDT is an increasing function with crystallinity ratio.

The example for PET demonstrates that when crystallinity ratio is relatively low, HDT values remain close to T_g .

Polymer	T_g (°C)	HDT (°C)	T_f (°C)
PE bd	-41	60	120
PE hd	-40	80	135
PP	0	100	165
POM	-50	125	177
PA 6 or 6.6	50 - 60	80 – 100	220 or 250
PET	80	85	255
PPS	88	260	288

Table 5.4. *Temperatures of glass transition, heat deflection, and melting of a few semi-crystalline polymers*

5.5.3.2. Yield and fracture properties

As for glassy amorphous polymers, the stress at yield σ_y is almost proportional to the modulus and therefore to the crystallinity ratio for rubbery amorphous phase polymers. For example, in the case of polyethylene:

$$\sigma_y \sim 0.04 E$$

We generally allow that the temperature and strain rate effects on σ_y can be represented by Eyring's law. However, at least for PE, many molecular flow mechanisms can coexist, each dominating in a certain strain rate and temperature domain.

When the plastic yield is approached, the chains present in the amorphous phase and interconnecting the crystalline lamellae ("tie chains") stretch and are able to reach their maximum extended length at the yield. Then, we can observe a variety of phenomena:

- if the interlamellar distance l_a is too small (meaning the sample has a high crystallinity ratio), then plastic strain is impossible, the fracture is brittle. For example, in PE, the fracture is systematically brittle as soon as $l_a \leq 6$ nm. This is why in applications such as gas or water piping, copolymers ethylene-butene, ethylene-hexene or ethylene-octene are used. The higher olefin, used in low concentrations, creates disorder in the chain and limits crystallinity to improve resilience;

- if the crystals are not very cohesive, then the tie chains can extract the segments which make them from the lamellae. The material becomes amorphized, plastic strains which can stretch the chains may occur, the material is ductile;

- in some cases, however, a cavitation process can occur in the amorphous phase, and acts as the initial stage of a brittle or semi-brittle fracture. We observe

crazing in semi-crystalline polymers. This generally differs from the crazing found in amorphous polymers because the fibrillae are bigger;

– finally, in some cases of slow strain, for example under fatigue, the fracture propagates in the interspherulitic zone. Examinations under the microscope reveal a “washing away” of the spherulites. Here also, we are dealing with brittle behavior. Practitioners know that spherulites with strong dimensions must be avoided.

Analyzing molecular mechanisms of semi-crystalline polymer fractures is relatively complex. With the thickness of the interlamellar amorphous layer and the “tie chains” density aside, the entanglement density in the amorphous phase, the chain length and the surface energy of the amorphous phase seem to play an important role.

Generally, semi-crystalline polymers have a better resistance to fatigue than amorphous polymers, which allows us to imagine using some of them for making hinges (for example, built-in caps on shampoo bottles made of polypropylene). With regard to high-performance composites, the semi-crystalline PEEK matrices offer the highest resistance to fatigue (aeronautic applications).

5.6. Plasticizers and impact modifiers

There are two types of additives which are frequently used in order to change the mechanical behavior of polymers: plasticizers and impact modifiers. In both of these, the mass fraction of the additive can reach several tens of percentages.

5.6.1. Plasticizers

Plasticizers are additives miscible in the polymer, therefore they are at least partially solvents. Their main characteristic, other than miscibility, is having a glass transition temperature T_{gs} which is lower than polymer one T_{gp} . When mixed into the polymer, these additives decrease the glass transition temperature. Let T_g be the glass transition temperature of the mixture, v_s and $(1-v_s)$ the respective volume fraction of the plasticizer and the polymer, and let α_s and α_{pb} be the respective coefficients of the free volume expansion:

$$\alpha_s = \alpha_{ls} - \alpha_{gs} \quad \text{and} \quad \alpha_p = \alpha_{lp} - \alpha_{gp}$$

where α_l and α_g represent the expansion coefficients in the liquid/rubbery state and glassy state, respectively.

The theory of free volume leads to:

$$T_g = \frac{(1 - v_s)\alpha_p T_{gp} + v_s\alpha_s T_{gs}}{(1 - v_s)\alpha_p + v_s\alpha_s}$$

Simha and Boyer showed that for polymers:

$$\alpha T_g \sim 0.113 = \text{constant}$$

By inserting this equation into the preceding formula, we obtain:

$$\frac{1}{T_g} = \frac{1}{T_{gp}} + A v_s \quad \text{where:} \quad A = \frac{1}{T_{gs}} - \frac{1}{T_{gp}}$$

A is a parameter which characterizes the plasticizer efficiency. Typical values of A for PVC plasticizer: $(1.5 \text{ to } 3) \cdot 10^{-3} \text{ K}^{-1}$.

In a given structural family, T_g is low when the molar mass is low. We understand why butyl phthalate is a more efficient plasticizer than didecyl phthalate, which is a more efficient plasticizer than an aliphatic polyester with a molar mass of 1 to 2 kg.mol⁻¹. However, butyl phthalate is very volatile and migrates easily, whereas the polymer plasticizer does not migrate. We can see that all industrial plasticizers are made of a compromise between the need for a certain level of efficiency (represented by factor A) and a reasonable resistance to migration. In current applications of plasticized PVC (flexible water hoses), the dioctyl phthalate may be sufficient. In more demanding applications in terms of durability (insulation for cables in nuclear plants), superior phthalates are preferable (didecyl, ditridecyl, etc.). In some critical applications (use in contact with hot water) we can be led to use polymer plasticizers, but by resigning ourselves to a weak plasticizing efficiency.

The modulus-temperature curves of a plasticized polymer and of the same unplasticized polymer take the shape seen in Figure 5.27.

The previous considerations show that plasticization can be explained by a decrease in T_g .

A more unexpected yet general effect is anti-plasticization: an increase in the modulus at the glassy plateau linked to the fact that plasticization partially prevents the β transition. This behavior has been observed both in PVC as well as in polycarbonates, polysulfones or epoxy networks.

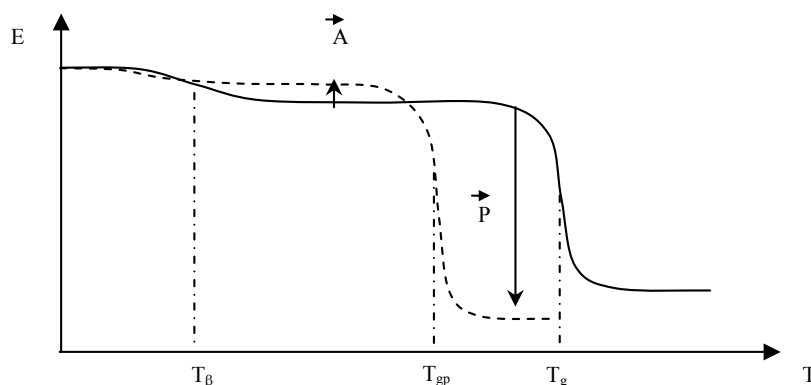


Figure 5.27. Shape of the modulus variation with temperature in the case of an unplasticized polymer (continuous line) and plasticized (dotted line). $T_\alpha \sim T_g$

Plasticization can be external as well as internal. For example, incorporating by copolymerization vinyl acetate (T_g of PVAC: 40°C) into PVC ($T_g = 80^\circ$) will plasticize the PVC (floor coverings, etc.). Internal plasticization is currently used frequently in the thermoset industry. In semi-crystalline polymers, plasticization is rarer. However, it is frequently used in polyamides 11 or 12 (aromatic sulfonamides). We, also, use plasticizers (oils) in elastomers, but in most cases, the real objective is not plasticization.

5.6.2. Impact modifiers

Impact modifiers are generally polymers which are non-miscible in the receiving polymer. They can be incorporated as external additives, mixed and dispersed mechanically. Or, they can be added as internal additives (non-miscible sequences in a copolymer block). Their fortuitous discovery was made over more than 50 years ago, when scientists were starting to realize that by mixing an elastomer (flexible, ductile) into a plastic (rigid, brittle), such as polybutadiene into polystyrene, a material with decreased rigidity but in acceptable proportions was obtained, whereas the strength and impact resistance were increased in considerable proportions (Figure 5.28).

Such properties however are only obtained when the blend morphology fulfills certain conditions: generally, we are looking for nodular morphologies (see section 5.2.5) with certain combinations (modifier volume fraction) = f (nodule size).

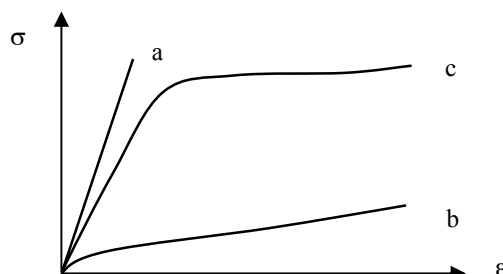


Figure 5.28. Diagram showing stress-strain curves of the receiving polymer (a) of the elastomeric modifier (b) and of the blend (c)

For some time, research in this area was confined to polystyrene: PS-PB blends, block copolymers, ABS type terpolymers, etc. It was then noticed in the 1970s that this approach could be generalized for all polymers: ABS as an impact modifier for PVC building profiles, EPR for polypropylene for car bumpers, polysulfones for structural adhesives, EPR for polyamides, etc.

Strengthening mechanisms have been the subject of a lot of research which has allowed us to highlight the following mechanisms:

- stopping crack propagation by nodules (crack blunting);
- nodules favor local shearing and nucleate diffuse shear bands which absorb a lot of energy.

That these two phenomena coexist may explain the interest in bimodal distributions of nodal sizes. The small nodules initiate shear bands, and the large nodules stop the cracks.

For an impact modifier to be efficient, it has to stick to the matrix so it prevents any decohesion. Adhesion is optimal in block copolymers because covalent bonds unite the blocks.

For polymer blends which are unbound from the beginning, chemical functions can be inserted into the additive, which promote “anchoring” onto the receiving polymer. This can be seen in the case of maleic anhydride grafted onto EPR, which ensures its bond with all kinds of polar polymers.

In some cases, a third body will preferably be put on the interface and ensure the bond between two phases. As an example, let us consider two non-miscible polymers called A and B. The third body could be a block copolymer $-(A)_n-(B)_p-$. Sequence $-(A)_n-$, which is miscible with polymer A will become entangled

in the chains of A. Sequence $-(B)_p-$ will do the same with B: the block copolymer will act as a fastener, binding the two phases together.

We are able to judge the efficiency of an impact modifier in a polymer by the variation in resilience (Figure 5.29) or the toughness that it induces at room temperature. The displacement of the ductile-brittle transition temperature (towards low temperatures) is also a good criterion (Figure 5.30).

In the last 30 years, the market for impact modifier has developed rapidly. The only thing which stands in the way of their expansion could be an eventual hardening of the limits connected to recycling, which is of course not an easy option for polymer blends.

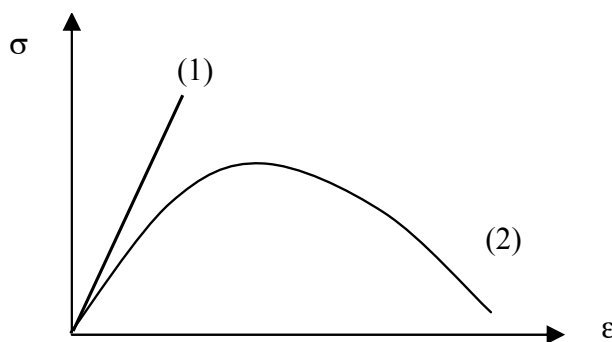


Figure 5.29. Stress-strain curves (instrumented impact) by a brittle polymer (1) and the same polymer by impact modifier (2)

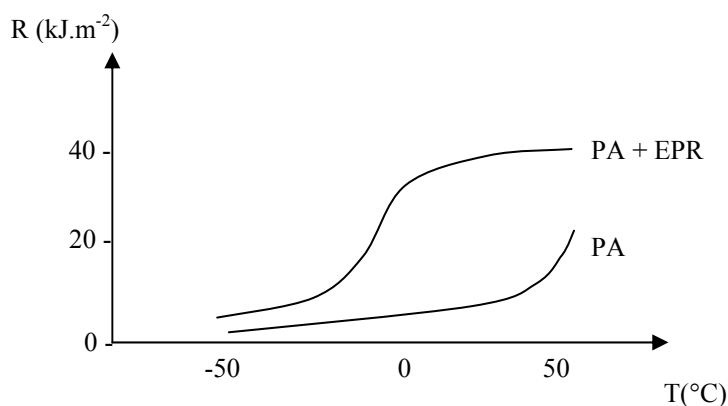


Figure 5.30. Resilience according to temperature for a polyamide (PA) and the same polyamide reinforced by EPR

5.7. Properties of a few industrial linear polymers

Polymer	Acro- nym	Type (a)	T _g (°C)	T _f (°C)	d _a (b)	d _c (c)	E (GPa)(d)
Low density polyethylene	PEbd	C	-43	120	0.85	1.00	0.2-0.3
High density polyethylene	PEhd	C	-43	140	0.85	1.00	0.8-1.2
Polypropylene	PP	C	-3	192	0.85	0.95	1.1-1.6
Polyoxymethylene	POM	C	-50	177	1.25	1.54	2.9-3.4
Polyamide 6	PA6	C	50	223	1.08	1.23	3.2
Polyamide 6,6	PA66	C	50	250	-	-	2.6
Polyamide 11	PA11	C	27	190	1.01	1.18	1.0
Ethylene polyterephthalate	PET	C	80	255	1.33	1.46	2-9
Polybutylene terephthalate	PBT	C	60	227	-	-	2.5-2.8
Polyphenylene sulfide	PPS	C	85	288	1.34	1.46	-
Polyether ether ketone	PEEK	C	141	337	1.26	1.32	3.6
Polyvinyl chloride	PVC	A	80		1.39	-	3.0
Polystyrene	PS	A	105		1.05	-	3.3
Polymethyl methacrylate	PMMA	A	127		1.18	-	3.3
Polycarbonate	PC	A	150		1.20	-	2.4
Polysulfone	PSU	A	190		1.24	-	2.6
Polyethersulfone	PES	A	210		1.37	-	2.7
Polyetherimide	PEI	A	210		1.27	-	3.1
Polyoxyethylene	PPO	A	210		1.07	-	2.4
Polyphthalamide	PPA	A	127		1.15	-	2.4
Polyamideimide	PAI	A	275		1.42	-	4.9

Table 5.5. *Properties of a few industrial linear polymers*

NOTES. –

- (a) semi-crystalline type (C) or amorphous (A);
- (b) amorphous-state density;
- (c) crystalline-state density;
- (d) sample modulus used under industrial conditions;
- (e) dry-state material modulus. Great decrease in humid state;
- (f) modulus greatly varying with orientation: 2 GPa for isotropic part, 9 GPa for strongly oriented fiber.

5.8. Conclusion

The cost of industrial polymers ranges between about 1 and 100€/kg. Indeed, commercialized tonnage is a function which greatly brings down the cost. Experts generally distinguish three classes of polymers: special polymers (such as thermostable polymers used in aeronautics or polymers for medical use); engineering polymers whose cost may vary between a few and several tens of €/kg (e.g. polyamides, polycarbonate, etc.) and commodity polymers (polyethylene, polyvinyl chloride, polystyrene, etc.) whose cost does not exceed a few €/kg. Evidently, building and civil engineering sectors are only interested in two of these categories; technical polymers for relatively low volumes of applications: waterproofing, concrete additives, etc., and commodity polymers for a high volume of applications: thermal insulation, window profiles, pipes, packaging, etc.

Compared to metals, synthetic polymers are young materials, only appearing around 50 years ago. But we can already see that their evolution has followed a different path. The history of metallurgy was first of all to research the best performances:

Native copper → bronze → iron → steel → special steels, etc.

The history of plastics processing was rather to research the best compromise between cost and performance. Of course, we can cite the spectacular successes of polymers as an example in their competition with traditional materials: polyamides replacing silk parachutes, polypropylene to replace the steel of car bumpers, epoxy-carbon composites to replace aluminum used in helicopter blades, etc. However, a large proportion of the current research effort is dedicated to the competition between plastics themselves. The fundamental question is: can we replace a polymer costing 20€/kg with a polymer which costs 2€/kg? An overview of scientific and technological literature shows us that the most “advanced” materials in this domain, meaning the object of the most intense research, are not characterized by the highest intrinsic performances. These are rather common polymers with mediocre performances, but, however, offering a compromise: ease of processing against usage properties and unbeatable costs.

We can easily see that this trend will increase in the future and win over all the material families because economic constraints will weigh down more and more on the following chain: synthesis → processing → use. Can a miracle, such as the (fortuitous) invention of polyethylene happen again? Theoretically, it is possible but seems improbable after more than 70 years of systematic research in macromolecular synthesis. The domain will not remain stagnate for as long: progress in knowledge will allow for a more and more tight structure control (on all scales) during synthesis and implementation. Researchers will continue to exploit

the quasi-infinite combinatory offered by the diversity of polymers (and for a given polymer microstructure), additives, fillers, possibilities for reactive processing, etc.

The effects of this research allow us to accommodate existing chemical families, perhaps for a long time to come, by trying to adapt them to the demands of sustainable developments (improvement in long term resistance, recycling). We will see new families of polymers emerge from “green” chemistry: vegetal or biochemically synthetic polymers. However, it is difficult to imagine these new materials being capable, one day, of supplanting the current common polymers.

Polymers are generally perceived as being bad by environmental activists, above all because of the massive and anarchic spreading of packaging in natural areas. However, whatever the threats to the environment which weigh down on industrial civilization, for now it is impossible to imagine its future without polymeric materials.

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Chapter 6

Formulation of Plastics

6.1. Introduction

How do we go from a polymer to plastic or rubber? Such is the question being asked now, and it is a question which brings out the art of the formulator. In fact, polymers are practically all unsuitable for direct use straight after polymerization. Therefore, it is necessary to use ingredients known as additives, working agents, etc.

For certain polymers such as PVC and rubbers, the use of additives and fillers enters the art of formulation. Beyond their capacities to implement the polymer, they make it possible to manufacture products which are especially adapted to the material's use and its need.

From this point of view, the considerable offer of the market in terms of available ingredients makes it possible to propose a wide competitive range of formulated products, perfectly adapted for each use. Therefore, any PVC producer can propose all kinds of window profiles where the formulations are different for each use. A manufacturer of bridge bearing plates will work with different elastomers and ingredients for a specific usage, and will offer a vulcanized product specific to their company and their know-how. Manufacturers of furniture, or decoration items and products, will propose materials made from polypropylene, PMMA or polystyrene, for close or identical uses.

Chapter written by Michel DE LONGCAMP.

These specificities related to the art of the formulation allow companies real competition in the field of technology.

These ingredients can be organic or inorganic. Either they come in phase juxtaposition, and react themselves against stresses, like a protective shield of the based polymer. Or, they are polymer solvents and react indirectly with it and not against stresses. Furthermore, they modify noticeably the molecular chain, as is the case in rubber vulcanization.

Here we are not trying to take up the scientific foundations of formulation (see Chapter 5) but rather trying to put ourselves in the skin of the “formulator”, a man of technology *par excellence*, who knows all the ingredients, how much should be used, the compatibilities between them, their necessary roles. It is he who has studied polymers and elastomers, and who knows the transformation and mixing modes.

The formulator is not strictly a scientist, but a technician who applies a science. Books will give him the formulation base, which will enable him to create marketable products which will meet the minimum need for the specifications.

The art of the formulator, is to live with his specifications, discovering the most adapted commercial ingredients, the best targeted polymer grade, the ideal plasticizers, the most skilled fillers in order to give a perfect response to the specifications in technical and economic terms, or even to meet the hidden needs and therefore to offer a “better than good” product.

Here, we may dare to put forward a comparison with cooking, a practice widely used in the medium of formulation. If we were to take some 500 traditional recipes in France, all the cookbooks, with a few exceptions certainly, will offer the same formulas, or close enough. But according to the place, the quality of the guests, the season, the chef will adapt the base recipe to please the most people. In the same way, if we were to put this same base recipe into the hands of many different chefs, each of them will make the same dish, but the end results will all be different from one another. Cooking is an art and chefs are great artists, just as formulation is an art, and formulators are great artists who, sometimes, verge on genius.

Finally it should be noted here that, in this chapter, we will only discuss polymer formulation which is intended to create industrial plastic products. Everything that relates to formulation on building sites to make products which repair, protect, inject or coat, whose base polymers are primarily epoxides, polyurethanes, polyesters and other acrylic resins will be otherwise discussed.

6.2. Ingredients used for plastic formulation

The formulation of plastics brings into play additives which are theoretically soluble in the polymer, and insoluble fillers which form a biphasic system with the polymer.

There are many types of additives: working agents, reticulating agents, stabilizers divided into anti-oxidants and anti-UV, plasticizers, fireproofing agents, pigments and dyes, inflating agents, anti-shocks. The great series of mineral fillers can be added to this list.

6.2.1. *Polymers*

Are all polymers and elastomers able to accept mixing with additives?

Not all polymers need a very sophisticated ingredient technology. Many specific polymers such as EVA, PMMA, PET, PVC, and technical polymers such as PA, PTFE and PVDF, are already stabilized for polymerization and are often proportioned so as to remain stable throughout their life. Moreover, the molecular structure of these last three polymers makes them naturally resistant to oxidation.

Polymers coming from petrochemistry, EP, PP are additived, but especially with fillers, pigments, lubricants, and generally in small amounts. This phase is almost always carried out by the polymerist and is not a part of industrial specialities. To raise the commerciality, the producer will act directly on the polymerization system and will therefore modify the structure of the molecular chain. For these polymers, the choices offered are related more to type or the grade of polymer, which is often numerous, than with its ingredient modification.

In conclusion, all polymers are “mixed”; many of which are additived during or after polymerization. Others are received a formulation due to the simple need to be put into action. Some, such as PVC, rubbers, some polystyrenes or polypropylenes, need a real reflection. These are the polymers which will be discussed in this chapter.

6.2.2. *Working agents*

In the case of PVC, we can clearly distinguish lubricants from plasticizers.

6.2.2.1. *Lubricants*

At high temperatures, considerable friction forces appear on the walls and between the PVC grains themselves, when the PVC is mixed. The purpose of lubrication is to control and regulate these friction forces. Therefore, we use:

- external lubricants, responsible for preventing the PVC from slipping on the walls of the transformation apparatus, which is generally an extruder; the formulator will choose a product which is not very compatible with PVC to create a film between the walls and PVC, such as polyethylene waxes or paraffins;
- internal lubricants whose role is to control internal friction between the PVC molecules, therefore causing the matter to a self-heat, and consequently leading to thermal degradation of the product. With these products being defined as internal to the matter, they must not migrate over time. The formulator will then choose products compatible with PVC like fatty-acid esters, generally from stearic acid.

6.2.2.2. *Plasticizers*

In general, these are mineral oils intended to make the incorporation of mineral and organic ingredients into the PVC or polyolefin mass easier.

6.2.3. *Cross-linking agents*

The use of cross-linking agents, such as organic peroxides (benzoyl peroxide types), has been known for a long time for making a very precise matter, a nitrile rubber/PVC mixture, used a lot before the 1980s for its resistance to ageing in a hydrocarbon solvent environment. To turn these two compatible polymers into a coherent mass, it was necessary to resort to a carbon/carbon by organic peroxide reticulation.

In certain cases, the formulator will have to use organic peroxides for polyethylene reticulation. This *chemically reticulate polyethylene* (CRP) allows for a usage under extreme temperature conditions – hot water piping (heating or medical), electric cable isolation under severe conditions, etc. – while maintaining raised mechanical properties.

6.2.4. *Stabilizers*

Some thermal stabilizers are primarily used to protect the polymer during its time period at a high temperature, during work.

At high temperatures, PVC breaks down by producing hydrogen chloride (HCl). This reaction is called dechlorination. Consequentially, it produces a strongly colored, infusible product, which blocks all the transformation machine's openings.

6.2.4.1. *Role of the stabilizers in PVC*

We require the stabilizers to:

- fix the released hydrogen chloride to prevent autocatalytic phenomena;
- react on the unsaturated bonds to remove polyenic structures responsible for yellowing.

The effectiveness of stabilizers depends on their chemical nature and their action method. The formulator will prefer to use stabilizer mixtures according to these action methods.

PVC stabilizers are generally used in concentrations of 1 to 3%.

6.2.4.2. *Nature of stabilizers*

We can classify stabilizers according to their chemical nature.

Lead-based stabilizers, with an excellent quality-price ratio, were certainly the most used. Today they are confined to manufacturing products which are classified as being non-accessible, such as electric cables and certain underground pipelines used for fluids evacuation.

Tin-based stabilizers do not present some of the disadvantages which are found for lead, but still remain a hot topic in terms of environmental concern.

Calcium-zinc and barium-zinc stabilizers can be found in abundance on the market. Their initial coloring is excellent; they present an average thermal stability and a brutal decomposition. Calcium-zinc stabilizers are used a lot in food packaging.

Organic compounds and secondary stabilizers such as Stearoyl Benzoyl Methane are also used in food quality packaging.

Taking into account the pressure and advance in studies on the environmental impacts of chemicals, there are many works in progress which aim to develop a new generation of stabilizers in order to replace products which contain lead and tin.

6.2.4.3. *Antioxidants*

Phenols, amines, sulfides, phosphites, etc., are used in practically all the aliphatic polymers with the exception of fluorides which are intrinsically stable.

Antioxidants are generally used in concentrations lower than 0.5% in plastics but to exceed 1% in elastomers.

PVC concerns specific stabilization methods, particularly based on the principle of substituting unstable chlorine atoms ($\text{Ca}^{++}/\text{Zn}^{++}$ soaps, organostannics, etc.).

6.2.4.4. *Anti-UVs*

These are used for applications in external exposure. They act by absorbing UV rays before they can come to degrade the polymeric structure. The formulator has many tools at his disposal whose level of effectiveness is linked to the polymer's basic structure:

- 2 hydroxy benzophenones, hydroxy phenyl benzotriazoles, substituted acrylonitriles, and benzylidene malonates are the most frequently used UV absorbers, in a concentration higher than 1%;
- tetramethylpiperidine type sterically hindered amines (HALS), are generally very effective radical captors, used in concentrations of 1%.

The formulator will use mineral-based anti-UV screens, such as titanium oxide which forms, using the flat structure of its particles, a real protective shield against the sun's rays, and by its very white color, a reflective screen without absorbing heat.

6.2.5. *Plasticizers, non-working agents*

Plasticizers are generally used to soften polymers.

The main plasticizers are dioctyl or dibutyl phthalates. Some are chlorinated, when it is a matter of using the naturally fireproof properties of PVC.

The dioctyl phthalate used at 30% transforms the initially rigid PVC ($T_g = 80^\circ\text{C}$) into an elastomer ($T_g \sim -50^\circ\text{C}$) which can be used for creating coated fabrics, flexible tubes, soft toys.

The aromatic chlorinated plasticizers are used in polycarbonate for making supple organic glass (contact lenses).

The polymers with low T_g (polyisobutene, polybutylene, low-density polyethylene, etc.) are used in polystyrene, very sensitive to shocks, making it less brittle and causing what is known as a *polystyrene shock*.

6.2.5.1. *Specific case of “plastisols”*

PVC offers an interesting domain with plastisols: the porous surface of the PVC grain makes it possible to absorb a large volume of the plasticizer.

The plastisols or “pastes” are made of suspensions in organic plasticizers, of low dimension PVC particles (0.1 to 3 μ) prepared by emulsion or micro-suspension processes, in the presence of additives such as stabilizers, fillers, pigments, and blowing agents. This formulation makes it possible to make coated pastes, which after the PVC’s gelation (the grains’ ability to bind them) creates fabrics for textile architecture, PVC/polyester composites.

Creating an object must pass through a *gelation* stage. Subjected to heat, approximately 140 to 210°C, the plastisol is transformed into a homogeneous mass. This temperature increase favors PVC particle coalescence, so the particles lose their individuality to form one continuous film. This phenomenon is more or less long according to the articles, their thicknesses, etc.

6.2.5.2. *Plasticizers used*

We distinguish:

- primary plasticizers with strong plasticization effect which can be used alone;
- secondary plasticizers used as a complement to the primary plasticizers.

The primary plasticizers are essentially phthalates: dibutyl phthalate, dibutyl benzene phthalate, di-2-ethylhexyl phthalate, diisodecyl phthalate.

The secondary plasticizers are adipates and sebacates (low temperatures), trimellitates (high temperatures), epoxidized soya oils (helps with thermal resistance of stabilizers), phosphates (fire resistance), etc.

6.2.6. *Various organic additives*

6.2.6.1. *Fireproofing agents*

Fireproofing agents are used to improve the polymer’s resistance to fire, which are considered flammable in their natural state. It is a matter of mixing species such as aryl phosphates, halogenous molecules and inorganic fillers such as antimony

trioxide, alumina trihydrate, etc. (see Chapter 8). They are generally used in high concentrations, susceptible to noticeably modifying the usage properties.

6.2.6.2. *Pigments and dyes*

All polymers can accept pigments and dyes in the mass.

All organic or mineral pigments can be used. The formulator favors mineral pigments in the case of products at risk from being exposed to the sun, and organic pigments for more varied colors.

In the case of “UV sensitive” polymers, the formulator will combine the pigments with a titanium oxide base which will screen the UV rays. In this case, the obtained colors will not be as bright as those obtained from the pure state.

The polypropylene and high density polyethylene, only slightly sensitive to UV rays, are often used for urban homes, materials used for children’s toys and playgrounds, because they allow a larger variety of colors, low-maintenance and in particular, child-proof products (no sharp angles, unbreakable products, etc.).

PMMA or PVDF type polymers, naturally resistant to UV rays, make it possible to create all possible colors, even allowing the use of pearled or metallic pigments to give mirror or 3D effects.

6.2.6.2.1. Specific case of PVC

Titanium oxide, used as an anti-UV agent, has a valuable use in PVC. Using titanium oxide has two distinct effects:

- the maximum use amount is 5%. If the amount is higher than this, the formulator risks being exposed to chalking (surface exudation of TiO_2 particles);
- the use amount is 1%, for its UV protective properties. It prevents the creation of bright colors in the mass and restricts the formulator to pastel colors.

6.2.6.3. *Blowing agents or porophores*

The azodicarbonamides are most often used for plastisols and rubber.

6.2.6.4. *Specific additives: fungicides, anti-static agents, odor agents*

In some very specific cases, the formulator will use them according to how the final product will be used.

6.2.7. Fillers

Under the category of fillers, we denote any inert or mineral substance which generally makes it possible to carefully modify the mechanical, electric, or thermal properties, the surface aspect or the cost price, when added to the polymer.

The principal fillers used are the following:

- calcium carbonate, natural or precipitated, which is characterized by weak plasticizer absorption and its beautiful surface shine; this is usually used for floor covering;
- synthetic silicas, also used for floor coverings;
- kaolin, for abrasion resistant properties;
- talc used as a fillers in polypropylene, for the parts under great mechanical stress.

6.3. Conclusion

The formulator can meet all a user's needs from the moment when he has the specifications expressed in terms of use at hand.

The difficulty today is in accepting a new vision of the conception of a work, and the differences in material behavior analysis.

Formerly construction products were determined: concrete, steel, glass, quarry materials, etc. It was these materials which fixed construction rules and the main contractor had to adapt to these rules. Today the spectrum of proposals for these products is already wider, thanks to the requirements of architects, and the birth of a chemistry which has made it possible to *formulate* certain concretes or to modify mineral steels and glasses, but still they remain conclusive.

In the case of plastics and all the “soft” materials, this rule no longer exists. Plastics force the architect to work from a blank page, to build without constraint, or better still, to build his own constraints.

Plastics are no longer construction material determiners, but to be determined. Filling a void, creating a shape, removing posts in a floating space, making enormous transparent surfaces without visible support, etc.

The 2008 Olympic Games held in Beijing, demonstrated considerable resources drawn from plastics especially on behalf of the plastic imagination of architects with the “Bird's Nest” and the *Water Cube*.

Soft products, materials to be determined, built without constraint; we are no longer in the domain of a simple evolution of behavior, but in a revolution of thought. It will soon be 30 years since this revolution began. There are no new concepts, or new products on the market which do not use plastic or organic materials or at the very least, organic chemistry.

This revolution is moving and will not stop, because it is through the formulator's subtlety, the ability to choose good polymer, the best feeds, perfectly adapted antioxidants, etc., that the materials will always correspond to the main contractor needs.

It is not our aim to propose that everything be built from plastic, but the use of the plastics in their field of excellence, thus perfectly formulated and adapted, allows a construction to be near perfection, by the will of the main contractors.

Chapter 7

Ageing and Durability of Organic Polymers

7.1. Definitions, general comments

7.1.1. *Ageing*

“Ageing” is any slow and irreversible phenomenon (under usage conditions) of a material’s structure, morphology or composition, under the effects of its own instability and/or interaction with the environment.

Any condition is considered to be slow when the kinetics are not apprehensible in a time-scale which is compatible with economic restraints.

The classic approach of predicting long-term behavior consists of carrying out accelerated tests simulating, as accurately as possible, natural ageing and to presume that the hierarchy of stability for several materials is the same in accelerated and natural ageing. *The modern approach* consists of developing a kinetic model derived from analyzing degradation materials. Accelerated ageing is, then, used to identify the model parameters.

7.1.2. *Lifetime*

The lifetime (t_f) is specific to a property (P) of the material, as crucial as possible for the application considered, and for which it is possible to define a critical value

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P_f . Beyond this value, the material will no longer be capable of fulfilling its function. The kinetic model must allow the following function to be established: $P = f(t)$, which describes the evolution of P over the ageing process. The lifetime is then defined by:

$$t_F = f^{-1}(P_F)$$

where f^{-1} is the reciprocal function of f . P_F is often called the end-of-life criterion.

7.1.3. Extrapolation principle

The *classic approach* consists of considering that the simple laws established for basic processes also apply to complex processes, such as ageing. For example, in thermal ageing (a rise in temperature leading to acceleration), we can write:

$$t_F = t_{F0} \exp\left(\frac{E}{RT}\right) \quad (\text{Arrhenius law})$$

The tests accelerated at different temperatures enable us to identify t_{F0} and E . Next, it is then sufficient to extrapolate to use temperature to obtain lifetime.

In the case of ageing by irradiation (photo or radiochemical), it may be useful to consider that the end-of-life is an isodose state, in other words:

$$\dot{d}_a t_{Fa} = \dot{d}_u t_{Fu}$$

where $\dot{d}$ is the dose rate (light intensity for photochemical ageing), indices a and u are specific to accelerated and natural ageing, respectively.

In fact, neither of the two laws above can be considered as being systematically valid for ageing. Using these laws without control may lead to important errors of appreciation.

For *kinetic approaches*, the ageing mechanism is divided into elementary processes. For each of these processes, the laws mentioned above are applicable, when reformulated in terms of elementary rates:

$$v_i = v_{i0} \exp\left(-\frac{E_i}{RT}\right) \quad \text{and} \quad v_j = G \dot{d}$$

The global kinetic function $P = f(t)$ includes all the associated elementary kinetic parameters in a more or less complex mathematical equation. Extrapolation under

natural ageing conditions will be achieved by extrapolating all the elementary parameters by their associated law.

Let us use a simple example from thermal ageing where the total rate is the sum of the rates of two elementary processes which obey the Arrhenius law:

$$v = v_{0a} \exp\left(-\frac{H_a}{RT}\right) + v_{0b} \exp\left(-\frac{H_b}{RT}\right)$$

The elementary process rates are equal at temperature T_c , such as:

$$T_c = \frac{H_b - H_a}{R \cdot \ln\left(\frac{v_{0b}}{v_{0a}}\right)}$$

Away from T_c , one of the processes is insignificant in relation to the other, and the Arrhenius law may be an acceptable estimation to calculate v :

$$v \approx v_{0i} \exp\left(-\frac{H_i}{RT}\right)$$

with $i = a$ or b .

On the other hand, around temperature T_c , v does not obey the Arrhenius law at all. In this domain, lifetime predictions bypass the identification of the parameters which characterize the elementary processes v_{0a} , H_a , v_{0b} , H_b and the calculation of the sum of the two Arrhenius terms.

In practice, cases when the total rate of a process results from the sum of elementary rates are not rare.

7.1.4. Induction period

In many cases, ageing kinetics are characterized by the existence of an initial period during which there is no noticeable evolution of the polymer usage properties (Figure 7.1).

Generally, an *induction period* is a period of time over which the material preserves its original properties. There are three main reasons which explain such behavior (largely nonlinear behavior, it must be said):

- induction phenomenon is specific to the chemical reaction responsible for ageing. Oxidation processes (radical reactions in branched chains) often manifest this characteristic at low temperatures (typically when $T \leq 150^\circ\text{C}$);
- induction phenomenon is related to the presence of an efficient stabilizer. So long as this stabilizer is not completely consumed, degradation remains insignificant;
- the chemical structure evolves under an ageing effect, but the considered properties only evolve beyond one threshold. Embrittlement phenomena often manifest this characteristic.

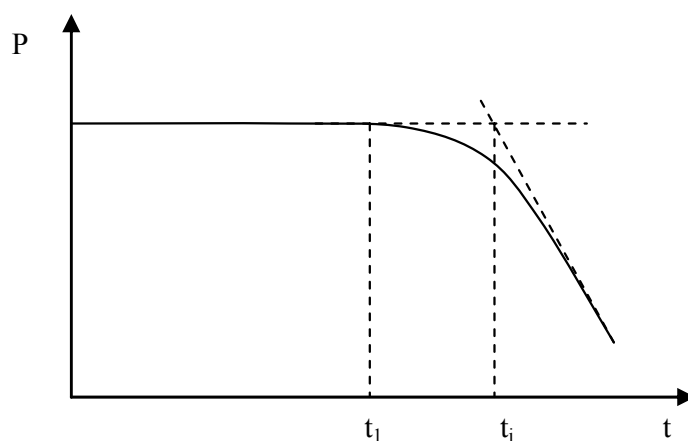


Figure 7.1. *Diagram representing kinetics of the evolution of usage property P with an induction period of length t_i*

Obviously the combination of two or three causes above is not excluded.

Figure 7.1 enables us to understand the remote amount of interest, so as not to say the uselessness, in punctual tests based on the study of one ageing duration length. For example, a duration test where $t_1 < t_i$ lets us establish that t_i is higher than the test time, but we cannot be sure, however, if $t_1 = 0.95 t_i$ or $0.1 t_i$ or $0.01 t_i$.

In conclusion, any analysis relevant to ageing bypasses the stage where the kinetic curves of the material's evolution are established in unique time scales which allow for a significant evolution, if possible to a state where it would then be considered unsuitable for the characterized usage.

7.1.5. Different types of ageing

7.1.5.1. Chemical ageing

Ageing induced by a chemical modification of the material's structure.

7.1.5.2. Physical ageing

Ageing affecting chain conformation, morphology or the material composition without changing the chemical structure of the macromolecules.

7.1.5.3. Thermal ageing

Ageing where the kinetics only depend on temperature and atmospheric composition. This can be either physical, chemical or both.

7.1.5.4. Wet ageing

Ageing induced by the interaction of the material with water present in the environment, either as a liquid or vapor. This interaction can be either physical or chemical.

7.1.5.5. Photochemical ageing

Chemical ageing induced by the interaction of a polymer with light rays (generally solar UV radiation), where oxygen from the atmosphere generally plays a large role (photo-oxidation).

7.1.5.6. Radiochemical ageing

Chemical ageing induced by the interaction of a polymer with ionizing rays (γ , β , α , neutrons, etc.), where oxygen from the atmosphere may play a large role, especially at low dose rates.

7.1.5.7. Biochemical ageing

Chemical ageing induced by the interaction of a polymer with living organisms (bacteria, moulds, etc.).

7.2. Physical ageing

7.2.1. Physical ageing by structural relaxation (broad meaning)

The two phenomena responsible for the solidification of polymers at the end of their processing operations are vitrification and crystallization. Both of which are kinetic phenomena which lead to a thermodynamic state out of equilibrium. Glasses

have an excess of unstable conformations and free volume (section 5.2.5). Semi-crystalline polymers are not completely crystallized; their melting point is clearly lower (often by a few tens of degrees) than its equilibrium value.

If, in their use conditions, a residual molecular mobility takes place in these polymers (β movements in glass, α movements in the rubbery amorphous phase of semi-crystallines), then they will slowly move towards an equilibrium (structural relaxation).

The general characteristics of this type of ageing (wrongly called “physical” ageing because there are other physical mechanisms of ageing) are the following:

- ageing results in a compaction of the matrices and a loss of enthalpy;
- the stress at the plastic yield increases;
- the creep compliance decreases;
- evolution slows down but may continue over recorded time.

The evolution of creep compliance $J(t)$ has been the subject of quantitative studies, particularly by Struik [STU 78] for organic glass.

The creep curves of samples aged during t_v , $10t_v$, $100t_v$, etc., take the shape seen in Figure 7.2.

If we say that $a_v = \text{Log} \left(\frac{t_{1v}}{t_{2v}} \right)$ is the logarithm of the ageing time ratio, and $a_n = \text{Log} \left(\frac{t_{1n}}{t_{2n}} \right)$ the corresponding interval of the creep curves on the logarithmic time scale, we observe that $\frac{a_v}{a_n} \approx 1$.

In other words, increasing the ageing time by a decade causes an increase in the characteristic creep time by approximately a decade.

This is a very general property of structural relaxation ageing, whether it is a question of polymers, molecular organic materials (glucose), sand heaps or emulsions.

The reduction in creep compliance, as with the stress increase at the plastic yield, would be an advantage in many applications. Unfortunately, it is compensated by an important reduction in ductility/toughness (Figure 7.3a).

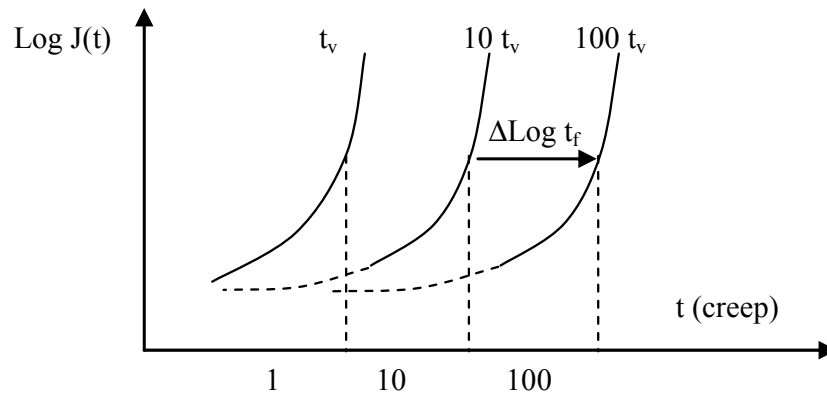


Figure 7.2. Creep curve (in a log – log scale), of aged samples t_v , $10t_v$ and $100t_v$ at a temperature lower than T_g

Increasing yield stress (up to 20 MPa for a polymer such as polycarbonate), the loss of ductility without altering the molar mass distribution, and the appearance of an endotherm in the immediate vicinity of T_g (Figure 7.3b) allows us to recognize structural relaxation ageing from another type of ageing, in the case of an amorphous glassy polymer.

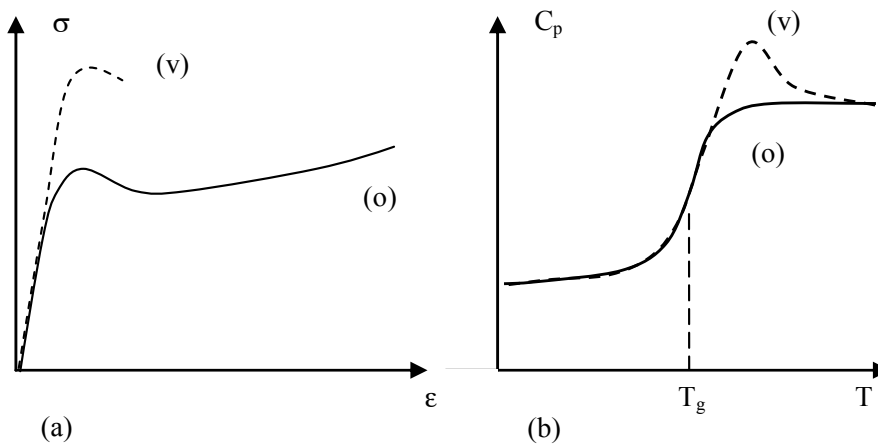


Figure 7.3. a) Shape of stress-strain curves from a new sample (o) and from a sample subjected to ageing under structural relaxation (v). b) Shape of (DSC) thermograms from a new sample (o) and from a sample subjected to ageing under structural relaxation (v)

7.2.2. Ageing by solvent absorption

Solvents plasticize polymers and therefore lead to a reduction in T_g and a reduction in the yield stress in a ductile system.

However the most important effects, in practice, appear when the polymer is subjected to static stress.

Indeed, plasticization favors damage, in particular by crazing.

For example, let us consider a creep test where damage is detected by an optical method.

The behavior is represented by Figure 7.4.

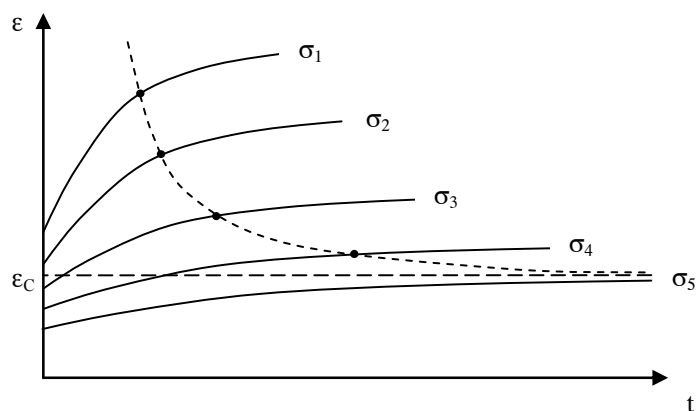


Figure 7.4. Shape of the creep curves in the presence of a solvent. $\sigma_1 > \sigma_2 > \sigma_3 \dots$ etc. The black points represent onset of damage. The envelope of the points has a horizontal asymptote at $\epsilon = \epsilon_C$

We can see that there is a critical strain ϵ_C , below which the material will not be damaged. Value ϵ_C is according to the polymer/solvent pair.

In simple cases (only slightly polar polymers, such as polyphenyleneoxide (PPO), ϵ_C varies with the solvent's solubility parameter, according to Figure 7.5.

We must remember that certain vapors (H_2O , CO_2) are very important. In addition, the plasticizers themselves can migrate from one polymer into the other and induce damage under stress.

Where complex parts are concerned, localized damage in the presence of solvent vapors may reveal the presence of residual stresses.

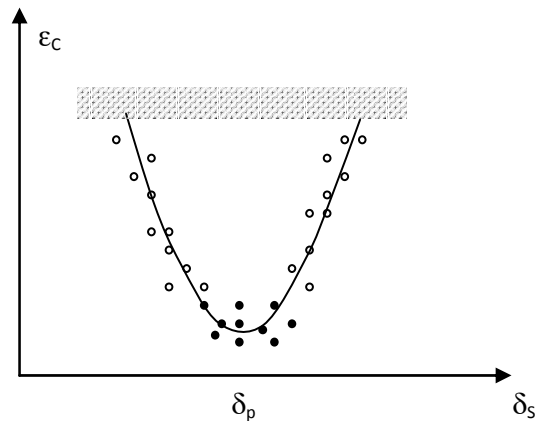


Figure 7.5. Shape of the critical strain variation ϵ_c with the solvent's solubility parameter in the case of PPO. The curve's minimum corresponds to $\delta_s = \delta_p$ (the polymer's solubility parameter). (○): crazes. (●): open cracks. The hatched area relates to the ϵ_c values observed in the air. NB For polar polymers (PMMA for instance), the behavior is more complex, the curve $\epsilon_c = f(\delta_s)$ may include several minima

Solvent penetration in a polymer results in swelling, which can also generate strains related to differential. Damage problems induced by water diffusion in organic matrix composites have been, and are still, the subject of active research, particularly in aeronautics.

7.2.3. Ageing by additive migration

Thermodynamically, a polymer + additive mix is out of equilibrium. Since the additive's concentration in the surrounding environment is nul, there is no equality in its chemical potential within the environment and the polymer.

To restore this equality and move towards equilibrium, the additive tends to migrate out of the polymer. This migration is made up of two stages (Figure 7.6).

The first stage is the movement into the environment for the molecules close to the surface, in other words, crossing over into the polymer/environment interface. In gaseous environments, (e.g. the atmosphere), the evaporation of the additive is responsible for this stage. In liquid environments, the additive's dissolution by the said liquid plays the same role. Let us note that a second polymer, in contact with

the first, may play the same role as a liquid. Polymers also have a tendency to switch stabilizers. Plasticizers (PVC, for example) are well-known for their tendency to migrate into all sorts of polymers.

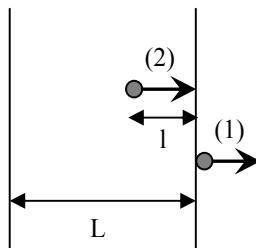


Figure 7.6. Diagram representing the two stages of a polymer's migration outside a polymer

The second stage begins as soon as the first molecules of the additive which leave during the first stage have created a concentration gradient. This is the “motor” of the molecular diffusion occurring in the core towards the surface. Duration t_d of the molecule's path of length l is given, in the case of diffusion which obeys the Fick law by:

$$t_d = \frac{l^2}{D}$$

We can see that t_d rapidly increases with the sample's thickness L .

Therefore, we can now distinguish two kinetic regimes.

7.2.3.1. Mode controlled by evaporation (or dissolution)

When L is low (fibers, films) and diffusivity D is high enough, evaporation is slower than diffusion and therefore controls the migration's total kinetics.

Thus, concentration C of the additive in the polymer decreases in an exponential way with time:

$$\frac{dC}{dt} = -HC$$

The evaporation rate constant H decreases with the additive molar mass and its cohesive energy density.

7.2.3.2. Mode controlled by additive diffusion

When L is high and D is low, diffusion controls kinetics. In the simplest of cases, the Fick law is applied:

$$\frac{\partial m}{\partial t} = D \frac{\partial^2 m}{\partial x^2} \quad (m = \text{mass variation related to additive loss})$$

In the initial time period, the mass decreases in proportion to the square root of the time. A concentration gradient is established in the thickness of the sample (Figure 7.7).

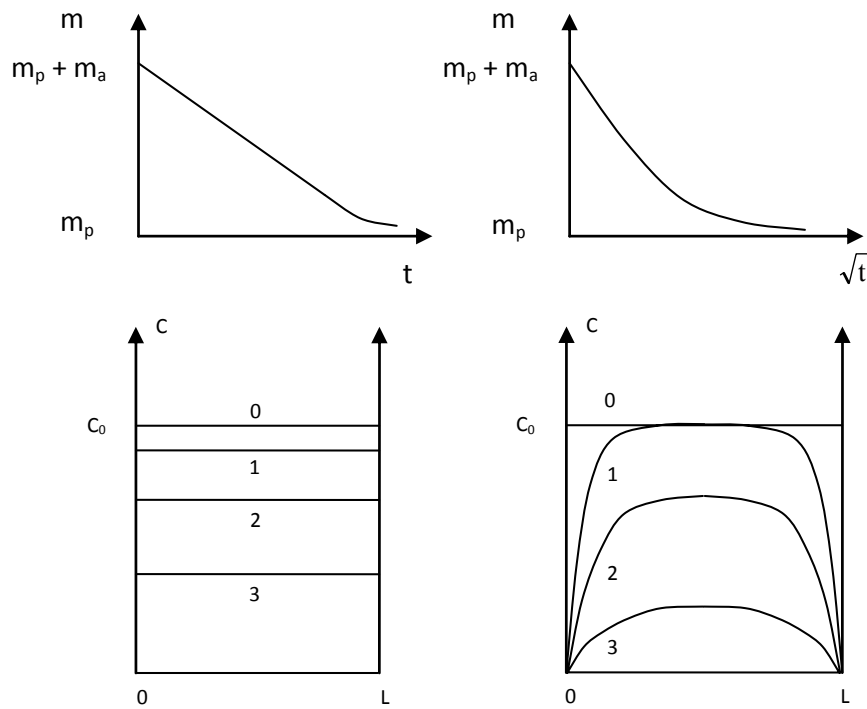


Figure 7.7. Migration controlled by evaporation (left) and by diffusion (right). Top: shape of the kinetic curves of mass evolution. $m_p + m_a$ = polymer mass + additive mass (m_p = polymer mass). Bottom: additive concentration profile in the sample's thickness at different times: $0 < t_1 < t_2 < t_3 < t_4$

When the additives have relatively high molar masses, their evaporation (or generally, their cross over from the polymer/environment interface) is slow. Their concentration at the surface is thus intermediate between the initial concentration C_0

and 0. This boundary condition must be taken into account to solve the diffusion equation.

When the additives are strongly concentrated (e.g. plasticizers) they change matrix properties, and their diffusivity then becomes a function of their concentration (D increases with C). There are some complications which may arise when the additive's migration is accompanied by a phase transition, for example, in the case of plasticized PVC we may expect the profile seen in Figure 7.8.

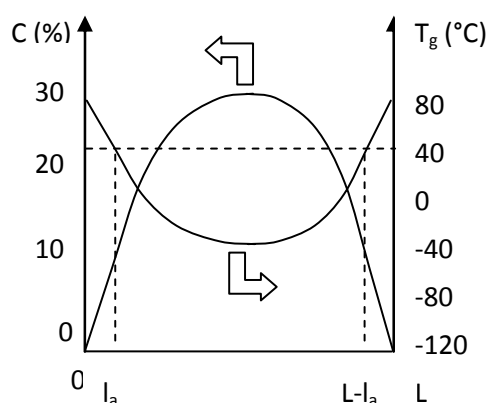


Figure 7.8. Presumed shape of the concentration profile in the plasticizer (mass fraction) and the local glass transition temperature in a plasticized PVC sample subjected to ageing at room temperature

We can see, however, that in the central area, the polymer has retained a rubbery state. On the other hand, in a superficial layer of thickness l_a , the polymer is glassy. As the diffusion coefficient varies from at least one order of magnitude at glass transition, the real profile will be more likely to take the shape seen in Figure 7.9.

In such cases, the diffusion front is very abrupt and the mass variation is a linear time function.

In terms of usage properties, a loss of additives may result in the loss of properties that they were supposed to bring originally: long term resistance for stabilizers, flexibility for plasticizers, etc. When the additives are initially strongly concentrated (plasticizers), their loss leads to volume shrinkage (mass loss). The volume shrinkage may generate strains and lead to crack growth.

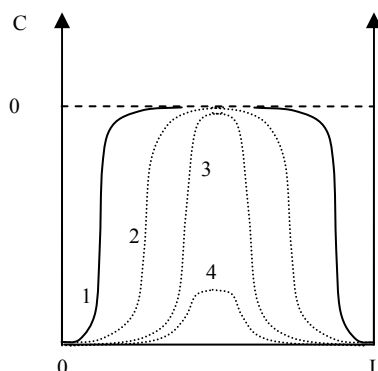


Figure 7.9. Real shape of the concentration profile in plasticization, in the example illustrated by Figure 7.7, at times $0 < t_1 < t_2 < t_3 < t_4$

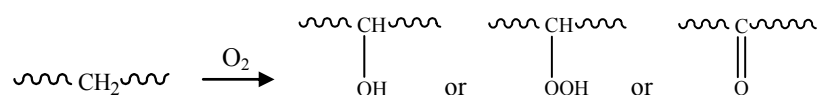
7.3. Chemical ageing – general aspects

7.3.1. The two large families of chemical ageing processes

It is important to distinguish the processes which only affect lateral groups, without changes to the macromolecular skeleton, from processes which alter the macromolecular skeleton. Indeed, the first processes do not affect mechanical behavior (at reasonable conversion ratio), whereas the second processes greatly affect the mechanical behavior, even at low conversion ratio.

7.3.1.1. Processes affecting lateral groups

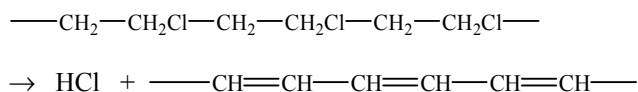
Halogenation and sulfonation processes etc., are likely to replace various hydrogen groups carried in the chain by chlorine atoms, SO_3 groups etc., but such processes are rarely encountered in an ageing context. In contrast, oxidation processes are very frequent. These processes also affect the macromolecular skeleton, but for now we will only deal with the consequences of altering lateral groups, e.g.:



A hydrocarbon group, which is only slightly polar, is transformed into an oxygenated polar group (ketone), or even a very polar group (alcohol). If this transformation occurs in a matrix which is initially rich in polar groups, there will be few consequences on the physical properties. On the other hand, if it occurs in a

matrix which is only slightly polar (polyolefin, hydrocarbon elastomers), then resultant changes in polarity may have significant consequences on all the physical properties linked to this characteristic, particularly dielectric permittivity, refraction index, surface energy, and wettability.

Some processes lead to the formation of colored species. In the case of PVC, such as sequential elimination of hydrogen chloride:



Sequences of more than five to seven conjugated double bonds absorb in the visible spectrum and absorption spreads towards large wavelengths when the number of conjugated double bonds increases. The material will appear yellow-brown or purple according to the distribution of the conjugated sequence lengths. These species have very high molar extinction coefficients, up to more than $10^5 \text{ l.mol}^{-1}\text{cm}^{-1}$. The coloring appears at low, or even very low, conversion ratio.

In polymers made up of aromatic nuclei, their oxidation leads to quinoid species which absorb near UV and violet. These materials (polystyrene, polycarbonate, PET, polyesters cross-linked by styrene, epoxides, etc.) undergo a degree of yellowing over ageing.

The oxidation of saturated polymers (PE, PP, for example) may also lead to colored species if the material initially contains traces of metallic impurities which can potentially form colored complexes with some oxidation products, such as carbonyls.

Lastly, some stabilization processes, particularly with aromatic amines or phenols, are also likely to create strongly colored species which can be distinguished from the species already present on the polymers, by the fact that they can be extracted by solvents.

7.3.1.2. Macromolecular skeleton modification process

Two types of processes can be distinguished here (Figure 7.10).

Of course, the two process types can coexist. If s and x are the respective numbers (moles) of scission and cross-linking events per mass unit, the average molar mass in number M_n (initial value M_{n0}) variation and weight (initial value M_{w0}) is given by the following system of equation:

$$\frac{1}{M_n} - \frac{1}{M_{n0}} = s - x$$

$$\frac{1}{M_w} - \frac{1}{M_{w0}} = \frac{s}{2} - 2x$$

We are able to see that if $s > 4x$, chain scission prevails.

On the other hand, if $s < 4x$, cross-linking will prevail.

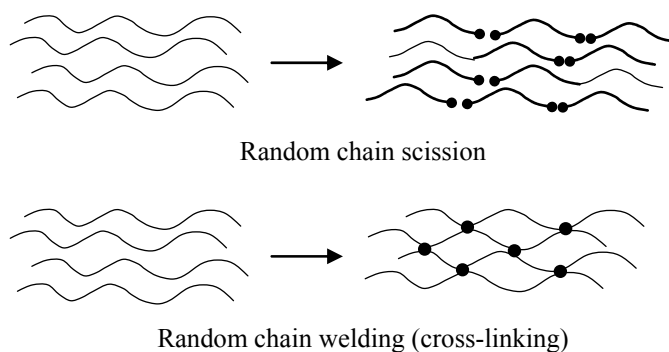


Figure 7.10. *Diagram representing two types of macromolecular skeleton modification processes*

So long as the material stays 100% soluble, then this system of equations enables us to determine s and x from average molar masses M_n and M_w . But if cross-linking prevails, the material bypasses the gelation point and an insoluble fraction appears. We can then apply the Charlesby theory:

$$w_s + w_s^{1/2} = \frac{s}{2x} + \frac{1}{M_{w0}x}$$

where w_s is the soluble fraction.

This equation is easy to exploit if s and x vary in a linear way with time, which is generally the case in radiochemical ageing at relatively high dose rates.

7.3.1.2.1 Consequences of chain scission

As seen in Chapter 5 (section 5.2.5), fracture properties of a linear polymer vary enormously around a critical molar mass M_c . We can then expect that the fracture

properties of an initially ductile/tough polymer drop significantly when its molar mass reaches value M_C' . Let us consider a chain scission process at constant rate v :

$$s = vt$$

In the absence of cross-linking:

$$s = \frac{1}{M_n} - \frac{1}{M_{n0}}$$

Therefore:

$$M_n = M_{n0} \left(\frac{1}{1 + vM_{n0}t} \right)$$

Let us consider an example where $M_{n0} = 100 \text{ kg.mol}^{-1}$, $v = 10^{-4} \text{ mol.kg.j}^{-1}$ and $M_C' = 20 \text{ kg.mol}^{-1}$. The evolution of M_n and the ultimate elongation are represented in Figure 7.11.

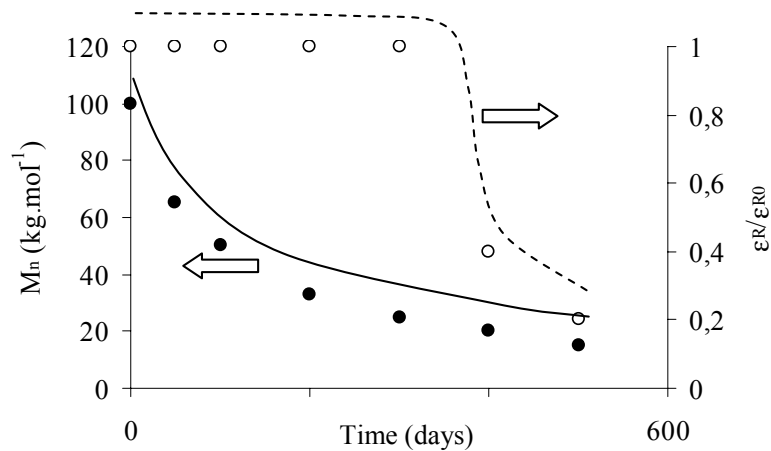


Figure 7.11. Variation in the number average molar mass M_n , and of the relative ultimate elongation ϵ_r/ϵ_{r0} in a polymer subjected to ageing by random chain scission at a rate of 10^{-4} moles scissions per kg per day

These results call for the following remarks:

– where the chain scission reaction occurs at constant rate, the molar mass varies hyperbolically;

– M_n varies monotonously whereas the ultimate elongation drops catastrophically when $M_n = M_C'$;

– embrittlement occurs when the number of chain scissions is:

$$s_c = \frac{1}{M'_C} - \frac{1}{M_{n0}} = 0.04 \text{ mol.kg}^{-1}$$

As an example, in a polymer such as polyamide 11 or PET, the concentration in monomer units is 5 mol.kg^{-1} . In other words, embrittlement occurs at a very low conversion ratio, which is sometimes difficult or impossible to detect by spectrochemical means. The elastic and yielding properties are practically unaffected at such conversion ratio. We understand, then, that embrittlement caused by ageing is an important aspect of research. Whatever the importance of other usage properties, no application can tolerate the geometric integrity of the samples being damaged by crack growth.

In some cases of superficial ageing, localized embrittlement may create a network of microcracks without a notable influence on the total fracture behavior. However, microcracking will change the appearance of the surface which may also have an economic impact in applications where questions of aesthetics are important.

In networks (vulcanized elastomers, thermosets), random chain scission can destroy chains which are elastically active. Typically, at low conversion ratio, for a quasi-ideal network:

$$v = v_0 - s$$

where v and v_0 are the concentrations in elastically active chains, before and after ageing respectively, and s is the number of chain cuts. Let us remember that v can be determined by measurements of the elasticity modulus in rubbery state:

$$v = \frac{G}{RT\rho} \quad (G: \text{shear modulus})$$

therefore:

$$s = \frac{1}{RT\rho}(G_0 - G)$$

Chain cuts can decrease the elastomer's modulus. On the other hand, they do not directly influence the thermosets modulus in glassy state.

Fracture properties tend to drop catastrophically, but the structure/property relationships are still relatively unknown in this domain.

7.3.1.2.2. Cross-linking consequences

For exclusive cross-linking (no chain scission), M_w and M_n increase, the polymolecularity index $p = M_w/M_n$ also increases, p and M_w diverge at the gelation point which corresponds to:

$$x_g = \frac{1}{2M_{w0}}$$

Here, we also see that gelation relates to a very weak conversion ratio. Two active sites are needed to make a cross-link, therefore the transformation rate at the gelation point is $y_g = \frac{1}{M_{w0}}$. In polyethylene, for example, for $M_{w0} = 100 \text{ kg.mol}^{-1}$

we would obtain that $y_g = 10^{-2} \text{ mol.kg}^{-1}$ whereas the concentration in potentially reactive sites ($-\text{CH}_2-$) is approximately 7,000 times greater. Of course, certain properties, particularly flow properties in molten state, change well before the gelation point. In particular, viscosity in molten state rapidly increases and the Newtonian plateau tends to disappear.

Elongation at break gradually decreases, whereas the stress at break increases, at least in an elastomer's initial ageing phase. Where thermosets are concerned, we know that T_g increases and that the ductility tends to decrease.

7.3.2. Diffusional phenomena in chemical ageing

Oxidation and hydrolysis (two frequent modes in chemical ageing) involve penetrating a small reactive molecule (O_2 , H_2O) from the environment in the material. We can define two characteristic times – one being diffusion, the other a chemical reaction – for a simplified approach to the problem:

– *in the case of diffusion*, characteristic time can be defined by:

$$t_D = \frac{L^2}{D}$$

where L is the sample's thickness and D the diffusion coefficient of the molecular reactant;

– in the case of the reaction, we can use the following definition:

$t_R = \frac{C}{v_c}$ where C is the equilibrium concentration of the reactant in the polymer, and v_c is the rate of the reactant consumption by the reaction in the sample's superficial layer where the reactant's concentration is effectively C .

The equality of the two times is achieved for:

$$t_D = t_R \text{ meaning that } L_C = \left(\frac{DC}{v_c} \right)^{1/2}$$

– if the sample's thickness is $L \ll L_C$, then diffusion is quick enough in relation to the reaction, in order to saturate the sample in its entire volume at any time;

– if the sample's thickness is $L \gg L_C$, then any molecular reactant is consumed in a layer with a thickness of the order of L_C and the sample's core is not degraded.

By comparing the total degradation rates of samples which differ in thickness, we can build the graph in Figure 7.12 which enables us to determine L_C .

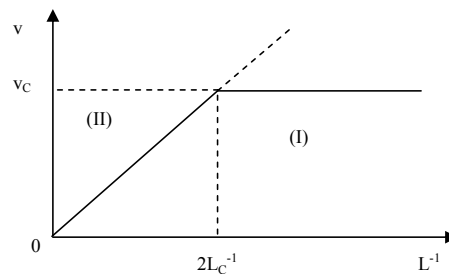


Figure 7.12. Shape of degradation rate variations with the reverse of the sample's thickness

Two regimes can be distinguished: the regime which is not controlled by diffusion (I) where the (total) degradation rate is independent of the thickness, and the regime which *is* controlled by diffusion (II) where the (total) degradation rate is in proportion to the reverse thickness since the thickness of the degraded layer (L_C) is independent of the whole sample thickness. The boundary value is $2L_C$ if the molecular reactant penetration is carried out by the two sides of the sample, which is often the case.

For a more rigorous and detailed approach to the problem, the relationship $v_c = v(C)$ expressing the reactant's consumption rate according to its concentration

in the case of a homogeneous reaction ($L \ll L_c$) must be established. The variation rate of the reactant's local concentration is, then, given by the equation:

$$\frac{\partial C}{\partial t} = -v(C) + D \frac{\partial^2 C}{\partial x^2}$$

where x is the spatial coordinate (in the direction perpendicular to the sample's surface) and D is the molecular reactant's diffusion coefficient.

Many authors assume rapid installation of a stationary state such as:

$$\frac{\partial C}{\partial t} = 0 \quad \text{therefore} \quad \frac{\partial^2 C}{\partial x^2} = v(C)$$

Therefore, we assume that the molecular reactant has a stationary concentration profile in the sample: $C = f(x)$, which is a result of solving the above differential equation.

In hydrolysis processes, for example, we can generally say that:

$$v_c = KC \text{ (pseudo first order process)}$$

In oxidation processes, v_c varies with C according to a pseudo-hyperbolic curve which can be approximate by:

$$v_c = \frac{\alpha C}{1 + \beta C}$$

where α and β are parameters which can be clarified according to the rate constants of elementary processes which are constitutive of the radical oxidation chain reaction.

Numerical solutions of kinetic equations and reaction-diffusion coupling equations free us from simplifying hypotheses, particularly those of a stationary state which is often difficult to justify.

Let us return to the scaling relationship of the simplified approach to the problem:

$$L_c = \left(\frac{DC}{v_c} \right)^{1/2}$$

– C generally hardly varies with temperature.

– D generally obeys the Arrhenius law: $D = D_0 \exp\left(-\frac{E_D}{RT}\right)$.

For v_C , we may also consider the Arrhenius law to be obeyed in a first approach:

$$v_C = v_{C0} \exp\left(-\frac{E_C}{RT}\right).$$

We can see that L_C should also obey the Arrhenius law:

$$L_C = L_{C0} \exp\left(-\frac{E_L}{RT}\right) \quad \text{with} \quad E_L = \frac{1}{2}(E_D - E_C)$$

With regard to thermal ageing, we generally have $E_C > E_D$, so that L_C is a decreasing function of temperature (Figure 7.13).

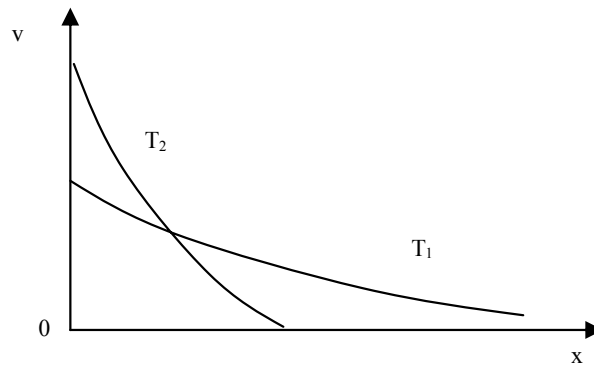


Figure 7.13. Diagram representing degradation profiles (thermo-oxidation) at two different temperatures: $T_1 < T_2$ and at a sensively equal total degradation rate

In the case of ageing by irradiation, D and C are independent of radiation intensity I, whereas v_C can be approximately obtained by $v_C \propto I^\alpha$. It results that:

$$L_C \propto I^{-\alpha/2}$$

L_C decreases slowly with I because α is generally lower than unity ($\alpha = 1/2$ in the simplest models).

The fact that the thickness of the degraded layer is generally a decreasing function of the “aggressiveness” of the exposure conditions may go against intuition, but it is a fact which has been checked many times.

7.3.2.1. Consequences of superficial deterioration on usage properties

Of course, surface properties (color, wettability, etc.) are not dependant on the degradation gradients. On the other hand, these gradients may play an important role in terms of mechanics.

Schematically, a polymer sample (initially ductile/tough and homogeneous) is gradually transformed into two layers by ageing. The inner layer remains ductile/tough, but the superficial layer is brittle and cracks easily. A crack which starts in the superficial layer will quickly make its way into the superficial/inner layer interface. It will either be blunted, or it will propagate, leading to a break in the sample (Figure 7.14).

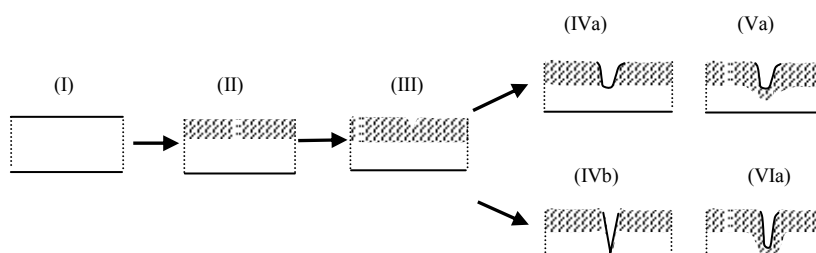


Figure 7.14. Diagram representing possible crack growth modes of a sample subjected to surface level ageing. The dots symbolize degradation: I is the initial sample, II is the aged sample before the embrittlement threshold, III is the sample which is close to the embrittlement threshold, IVa is a sample with blunted crack, with the crack making its way to the degraded/non-degraded interface, IVb shows the crack crossing the degradation front, Va and Vb show the progression of the degradation front at the top of the crack

As a first approach, we may consider that the weakened superficial layer is equivalent to a notch of the same depth. Fracture mechanics ([GRI 21]) enable us to predict that there is a critical notch depth, which will not initiate crack growth if it is not reached. This critical depth depends on the material’s strength, which depends on crack propagation rate.

Therefore we expect that a very rapid ageing process, leading to a low level of thickness of the oxidized layer, changes fracture behavior comparatively less than a slower ageing process. This has been checked many times in experiments.

7.3.3. Towards a non-empirical lifetime prediction

Ageing is a complex phenomenon but which can be broken down into elementary mechanisms which obey simple kinetic laws (Arrhenius law, proportionality of rate to light intensity, etc.). However, the “target” of chemical ageing is the molecular scale structure, but the usage properties depend on higher scale structures [AUD 07]. Moving away from these reports, we can develop a strategy for predicting non-empirical lifetimes, represented in the following diagram (Figure 7.15).

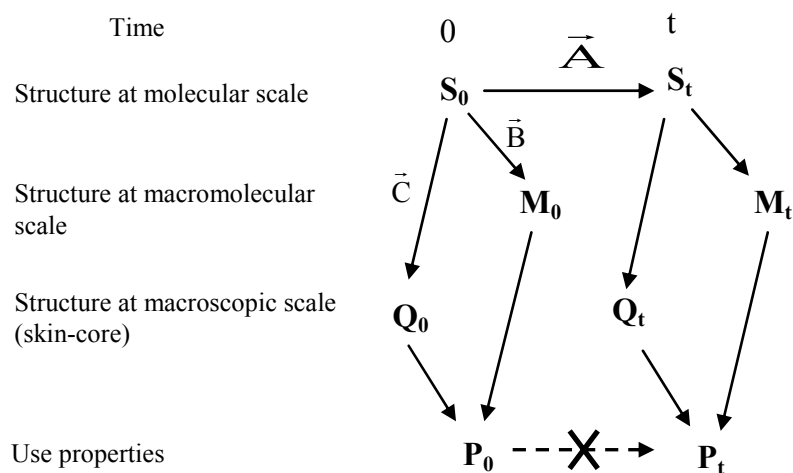


Figure 7.15. Diagram illustrating the strategy for predicting non-empirical lifetime

Vector $\vec{A}$ represents a chemical kinetics model, showing the evolution of the material to the molecular scale. Vector $\vec{B}$ symbolizes the path from the molecular scale to the macromolecular scale. This process involves knowledge of the elementary event of scission/cross-linking, and reaction statistics. Vector $\vec{C}$ represents reaction-diffusion coupling. All the other vectors show relationships coming from polymer physics.

For different reasons (mechanism hyper-complexity, gaps in polymer physics, etc.) some of the relationships involved in this diagram cannot be translated in mathematical terms. On the other hand, achieving all the procedure steps in a non-empirical way may constitute an unrealistic research program from an economical point of view. It will then be a matter of injecting a minimum of empiricism into the model so that it works, but by making the conducted hypotheses as clear as possible.

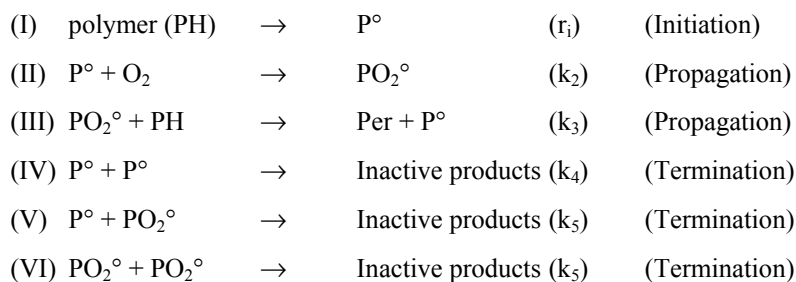
From this, the chosen strategy seems to be the best possible compromise between the need for scientific rigor, which guarantees the reliability of the prediction, and economic constraints.

7.3.4. Oxidation – general aspects

For the majority of practical cases in thermal, photochemical or radiochemical ageing, the main cause for ageing is oxidation of the polymer by interaction with oxygen in the atmosphere.

In all cases oxidation results from radical chain reactions and the kinds of ageing mentioned above, they only differ by initiation (in mechanistic terms).

The standard mechanistic scheme, drawn up by an English team in the 1940s [BOLL 46], is the following:



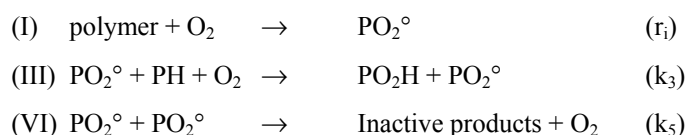
As we have seen, initiation may be thermal, photochemical or radiochemical. It can be the result of a reaction which directly involves a non-degraded part of the polymer (radiochemical) or a reaction product, particularly a peroxide or hydroperoxide (Per).

Propagation involves two chemical processes, the second one (III) regenerating radical P° involved in the first one (II). Adding O_2 to the radicals (II) is very fast ($k_2 \sim 10^8$ to 10^9 L.mol⁻¹.s⁻¹). The reaction between peroxy radicals (PO_2°) and the polymer is much slower ($k_3 \sim 0.01$ to 10 L.mol⁻¹.s⁻¹, typical values at room temperature). PO_2° radicals can act by abstracting hydrogen or adding to double bonds. In the first case, the product Per is a hydroperoxide (POOH). In the second, it is a peroxide (POOP).

The terminations (when there are no stabilizers) are bimolecular. Two radicals are deactivated mutually. We then have:

$$k_4 > k_5 \gg k_6$$

When there is excess oxygen (low thickness sample, high O₂ pressure, low initiation rates), radicals P° are quickly transformed into PO₂° by reaction II. The probability of their reacting by other means becomes very low, and the scheme is simplified as follows in the case of propagation by hydrogen abstraction, for example:



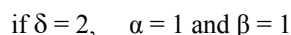
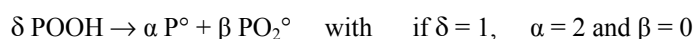
We can therefore distinguish two important considerations:

Reaction (I) is carried out at constant rate r_i (radiochemical initiation). Therefore, a stationary state is quickly established, and the oxidation products gather at constant rate (Figure 7.16).

We can easily show that products from initiation and termination are formed at a rate which is proportional to r_i . On the other hand, hydroperoxide (propagation product) is formed at rate $v(\text{POOH}) = k_3[\text{PH}]\left(\frac{r_i}{2k_6}\right)^{1/2}$ (proportional to $\sqrt{r_i}$).

$$\text{Oxygen is absorbed at rate: } v_{ok} = \frac{r_i}{2} + k_3[\text{PH}]\left(\frac{r_i}{2k_6}\right)^{1/2}.$$

Reaction (I) is the decomposition of peroxides or hydroperoxides formed during propagation. Initiation can be written as:



When $\delta = 2$ (more common at temperatures higher than 150°C), the kinetics are comprised of an induction period followed by a strong auto-acceleration preceding a steady state (Figure 7.16).

This type of reaction can be called a “closed loop” reaction because it produces its own initiator: hydroperoxide.

The kinetic analysis of the two process types show that kinetic behavior depends, in both cases, on two main factors: one of which is extrinsic (relating to factors which are external to the polymer's structure), for instance the initiation rate

constant k_i or initiation rate r_i which depend on the radiation intensity in photo or radiochemical ageing. The other factor is intrinsic e.g. only dependent of polymer structure, for instance the ratio $\frac{k_3}{\sqrt{k_6}}$ which characterizes the polymer oxidability.

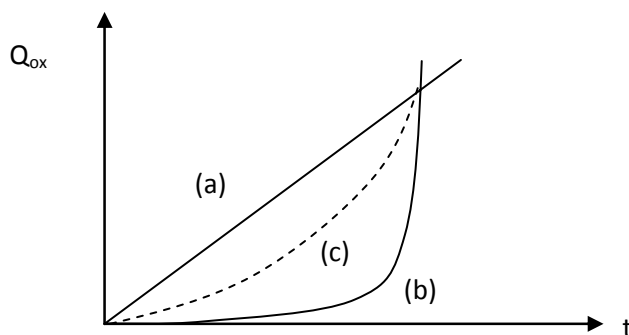


Figure 7.16. Shape of the kinetic curves of oxidation (a) for constant rate initiation (radiochemical ageing) (b) initiation by bimolecular decomposition ($\delta = 2$) of hydroperoxides (thermal ageing). In cases of unimolecular initiation ($\delta = 1$) of hydroperoxide (c) initial auto-acceleration is more progressive (some cases of photochemical ageing)

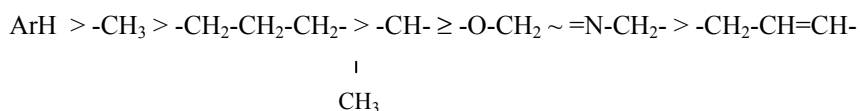
For “closed loop” processes, where $[\text{POOH}]_0$ and $[\text{POOH}]_\infty$ are the initial and steady state hydroperoxide concentrations respectively, the ratio $\frac{[\text{POOH}]_\infty}{[\text{POOH}]_0}$ determines the amplitude of the auto-acceleration effects.

Polymers which do not contain CH bonds (polytetrafluorethylene) or polymers only containing aromatic CH (PEEK, poly(ether sulfones), polyimides, etc.) are generally stable under oxidation. Polymers only containing methyls (polydimethylsiloxane) or methyls and methylenes (poly(methyl methacrylate), polycarbonate, polyethylene) are moderately stable. Polymers containing tertiary CH (polypropylene), CH in α of heteroatoms (polyoxymethylene) or allylic CH (polydienic elastomers) are relatively instable. Let us note that it is a matter of a comparison of relatively little practical use because another (physical) factor plays an important role: oxygen diffusivity. The diffusivity is notably higher in elastomers than in glassy polymers. In other words, with equal reactivity, these latter will seem more stable because the thickness of their oxidized superficial layer will be lower.

Another potentially important factor: the property sensitivity to chemical acts of oxidation. For example, polypropylene becomes brittle in a number of chain scissions which are about 10 times smaller than for an amorphous polymer.

According to mechanical criteria, it will seem 10 times less stable than an amorphous polymer with the same reactivity.

Despite these reservations, the classification of groups according to the following decreasing order of stability is completely valid:



7.3.5. Stabilization

Chain reactions, like radical oxidation, particularly when they produce their own initiation, have a major disadvantage in terms of practice: small problems may lead to big effects, in light of the strong auto-accelerating character of these reactions. But this disadvantage turns into an advantage when we plan to produce stabilization by additives (antioxidants). Indeed, since the reaction starts slowly and auto-accelerates, a small quantity of the stabilizers when adequately chosen may be enough to efficiently inhibit the process, a possibility which does not exist for step by step reactions, such as hydrolysis for example.

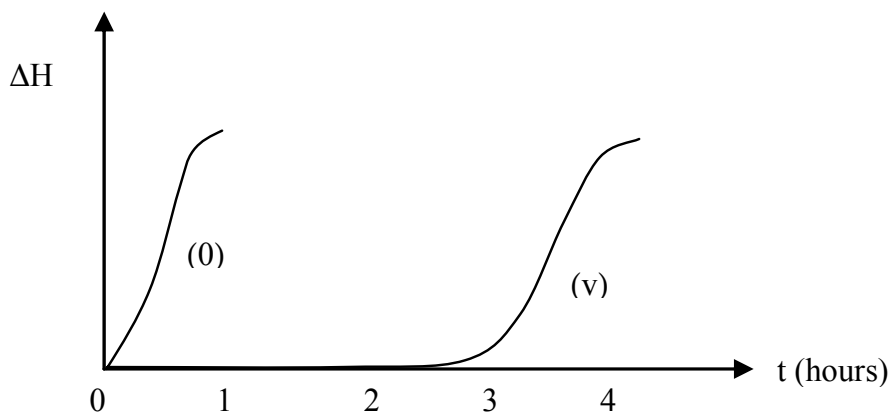
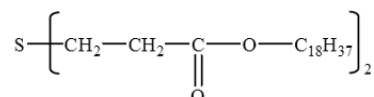


Figure 7.17. Shape of thermograms at 190°C (rise in temperature under nitrogen, oxygen is admitted in the cell when the thermal equilibrium has been reached): a non-stabilized polyethylene (0), the same polyethylene stabilized by 0.3% of a phenol-phosphite combination

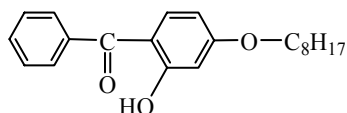
It generally seems difficult to change the propagation process. Yet, we can slow down initiation, for example, with stabilizers which destroy the hydroperoxides by non-radical means (sulfurs, phosphites). Or we can accelerate termination with stabilizers capable of capturing radicals P° or PO_2° (phenols, aromatic amines, hindered amines, nitroxyl radicals, etc.) In polyolefins, we may reach an efficient stabilization with stabilizing mass fractions lower than 0.5%. In polydienic elastomers, stabilizers can be used in concentrations higher than 1%. The most common appreciation method of stabilizer efficiency consists of determining the induction time at high temperatures (Figure 7.17).

It is important to note that the *effectiveness of stabilizers* also depends on physical factors, in particular:

– *solubility in the polymer*. If the solubility level is low, the concentration level necessary for good levels of stabilization may not be reached. We may note that many stabilizers are comprised of long alkyl chains for instance in distearylthiodipropionate:



Thermal antioxidant hydroperoxide decomposer;



UV absorber;

– *diffusivity in the polymer*. If the diffusivity level is too high, stabilizer loss through migration might decrease its efficiency. To reduce diffusivity, we can increase the molar mass (alkyl chain grafting, polymer stabilizers, etc.).

In addition to these significant factors, the choice of stabilizer must take other characteristics into account, such as:

– *compatibility with the considered use* (color, smell, toxicity, etc.);

– *interaction with the environment*. For example, phenolic stabilizers create highly colored species in the presence of nitrogen oxides; some hindered amines react with certain biocides used in farming, etc.;

– *interaction with other polymer additives*. For example, organic sulfides are not compatible with metals because they create highly colored metal sulfides.

Not all interactions are problematic, some stabilizers have an increased level of efficiency when combined with another additive. We can call this a secondary stabilizer. This is the case for combination of zinc and calcium soaps in PVC. Synergy mechanisms are very varied. In phenol-hydroperoxide decomposer systems, synergy is essentially the result of a kinetic effect due to the fact that each stabilizer exerts a favorable strain on a different step of the oxidation chain reaction. For Ca/Zn soaps in PVC, the “primary” stabilizer is the zinc soap, but the PVC-Zn reaction generates zinc chloride which is a powerful catalyst for the degradation of PVC. The role of Ca soap is to eliminate zinc chloride by a double decomposition reaction which generates Zn soap.

7.4. Thermochemical ageing

7.4.1. *Intrinsic thermal stability*

In the absence of oxygen, polymers will decompose through their own instability, with this being controlled by thermochemical factors. Generally, it is a matter of radical processes initiated by a break in the weakest bond (meaning the bond with the weakest dissociation energy).

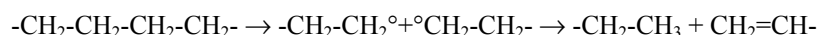
Aromatic bonds C-C and C-H and C-F bonds are among the most stable ($E_d \sim 500 \text{ kJ.mol}^{-1}$). Polymers which only carry this type of bond are known as “thermostable”.

The more the carbons are substituted, the less stable the aliphatic bonds C-C become:

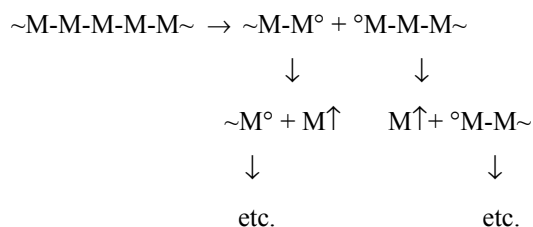


Polymers containing tetrasubstituted carbons (polyisobutylene, PMMA, poly(α methylstyrene), etc.) are particularly unstable.

However, total thermal stability does not only depend on bond weakness, but also on the tendency (or not) of primary radicals to initiate a chain propagation process. In polyethylene, for example, the radicals are easily deactivated by disproportionation:

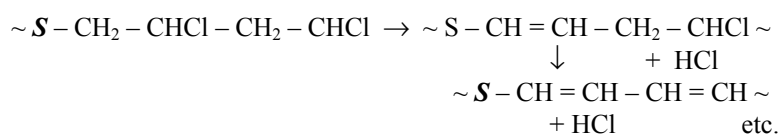


In polyisobutylene, as in other polymers which contain a quaternary carbon, and in polyoxymethylene, the radicals begin a “zip” process to eliminate the monomer:



This process is called “depolymerization”. Polymers which depolymerize are those which possess the lowest thermostabilities.

PVC is subject to a lateral group “zip” elimination reaction:



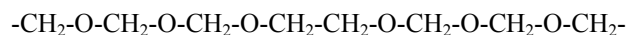
S is a structural irregularity (for example, double bond formed during polymerization) which makes the first elimination act easier.

For step by step processes (such as polyethylene thermal degradation) there is no known method of stabilization.

On the other hand, for chain processes (depolymerization, sequential elimination of HCl, etc.) it is possible to plan stabilization by:

– removing “weak points” through chemical modification during synthesis (blocking terminal alcohols in POMs) or by a reaction with a stabilizer during processing (PVC stabilizers);

– disfavoring propagation by an adequate comonomer, in the case of POM, for example:



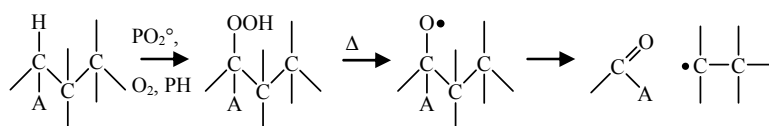
Inserting dimethylenic units into the chain by copolymerization can slow down the depolymerization process. The POM copolymers can be distinguished from “homopolymers” by their melting point which is lower by 10 to 20°C.

7.4.2. Oxidative ageing

Bonds present in industrial polymers possess dissociation energies which are rarely lower than 270 kJ.mol^{-1} . Oxidation by atmospheric oxygen makes peroxides and hydroperoxides appear (as we have seen) whose dissociation energy of the bond $-\text{O}-\text{O}-$ is in the order of 150 kJ.mol^{-1} . These groups decompose at temperatures which are clearly lower than for the groups carried by the monomer unit. This is why thermal ageing of polymers is controlled, in the vast majority of cases, by oxidation – at least in usage conditions. As we have seen, stability then depends above all on the reactivity of $-\text{C}-\text{H}$ bonds via the ratio: $\frac{k_3}{\sqrt{k_6}}$

Thermo-oxidations at moderate temperatures ($<150^\circ\text{C}$) have the following common characteristics:

- an induction phenomenon. The induction period is a decreasing function of temperature. Its apparent activation energy in the absence of a stabilizer is generally in the order of $100 \pm 20 \text{ kJ.mol}^{-1}$. These values are higher in the presence of stabilizers;
- when there is an oxygen excess (no termination of P° radicals), oxidation often results in a predominance of chain scission particularly related to the β scission of alkoxy radicals:



Cross-linking only prevails when the polymer carries double bonds onto which the radicals can easily be added (polybutadiene):

- in thick objects, thermo-oxidation is controlled by oxygen diffusion. The thickness of the oxygenated layer is a decreasing function of temperature;
- oxidation results in the accumulation of stable oxygenated groups: carbonyls, ethers, alcohols, etc., which may be titrated at relatively low concentration by IR spectrophotometry. However, in general, molecular mass measurements are more sensitive;
- although in a first approach, oxidation can be considered as a hydrogen substitution by heavier oxygenated groups, it generally leads to mass loss related to the elimination of volatile fragments (Figure 7.18).

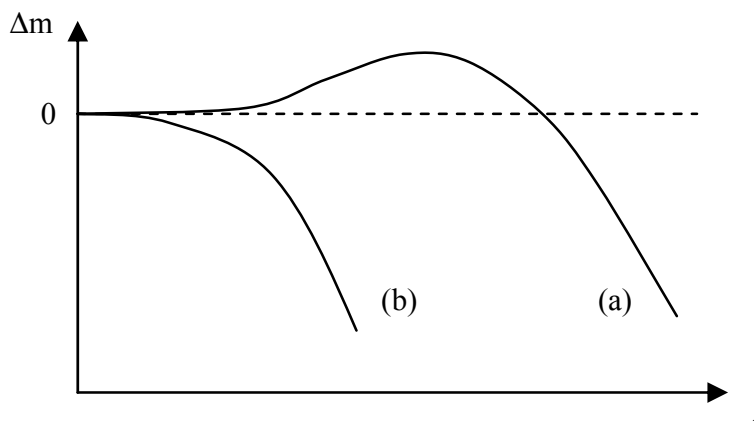


Figure 7.18. Shape of mass variations during thermal oxidation. (a) polymer with a relatively low initiation rate. Mass gain prevails during the induction period. Mass loss prevails after the mass gain has ended; (b) polymer with a relatively high initiation rate: mass loss prevails as exposure begins.

Polypropylene and polybismaleimides for example, belong to family (a) (Figure 7.18). Polyoxymethylene and epoxides cross-linked by amines rather belong to family (b). In all polymers oxidizing at low temperatures (polyolefins, polydienes), antioxidants generally have a noticeable effect, even spectacular, on the induction periods. This effect is a lot less important, even not important at all, when polymers oxidize at higher temperatures (thermostable polymers, particularly).

7.4.3. Lifetime in thermal ageing

The lifetime versus temperature curves take the shape represented in Figure 7.19.

With regard to low temperatures (of practical interest for users) we conventionally define a duration of 5000, 20,000 or 100,000 hours depending on the application, and we define the corresponding temperature on the curve, which we call *maximum continuous operating temperature* (T_{mu}).

Typically $50^{\circ}\text{C} \leq T_{mu} \leq 100^{\circ}\text{C}$ for commodity polymers, such as PVC, PP, ABS, etc. and $250^{\circ}\text{C} \leq T_{mu} \leq 300^{\circ}\text{C}$ for thermostable polymers, such as polysulfones, polyimides, etc. All industrial polymers are in between these two limits.

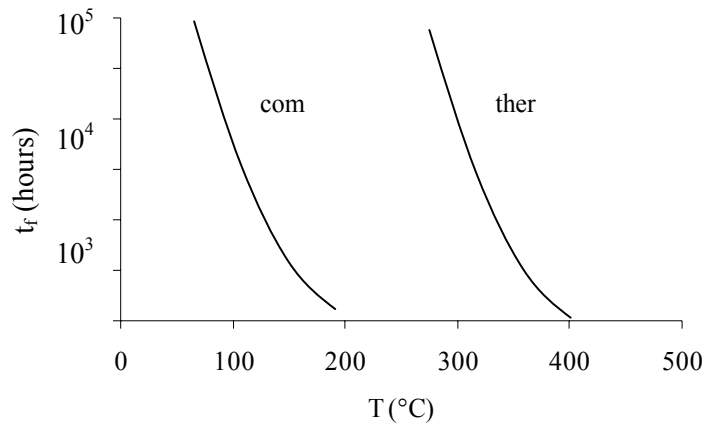


Figure 7.19. Lifetime (time to embrittlement) versus temperature. Curve shape for a commodity polymer (com) and for a thermostable polymer (therm)

For high temperatures (of practical interest for processing practitioners), knowing the “maximum thermal stability” is necessary because this “maximum” constitutes one of the “processability window” boundaries (see section 5.4). Certainly, for a given polymer, these boundaries are moved according to the severity of the end-of-life criteria and the efficiency of the stabilizers.

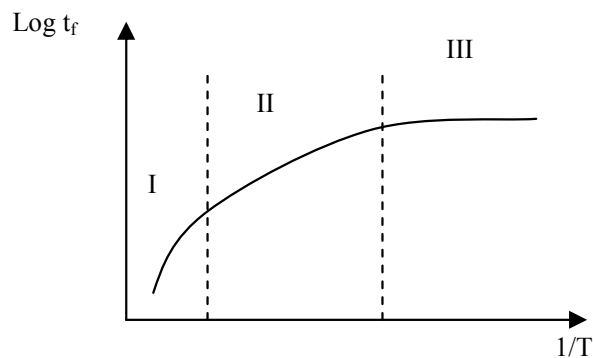


Figure 7.20. Shape of the Arrhenius graph for lifetime in a wide temperature interval

From very early on, we have tried to give a mathematical form to curves $t_F = f(T)$. In the 1940s, the Arrhenius law was first proposed [DAK 48]. In its simplest form, it is written: $\text{Log } t_F = A + \frac{B}{T}$ which allows for linear extrapolation.

This method has given way to diverse standards and recommendations. The T_{mu} shown in industrial polymer technical notices are always obtained in this way. However, when we carry out experiments in a wide temperature interval, it is not rare to find that we obtain graphs with the shape of Figure 7.20.

We observe a general tendency for the apparent activation energy (B) to increase when the temperature increases, with three or more domains which are easy to distinguish:

- domain I: oxidation is controlled by diffusion, the polymer is subjected to thermolytic degradation;
- domain II: this is the domain of “closed loop” oxidation, with an apparent activation energy in the order 80 to 120 kJ.mol⁻¹ in the absence of stabilizers, 120 to 200 kJ.mol⁻¹ in the presence of stabilizers;
- domain III: this is also a closed loop oxidation domain, but at low temperatures the termination reactions are controlled by diffusion of radicals and the apparent activation energy tends to decrease.

This type of behavior has been observed on many different occasions, for example in polyethylene and elastomers.

Kinetic modeling allows us to take this phenomenon into account and to carry out lifetime predictions which are more realistic than simple linear extrapolation from system II.

7.5. Photochemical ageing

7.5.1. *Introduction: solar radiation*

For light radiation to induce photochemical processes in a polymer, first of all it must be absorbed, and then this absorption must lead to photoexcited species which are capable of giving way to irreversible chemical processes. In solar radiation on the earth surface, (Figure 7.21) radiation with the lowest wavelengths essentially belonging to the UV component ($300\text{ nm} \leq \lambda \leq 400\text{ nm}$) are potentially capable of inducing such processes.

Total solar energy, in the order of 300 kJ.mol⁻¹ in the North of Europe and 800 kJ.mol⁻¹ in desert tropical areas, in France between ~ 360 kJ.mol⁻¹ in the North and ~ 460 kJ.mol⁻¹ on the Mediterranean. UV energy varies between around 2% (in the winter) and 7% (in the summer) of the total energy in the temperate zone, where the seasonal variation tends to increase with latitude.

Cloud cover, altitude-latitude and surface orientation are at the root of local variations which are sometimes difficult to model. The first difficulty encountered in the study of photochemical ageing is the complexity of the fluctuations of all kinds of “photoactive” solar energy.

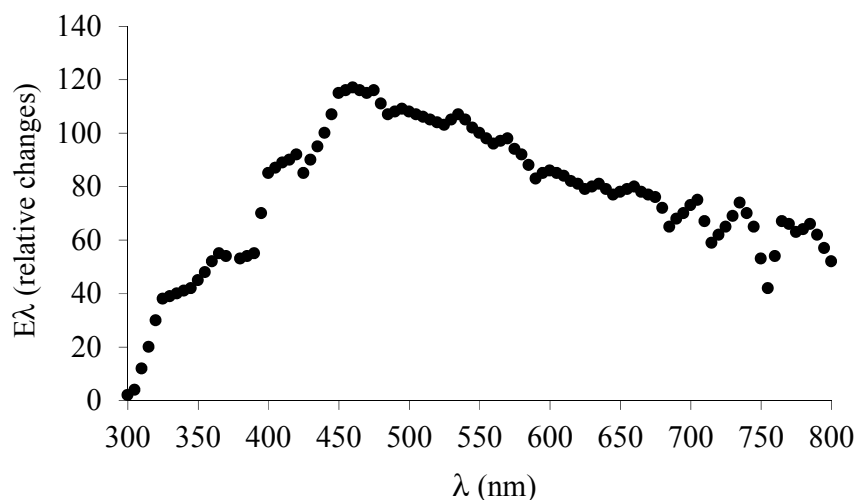
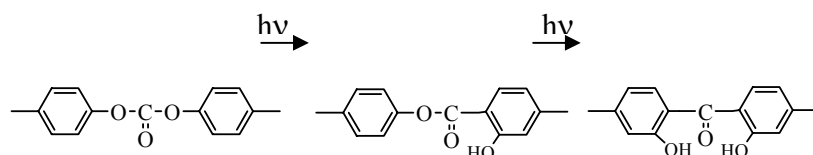


Figure 7.21. Solar radiation. Spectral distribution according to ICI E1.3.1 D.65 (ICI = International Commission on Illumination)

7.5.2. “Intrinsic” photochemistry and photo-oxidation; photo-oxidation and thermo-oxidation

Some industrial polymers are “intrinsically photoreactive”. In other words, carefully purified and irradiated under nitrogen by solar UV ($\lambda \geq 300$ nm), they are subjected to photochemical ageing.

The most well-known case is aromatic polymers comprised of ester groups, particularly polycarbonates. They are subjected to “photo-fries” rearrangement.



The species which result from this reaction strongly absorb in the near UV and violet, which leads to the following consequences:

- the material is subject to yellowing;
- the photo-transformed layer strongly absorbs UV. Therefore it plays the role of a protective screen for the under layers. The photo-transformation is therefore self-retarded.

As this reaction does not modify the macromolecular skeleton, there are no consequences on the polymer's mechanical behavior.

These examples aside, most industrial polymers do not present intrinsic photoreactivity in solar UV. Irradiated in the inert atmosphere, they evolve either very little or not at all. However, the presence of atmospheric oxygen completely changes the behavior because the “primary” products (hydroperoxides) and some “secondary” products (ketones) of radical oxidation are greatly photoreactive and the photoexcitation which is created from free radicals capable of initiating new radical chains, hence the strongly self-accelerated character from photo-oxidation.

Thus, polymers which are transparent in UV in pure state (polyethylene, polypropylene, polydienes, etc.) can be catastrophically photodegraded because they still contain impurities or structural irregularities capable of initiating the reaction in a “closed loop”.

As photo-oxidation is nearly always accompanied by chain cuts from hydroperoxide or ketonic photolysis, this leads to embrittlement:

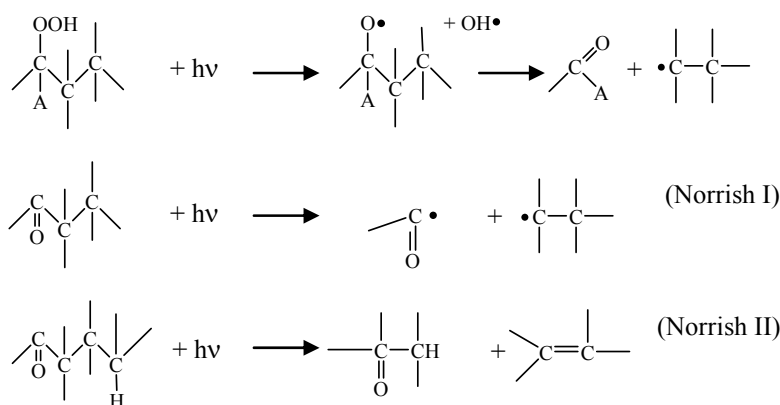


Photo-oxidation presents many similarities with thermo-oxidation at low temperatures. The radical chain propagation mechanism is the same, however it differs by two characteristics:

– initiation by POOH decomposition is unimolecular, whereas it is often bimolecular in the case of thermo-oxidation. Initial autoacceleration is more gradual in photo than in thermal ageing;

– the POOH decomposition rate by photochemical means is higher (under normal irradiation conditions) than in thermal ageing. The induction period is therefore very short, even non-existent. However, if we sufficiently reduce the irradiation intensity, we observe an induction period.

If the test temperature is high enough and the exposure time long enough, initiation of POOH by thermal decomposition may coexist with photochemical initiation. Thus, if we express the oxidation rate by an approximate relationship:

$$v = KI^\alpha \exp\left(\frac{E}{RT}\right)$$

We observe that α tends to increase with I and decrease with T , whereas E tends to increase with T and decrease with I . These dependencies demonstrate well the non-validity of this type of relationship.

7.5.3. Photostabilisation. UV screens

Since as a first approximation the initiation rate is proportional to the absorbed light intensity, the first possible means of stabilization consists of decreasing the light intensity by incorporating into the polymer strong UV absorbing additives.

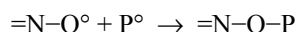
These additives may be pigments such as carbon black or titanium dioxide (white) glow. This latter must be surface treated to inhibit the well-known photocatalytic effect. These pigments are efficient in concentrations of several percent.

(Organic) plastosoluble additives, greatly absorbing in the 300-400 nm interval, and transparent in the visible spectrum can also be used (Figure 7.22).

These stabilizers, generally used in mass concentrations of 0.1 to 1%, are only really efficient in thick objects (typically ≥ 0.1 mm). The most frequently used are hydroxybenzophenones, hydroxybenzotriazoles, benzylidene malonates and substituted acrylonitriles. We will note that the first two families contain a phenolic group potentially capable of playing an antioxidant role.

We also use *radical scavengers* (tetramethylpiperidine type hindered amines) which may react with practically all species involved in the oxidation chain reaction:

PO_2° , P° and perhaps POOH . Nitroxyl radicals, very useful in termination reactions, are important intermediates in stabilization processes:



These stabilizers may also play the role of an antioxidant in the thermo-oxidation processes.

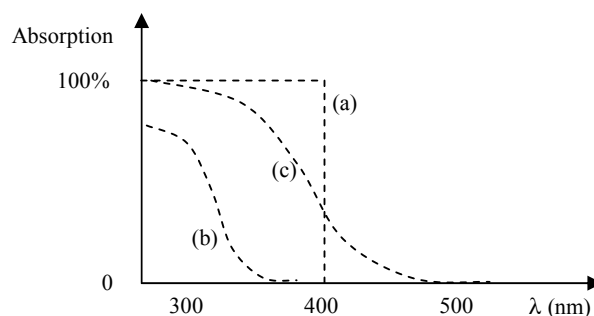


Figure 7.22. Absorption spectrum of UV absorbers: (a) ideal UV absorber; (b) UV absorber with limited protective power but colorless; (c) efficient UV absorber but yellow (it absorbs at $\lambda > 400$ nm in violet)

7.5.4. Towards a lifetime prediction in photoageing

For now, the generally used solution is based upon carrying out accelerated ageing tests constituting the best compromise between an exposure duration as low as possible and a simulation as close as possible to natural ageing. It is hypothesized (although not expressed) that if it is a “good” simulation, then there is a “good correlation” between the results for natural and accelerated ageing. This hypothesis has no scientific or logic grounding.

However, where a non-empirical alternative may exist for thermo-oxidation, carrying this out for photo-oxidation requires much more delicacy, as the following additional problems may arise:

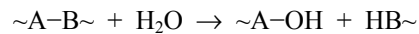
- distribution of initiation in the sample’s thickness does not simply depend on the reaction/diffusion coupling, but also on the screen effect of absorbent species, and this effect may vary as the reaction conversion increases;
- in principle, we know how to write kinetic equations for monochromatic irradiation, but the path for polychromatic irradiation is very complex;
- as already seen, daily, seasonal and geographical fluctuations in solar irradiation are difficult to model.

None of these problems is irresolvable, but due to the fact that researchers dedicate their time to analytical aspects and mechanisms, and that experts in the field are happy with just simulation tests, means that there has been no satisfactory solution proposed to date.

7.6. Hydrolytic ageing

7.6.1. Introduction

Hydrolytic ageing involves an ageing process resulting from the chemical interaction of a polymer with water. The main chemical act is a hydrolysis process which can be schematized in the following way:



In the most important examples in terms of practice, the broken bond is a molecular skeleton bond. Each hydrolysis process is therefore a chain scission. In all the chain scission cases, hydrolysis leads to polymer embrittlement at a low conversion rate, hence the interest in this type of ageing.

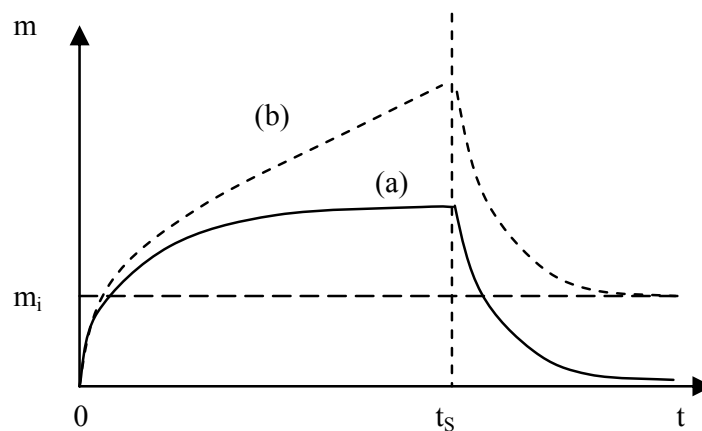
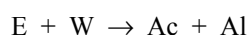


Figure 7.23. Shape of mass variations in a sample placed in a humid atmosphere ($t < t_s$) and a dry atmosphere ($t > t_s$). (a) “Pure” physical ageing: the mass gain curve tends towards equilibrium, we find the original mass after a drying process. The absorption and desorption rates are equal (when there is no damage). (b) Sample under hydrolysis (without extracting small molecules). Each hydrolysis process leads to a mass gain of 18 g/mol. The mass in dry state increases irreversibly. Note: the mass in dry state may increase, decrease or vary in a non-monotone manner (see further on) according to chemical ageing cases

For a water molecule to react with a group in the middle of a sample, this molecule must penetrate the said sample. In doing so, this will change the sample's properties and lead to physical ageing (see section 7.2). We know cases of "pure" physical ageing by water absorption for hydrophilic but not hydrolysable polymers. However, there is no such thing as "pure" chemical ageing; all hydrolytic ageing is accompanied by plasticization, swelling, etc., which are characteristics common to physical ageing. We recognize this latter kind of ageing by the fact that it is reversible (so long as the material is undamaged): drying will restore the original material properties. In contrast, chemical ageing is irreversible (Figure 7.23).

7.6.2. *Quasi-irreversible hydrolysis*

Polycarbonate, linear saturated polyesters, unsaturated polyesters cross-linked by styrene will hydrolyze until high conversion rates are reached, without any significant rate decrease being observed. For these polymers, we may consider (at least as a first estimation) that hydrolysis is irreversible. This leads us to write:



where E is the ester group, W the water molecule, Ac and Al respectively the acid and alcohol groups from hydrolysis. Each act of hydrolysis leads to one chain scission. We can write, then, in a system not controlled by diffusion that:

$$\frac{ds}{dt} = k[E][W] = k([E_0] - s)[W]$$

It should be noted that s is the number of chain scission, [W] represents the water concentration in the polymer and k is the rate constant.

Since embrittlement occurs at low conversion rates, we have $s \ll [E]_0$ and hydrolysis hardly changes the polymer hydrophilic properties. Therefore:

$$\frac{ds}{dt} = k[W]E_0 \approx \text{constant}$$

meaning:

$$s = K.t \quad \text{where } K = k[W][E]_0$$

The end-of-life criteria is the ductile-brittle transition occurring at $M_n = M_c'$.

The number of chain scissions s_F at the end life is:

$$s_F = \frac{1}{M_c'} - \frac{1}{M_{n0}}$$

The t_F lifetime is therefore:

$$t_F = \frac{s_F}{K} = \left(\frac{1}{M_c'} - \frac{1}{M_{n0}} \right) \frac{1}{k[W][E]_0}$$

where k obeys the Arrhenius law: $k = k_0 \cdot \exp(-E/RT)$ and $[W]$ is determined by the equality of chemical potentials of water in the medium and in the water.

For a material with few hydrophilic properties:

$-[W] = [W]_s$ (saturated water concentration in the material) in the case of immersion in pure water;

$-[W] = [W]_s \frac{HR}{100}$ (where HR is the relative hygrometry) in the case of exposure in humid atmospheres.

This means that in all cases:

$$t_F = \frac{1}{[E]_0} \left(\frac{1}{M_c'} - \frac{1}{M_{n0}} \right) \left[\frac{1}{k_0 \exp\left(-\frac{E}{RT}\right)} \right] \left[\frac{100}{W_s \cdot HR} \right]$$

where $HR = 100$ for immersion in pure water.

Therefore, we have a non-empirical relationship which connects lifetime to three factors: one which represents the effect of the polymer structure, another which shows the effect of temperature, and a final factor which represents the effect of the medium composition.

Structure-reactivity relationships are relatively well known in this field. For example, where polyesters are concerned, for a given diol such as propylene glycol, we obtain, in order of increasing stability:

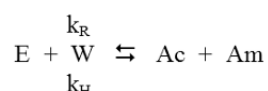
maleate < orthophthalate << acrylate

In the same way, for a given diacid, for example a maleate:

ethylene glycol < propylene glycol < neopentyl glycol

7.6.3. Reversible hydrolysis

In some cases, such as for polyamide 11, hydrolysis is self retarded as soon as exposure begins and the molecular mass rapidly stabilizes, which indicates that a reversible process exists:



where Ac and Am respectively indicate the acid and amine resulting from hydrolysis. Here, E is the amide. In most cases, initial acid and amine concentrations are equal $[\text{Ac}]_0 = [\text{Am}]_0$.

We can then say that:

$$\frac{ds}{dt} = k_{\text{H}}([\text{E}]_0 - s) [\text{W}] - k_{\text{R}}([\text{Ac}]_0 + s)([\text{Am}]_0 + s)$$

It is easy to show that the molar mass at equilibrium M_{ne} is given by:

$$M_{\text{ne}} = \left(\frac{k_{\text{R}}}{k_{\text{H}}[\text{E}]_0[\text{W}]_0} \right)^{1/2}$$

The molar mass decreases according to a pseudo-exponential law with a time constant of:

$$Z = \frac{M_{\text{ne}}}{2k_{\text{R}}}$$

Of course, embrittlement occurs if the critical molar mass M_{C}' is higher than M_{ne} , which is the case for PA11, at least at high temperatures. Integrating the above differential equation allows us, in principle, to determine the lifetime in a non-empirical way.

7.6.4. Role of solutes in water

Hydrolysis proceeds by an ionic mechanism which is likely to be accelerated by acids, bases or both. However, as ionic species are not soluble in the polymer, only non-dissociated species are likely to penetrate the material and to exert their catalytic role.

Merdas *et al.* [MER 02] summarize the effect of different factors in the following expression on hydrolysis rate V :

$$V = K (1 + \gamma [AH])^{1/2}$$

where $[AH]$ is the acid concentration in the polymer, γ a parameter essentially related to the acid dissociation constant, and K a prefactor which comprises the different factors which influence hydrolysis in pure water. The catalysis effect becomes noticeable when, typically:

$$\gamma [AH] \geq 0.1$$

Catalysis is important under the following conditions:

- weak organic acid (benzoic acid, for example): γ is weak but $[AH]$ is strong because acid is soluble in the polymer;
- strong acid (HCl , for example): γ is strong but in moderate pH levels ($pH \geq 2$, for example), the acid is completely dissociated, the ions are not soluble in the polymer, therefore $[AH] \sim 0$, the effect is weak. At low pH levels, on the other hand, a significant fraction of the acid is not dissociated and can penetrate the polymer. Thus, the acid's catalytic effect may be very strong. Additionally, the acid displaces the equilibrium, the reaction becomes quasi-irreversible, and very weak molar masses may be reached.

Let us add to this that if the catalytic effect of the solute is very strong, the hydrolytic attack will then be controlled by the water diffusion. We then have a very deep degradation in a very thin superficial layer, and the sample is destroyed by erosion (polyester fibers in soda, for example).

We must not forget that water generally contains dissolved oxygen and disinfectants (chlorine, for example) which may play the role of radical initiators. Oxidation may be superposed onto hydrolysis. In the case of PA11 for example, autoclave hydrolysis tests must be carried out in an inert atmosphere because when $T \geq 100^\circ C$ the oxygen's contribution to chain scission is significant.

7.6.5. Secondary effects of hydrolysis: composites

7.6.5.1. Osmotic crack growth

For unsaturated polyester fiberglass composites (boats, swimming pools), variations in mass related to water absorption have a very distinct shape which can be shown in Figure 7.24.

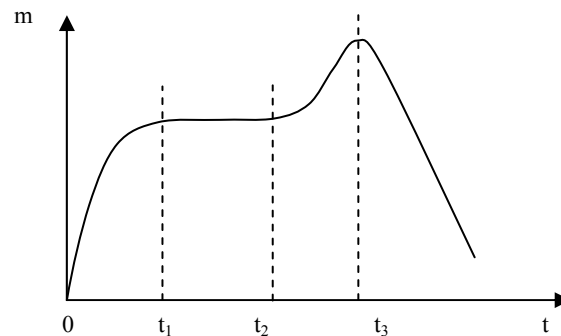


Figure 7.24. Shape of variations in mass in thin (<1 mm) samples of composites subjected to osmotic crack growth

The reason for this behavior has been explained as follows: the initial phase is simply water absorption by the classic dissolution-diffusion mechanism. At t_1 , the system reaches a sorption equilibrium.

However, water reacts with the polymer. As the polymer is rich in chain ends, the chain scissions on dangling chains create a set of small organic molecules (monomers, oligomers). When these small molecules (which are more polar than the polymer) reach their solubility threshold, they demix and form liquid micro-pockets with high hydrophilicity, at time t_2 .

The presence of water in these micro-pockets generates osmotic pressure, therefore the resulting stress state tends to propagate cracks from the micro-pockets which constitute initiating flaws. Between t_2 and t_3 the mass increases because the cracks let in more and more water.

At t_3 , the cracks coalesce and the sample empties its solutes contained in the dip. The mass decreases rapidly.

In composites, cracks form in a subcutaneous layer and propagate in parallel to the surface, hence the formation of blisters, well known by users.

The aptitude of a given material generating blisters in the presence of water is essentially related to the quantity of small molecules which gather in the matrix, which depends on three factors:

- the concentration of initially present molecules (particularly the initiation system of polymerization and its reaction products);
- the initial concentration of free chain ends (as strong as the initially unsaturated polyester's molar mass was low);
- the polymer's hydrolysis rate (which creates new chain ends).

The effect of these various factors has been vigorously checked in experiments [GAU 99].

7.6.5.2. *Interfacial hydrolysis*

In some cases of composites based on hydrolysis resistant matrices (vinyl ester, non-hydrolysable thermoplastics), wet ageing leads to a degradation of mechanical properties which cannot be attributed to a matrix-water interaction. Microscopic or mechanical analyses (interlaminar shear resistance for example) demonstrate that a fiber-resin decohesion exists.

Additionally, it seems that the material stability in given conditions narrowly depends on the nature of the coupling agents used. Therefore, we are displaying a case of hydrolysis reactions affecting the fiber/resin interphase.

If there are many methods of experimentation to demonstrate this phenomenon in a qualitative way, there is no method (to our knowledge) of indisputably quantifying the number of chemical events responsible for the observed evolution.

For the moment, it is not possible to carry out a fine kinetic analysis for this type of ageing.

7.6.6. *Stabilization*

With hydrolysis being a step by step mechanism where each chemical event is independent of the previous ones, there is no real useful method of stabilization. In some cases, PET geotextile fibers for example, some manufacturers propose fibers coated with a polymer layer with a very low hydrophilicity (PE, PTFE). However, water diffusion in these coatings is relatively quick and we do not know whether the stabilizing effect is particularly impressive.

This might be the case eventually, though, when the fiber is located in a particularly aggressive environment (e.g. basic) because it will then significantly slow down the superficial attack. At the moment we lack hindsight to fully understand the efficiency of these solutions, but we may doubt its total efficiency.

7.7. Conclusion

We have tried to present the main ageing processes in organic materials which are likely to be found in the civil engineering domain. This presentation has aimed for neither exhaustivity nor depth of analysis. Yet, with the basic elements for comprehension, the reader will be able to find the following messages implicitly:

- There is not one single mode of ageing, but many modes likely to superpose and interact.
- Ageing is not a mysterious phenomenon which obeys its own laws, but a more or less complex set of physical and chemical mechanisms, each obeying already known laws.
- Vigorous research in the last 50 years has enabled the identification of most of these elementary mechanisms. The main point of this research is the development of kinetic models able to simulate the behavior of such systems whose complexity (e.g. processes involving many tens of elementary reactions, with reaction/diffusion coupling, etc.) seems to defy analysis.
- The temptation, when faced with rather complex problems, is to look for empirical solutions, but these, potentially relevant in interpolation, are not adapted to the problem of predicting lifetime, which is an extrapolation problem.
- We now have powerful numerical methods accessible to non-specialists, to solve kinetic schemes, long ago considered to be irresolvable. These methods enable us to avoid simplifying hypotheses, necessary for analytical solutions, but sometimes difficult, or even impossible, to justify.
- Problems concerning non-Fickian diffusion, thermo-oxidation and hydrolysis have now already gained satisfying solutions, even if the kinetic schemes can still be perfected. However, significant efforts still needs to be made in the field of photo-oxidation and ageing of the interfacial zone in composites, glued joints, etc. Some problems, particularly mechanical stress/physical chemical ageing coupling, are still very far from being solved and must also be researched in the future.

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Chapter 8

Fireproofing Polymeric Materials: Problems and Solutions

8.1. Introduction

Polymeric materials are associated with the technological evolution of the 20th century. However, plastics and composites present us with a major defect, a defect for which only partial solutions have been found: *fireproofing*.

If man has been using fire for several centuries, it is only since the 19th century that the creation and the development process of fire has been established in a formal way. Fire occurs when a source of ignition (for example, a match, a cigarette, a stove or an air-heater) are put in the way of a flammable product such as a chair, a wall, or a sheet of paper. The heat provided by the source is then likely to break chemical bonds in the material, creating (via a generally endothermic process) small fragments which vaporize. If the temperature is raised high enough, these fragments react with oxygen in the air to produce more heat. Part of this heat is reassigned to the combustible source by radiative and/or convective processes, maintaining the fragmentation and molecular chain unzipping process, and thus contributing to feeding the flame. Threats to life and goods therefore come from a process where the heat flow coming from combustible material is higher than the sum of the dissipated heat in the combustion environment, and in the marginal enthalpy which is necessary in order to maintain the stationary flow in the pyrolysis gas phase.

Chapter written by Serge BOURBIGOT.

Historically, the synthesis of “fire retardant” (FR) materials preceded the comprehension of the mechanism of fire. It dates back to the 17th century in Europe, when the drapes of Parisian theaters in 1638 were treated, and materials were woven to obtain “fireproof” clothing, in Oxford in 1684. The works of Gay-Lussac completed at the beginning of the 19th century on non-natural cellulose carbonization in the presence of the orthophosphoric acid comes under this approach [GAY 21].

Currently, a material’s fireproofing is optimized by:

- increasing their fire resistance;
- reducing flame propagation by diluting combustible gases and/or oxidants. This reduction is obtained by emitting an inert gas, and/or by modifying the flame regime. The latter is obtained by emitting species of radical gases which act as termination agents for the radical chain reactions responsible for the flame;
- or, by decreasing the heat flow emitted during combustion by lowering the “fuel rate” released in the gas phase and/or by modifying their composition and therefore their heat value.

In the construction industry, furnishing, transport, electric and electronic applications, synthesized polymers (plastic, thermoplastic, and thermosetting resins) have a general use due to their ease of implementation, and their low trading prices. These materials, in particular frequently consumed polymers (polyethylenes, polypropylenes, polyamides and polystyrene) and their alloys or mixes are easily flammable. The generalization of their use therefore requires the user to obtain the “fire retardant” property. Formulating FR polymeric materials must take account of their low price, their implementation conditions and their intrinsic properties (rheological and mechanical properties, and resistance to ageing, ultraviolet rays and bad weather conditions).

Several methods are proposed to the industry expert for the choice or the formulation of FR polymeric material. They consist of:

- using polymers, such as certain thermosetting resins; (phenol/formaldehyde resin) or certain thermoplastics (sulfonic polyphenylene, aromatic polyamides (aramides), poly(bismaleimides), intrinsically resistant to heat and/or FR [BOU 02];
- adding functionalized monomers to monomers during the polymer cross-linkage. Raw materials are generally highly priced and this application remains comparatively confidential (for example, see the case of polyester in [CHE 05]);
- adding FR additives during the synthesis or the forming of the polymer [BOU 07].

This article is placed within the framework of this last strategy and will not consider intrinsically fireproof materials, or the chemical modification of the material. The “additive” method is the most commonly used and is that which represents the best compromise between process/cost/performance at the present time.

This chapter’s objective is therefore to present the various possible approaches which can be followed to improve the behavior of polymeric materials towards fire by incorporating additives. After a short overview of combustion phenomena, we will present three fundamental concepts which are intended to improve a material’s reaction to fire (*material’s contribution to fire*) which are: “poisoning” the flame by a gas phase mechanism, cooling and ceramizing a material, and the concept of intumescence. The use of nanotechnologies will be also approached. Lastly, a final section will deal with the fire resistance of materials (*a material’s capacity to block the path of fire/or smoke*) by using organic paints.

8.2. Combustion principles

The combustion process of polymeric materials is a complex process, comprised of many stages, some of which are still unexplored (Figure 8.1) [TRO 03].

These cannot be described quantitatively, but can be described qualitatively. We can mainly distinguish four stages which are: heating, decomposition, ignition and propagation, respectively:

- *Heating*: application of an external heat source, such as radiant heating or a flame, will firstly lead to an increase in the temperature of the polymeric material. In this initial phase, the thermoplastics will tend to soften or melt, which is not the case for thermosetting polymers which have a three-dimensional cross-linked molecular structure.

- *Degradation*: starting from a critical temperature, the thermally weaker bonds break. Degradation will lead to the formation of radicals which will react to form organic molecules of low molecular weight, which are generally flammable. The composition of degradation products will depend on the chemical nature of the polymer and the oxygenic composition of the environment.

- *Ignition*: the ignition stage of a polymeric material will depend on many variables, such as the concentration of oxygen in air, the temperature or the physical and chemical properties of the polymer. When the release rate of the volatile products reaches a sufficient value for the gas mixture to be produced – air is flammable, thus appears a flame. Combustion will be maintained so long as there is sufficient energy transferred to the surface and in the polymer’s mass to maintain its decomposition, which generates the production of combustible gases.

– *Propagation*: fire propagation is achieved via heat transfers which can be conductive, convective or radiative. These three modes of transfer coexist and interact during the fire. According to the fire conditions and the moment when the fire develops, either one of these modes may prevail.

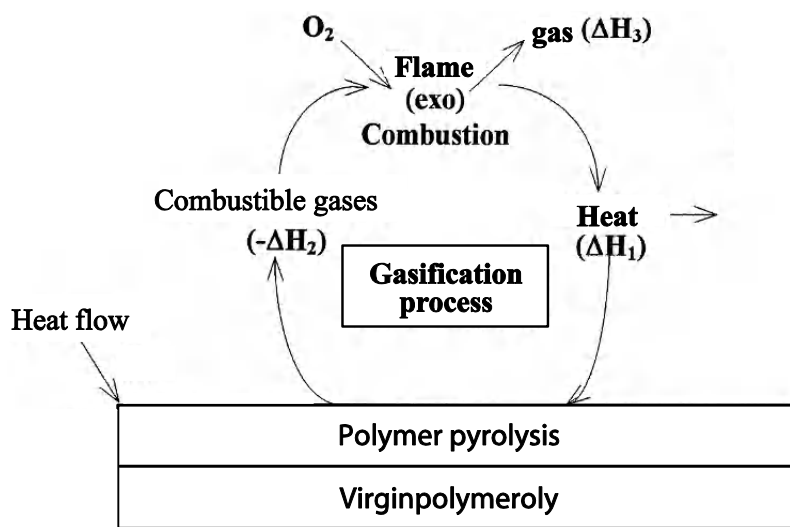
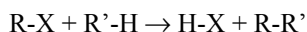


Figure 8.1. Diagram of polymer combustion

8.3. Action in gas phase

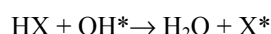
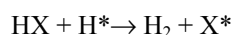
Fireproofing a material will consist of treating it in such a way so that the loop shown in Figure 8.1 is interrupted. Flame retardant additives may present an action mechanism in the gas phase. In this case the inhibiting action will be exerted on the level of the flame or in an action mechanism in condensed phase by disturbing the material's thermal degradation [LEW 98].

Halogenous derivatives mainly represent an action mechanism in gas phase which consists of inhibiting the radical reactions either by transfer reaction, or by recombination reactions. There is a first reaction stage between flame retardant additive (written as RX) and the polymer (noted R' -H), which leads to the release of halogenated hydracid:



The inhibiting role will be carried out by this acid, which will transform the H* and OH* radicals, which are radical chain conductors, into less reactive X* radicals.

By dissipating the energy from the OH* radicals by this type of trapping, the heat balance will be modified which will lead to a significant reduction in the combustion velocity:



Brominated derivatives are the most effective. This effectiveness is related to their ease of releasing HBr. In this hypothesis, the most effective derivatives will be the organic brominated derivatives and in particular those containing the weakest C-Br bond energies. Adding antimony trioxide, zinc hydroxystannate or zinc borate to halogenated compounds may lead to synergy effects.

8.4. Cooling and ceramization

A large category of flame retardants consists of metal hydroxides [HOR 05]: aluminum hydroxide (6% weight of annual growth in the United States) and magnesium hydroxide (8% of expected growth for 2009). The demand for such compounds allowing the development of improved fireproofing composites while responding to the double criterion “low smoke, zero halogen”, all while maintaining acceptable production costs, increased considerably because of the evolution of international legislation. Mineral hydroxides must, however, be incorporated in great quantities (around 60%) to show real effectiveness, which generally involves a reduction in the mechanical performances of the composite. In order to make up for this disadvantage, these can be treated on the surface, for example by silanes or fatty-acid derivatives, to ensure a better cohesion between the polymer and the filler.

Metal hydroxides are widely used as flame retardants in polymeric materials because of their low cost (aluminum trihydroxide) or their relatively high decomposition temperature (magnesium hydroxide) which allow high process temperatures (up to 280°C). They impart a widely improved fireproofing property on the material, compared to the material alone which makes it possible for the fireproofed material to answer to severe specifications. These additives present an endothermic degradation under fire conditions ($\Delta H = 1,050 \text{ J/g}$ for $\text{Al}(\text{OH})_3$ and $\Delta H = 1,350 \text{ J/g}$ for $\text{Mg}(\text{OH})_2$) with water release. This degradation causes an ignition delay but does not ensure substrate protection. However, this dehydration leads to oxide formation (aluminum or magnesium oxide) which forms a protective ceramic layer on the composite surface, promotes material carbonization and constitutes a barrier which protects the composite and delays its degradation.

8.5. The concept of intumescence

In French, the term “intumescence” (*intumescence*, an action denoting an object which swells (Littre, Dictionary of French Language)) has remained a literary expression for a long time. As an example, Victor Hugo defined the formation of fog banks on the sea as *l'intumescence de la mer*, “the swelling of the sea”. The verb, *to intumesce*, was used by the Elizabethan actor John Webster (1580-1624) with two meanings: “to grow or increase volume with heat” or “to present an upwards swelling by boiling”. Webster’s definition allows a totally exact description of the performance of a coating or an intumescent/swelling material which, heated beyond critical temperature, start to melt while boiling, then while swelling. The result of this process is the formation of a multicellular (alveolar) barrier, thick and non-flammable, which likely to protect the substrate or residual material from heat or flame action [BOU 07].

The concept of intumescence was initially applied to paint type coatings but was quickly extended to polymeric matrices. Intumescent formulations generally contain three ingredients: an acid source, phosphoric acid salts, such as ammonium phosphate or ammonium polyphosphate which release acid at temperatures of 150°C; a carbon source agent, which is generally a polyhydric compound and a swelling agent, of compounds such as guanidine and melamine which, when subjected to temperature effects, release a large quantity of non-combustible products such as ammonia (NH₃) or carbon dioxide (CO₂) which will allow the carbonaceous coating to expand.

Intumescent formulations will generally contain a compound belonging to each class. However some compounds can fulfill several functions. Ammonium polyphosphate, for example, can be both an acid source and a swelling agent at the same time. Moreover, associating the three ingredients does not necessarily lead to a intumescence phenomenon. It is, however, necessary for the chemical and/or physical processes leading to the “char” formation (carbonaceous material, pitch) to proceed in an appropriate sequence while the temperature increases.

8.6. Nanocomposites

Nanocomposites constitute a particular composite material class. Although they have the same composition, in particular with regard to the nature of the matrix, their difference lies in the size of the components (matrix or strengthening agents) and in the fact that certain specific properties only appear on a nanometric scale. There are many definitions of the term “nanocomposite”. However, one characteristic remains common: the nanometric size of the strengthening agent(s) in the matrix or the multiphasic domains which make up the composite. At least one of

the strengthening agents' morphological dimensions are lower than 100 nm. The improvements and new methods aim to obtain a better control over their size, their morphology and their surface properties. We only use them in rates generally lower than 10% in a mass for cost reasons, but also, in particular for clays, due to an important increase in the mix viscosity with the capacity factor.

At the end of the 1990s, the work of the NIST (*National Institute of Standards and Technology* in *Gaithersburg*, MD, United States) showed that montmorillonite clays contributed a significant increase in fireproofing the polymer in which they were nanodispersed. [GIL 97]. Other groups adhered to this concept of hybrid polymeric materials by using different types of nanoparticles such as TiO_2 or SiO_2 particles, Lamellar double hydroxides, carbon nanotubes or silsesquioxanes [WIL 07]. All these polymeric matrix nanocomposites show an improved fireproofing associated with other characteristics such as high mechanical properties which makes them potentially appealing for multifunctional material designs. Typically, the nanocomposites' heat release rate, a parameter currently referenced in building regulations and aeronautics, is reduced between 50 and 70% compared to the polymer alone.

The use of the carbon nanotubes leads to a similar effect in polypropylene: the heat release rate of the nanocomposite is reduced from 80%, by using only 1% of the carbon nanotubes weight, compared to polypropylene alone. But with regard to the difference in clays, the residue after nanocomposite combustion is compact and non-friable, which opens up interesting prospects for development (thermal barrier) [KAS 04].

8.7. Intumescent coatings for protecting steel

In the event of fire, the steel structures of a building must be stable as long as possible, at least, during the time needed to evacuate people. An undeniable advantage of steel is that it is fireproof (M0 classification of construction materials). However, fire stability duration treatment of an untreated metal profile only rarely exceeds half an hour when it is under a live load. To increase the stability of a steel to fire, one solution consists of using intumescent paint. When cold, the paint film varies in thickness from 0.5 to 4 mm. Brought to a temperature between 180°C and 300°C, the product swells and is transformed into "foam", reaching thicknesses of 30 to 40 mm, which ensures protection of the metal element (Figure 8.2). These paints are applied by traditional methods: gun or brush, but yet they require rigorouslyness in their application, in order to ensure homogeneity of the protection. Steel esthetics conservation constitutes the main interest of this type of protection which can even reach protection lengths of 1 hour, or even 1.5 to 2 hours for certain solutions. Intumescent paints also present interesting durability properties and can be used inside or outside.

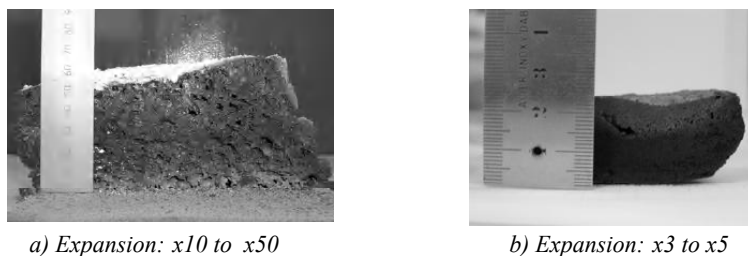


Figure 8.2. Example of a piece of “char” developed from intumescent paints (a: acrylic base paint; b: epoxy base paint)

Figure 8.3 displays the temperature evolution obtained on the back face of the sample (metal substrate) according to time for different intumescent paint formulations during test UL 1709 (temperature measurement according to time on the back face of a steel plate coated with intumescent paint and subjected to a temperature curve reaching 1,100°C in stationary mode).

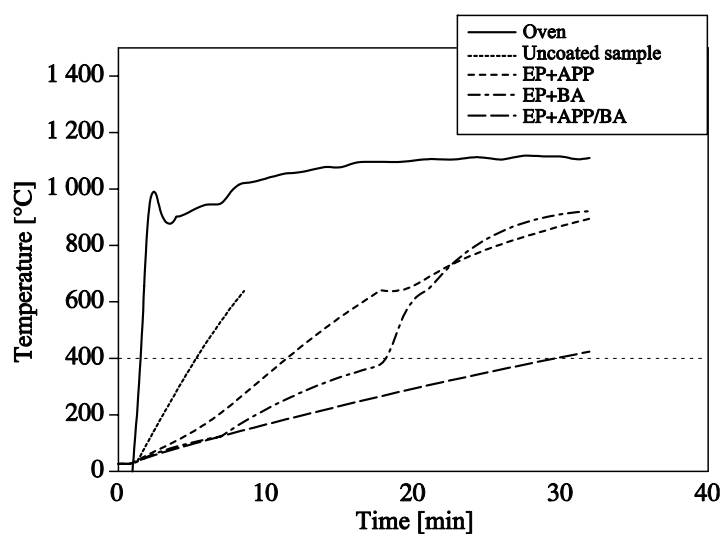


Figure 8.3. Temperature profiles of intumescent paints (series 1) in test UL 1709

The time needed to reach 400°C, still called the time of failure, is one of the characteristics parameters for fire protection. The longer the time, the more effective the paint. The time of failure of the metal substrate coated in epoxy resin (EP) is close to the time of ruin for the uncoated sample. When ammonium polyphosphate

(APP) is built in to the resin, we notice that the time of failure increases. A process of intumescence and carbonization is observed, but the formed carbonaceous coating shows a weak adhesion with regard to the substrate, and the change in curve to approximately 610°C can be attributed to a fall in the protective coating leading to a large rise in temperature. The formulation made up of epoxy resin and boric acid (BA) leads to a more noticeable increase in the time of failure. We also notice the development of an intumescence process. However, similarly to the phenomenon observed in the case of the EP+APP formulation, the protective coating does not sufficiently adhere to the plate, and its fall (after approximately 18 minutes) leads to a fast increase in temperature. The best result is obtained when the APP and the BA together are added to the resin [JIM 06]. In this particular case, the intumescent coating adheres perfectly to the substrate, and protection is maintained over a long period of time.

8.8. Conclusion

The fire resistance of polymeric materials can be increased by using intrinsically fireproof matrices or by the addition of a flame retardant additive, acting or not acting synergistically with other additives. These fireproofing systems will be able to present a chemical and/or physical action, the goal being to stop one of the combustion process stages.

We may notice here that we have not tackled the problem of smoke toxicity during a fire. This is indeed a complex question, important, not to be disregarded but which would require a long article to be dealt with correctly, which would be outside the scope of this chapter.

A polymeric material is a complex material integrated within an environment, able to undergo many physical and chemical suitable variations which are likely to affect its properties. It is therefore necessary to take stock of many parameters so as to reach a compromise, offering the best possible performances for the material. Today still, many questions remain regarding the action mechanisms of certain flame retardants, which leaves us with great prospects in terms of research and comprehension.

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Chapter 9

Organic Materials, Waste and Recycling

9.1. Introduction

Organic materials occupy a large space in the material sector, and are used because of their interesting usage properties. They can be found in very diverse applications, such as packaging, transport, health, agriculture, industry, buildings or in electric products. In this material category (plastics, inks, paints, varnish, etc.) the polymer objects are most often selected in order to fulfill certain specific applications with adapted properties, for a defined length of time, according to specifications. Effectively, throughout its lifecycle the end product will be subjected to certain attacks which will lead to its degradation and limit its use.

Therefore, as soon as they are processed, the polymers are subjected to thermal and mechanical stresses (extrusion, injection, thermoforming, rotomoulding, etc.) which are likely to deteriorate the matter and to change its properties. When in use, the material will be subject to various attacks (light, heat, pollution, mechanical cycles, etc.) which will lead to its ageing, depending on the intensity of the storage and use exposure parameters (time, temperature, light, moisture, weather conditions, etc.). All these attacks, imposed on the matter, essentially lead to its oxidation (and/or its hydrolysis) which disturb the initial structure of the polymer. This deterioration ends up reducing the mechanical properties of the materials until the end of the first life.

Chapter written by Vincent VERNEY.

When they are used up, polymer objects turn into waste. Several solutions exist to valorize this waste by developing it: either re-use, recycling or finally using it for energy. When it is not possible to develop the waste into something useful through valorization, the ultimate solutions are landfilling and incineration without re-using it for energy purposes.

At this stage of the polymer lifecycle, the level of degradation can strongly influence the future of the material. Indeed, when recycling matter, the polymer is then subjected to new thermal and mechanical attacks which also lead to degradation, and a negative impact on its properties. The degradation level of recyclable waste is therefore very important with regard to the end properties of recycled polymers.

The matter can be used with the same function as before or with a new application, where the properties of the recycled material are more adapted. When the properties of the recycled matter are not sufficient, improvements can be made either chemically, or by using additives.

Finally, we must not forget that the question of the future of this waste cannot be removed from the question of their origin. As a result, we must take into account the topics of the interaction between the materials and the environment from the first origin of the matter, to its final recycling stage through its usage.

9.2. Assessment

9.2.1. Definitions

For reasons of clarity, it is important to define things accurately:

- *re-use, re-usage*: as their names indicate, re-using an object;
- *regeneration*: acquiring polymer granules after reformulation of the new matter made from waste;
- *recycling*: making a new object or new matter for a new application; recycling can be an “isofunction” or a “heterofunction”. It can be an “isosector” (in applications) or a “heterosector”. Recycling can involve “mechanical” recycling or “chemical” recycling (acquiring a new chemical compound from waste);
- *valorization*: valorization can refer to “matter” in the case of recycling, or even “energy” in the case of incineration with energy recovery.

Since the beginning of the 1970s, the increase in the worldwide production of plastics is impressive by its large measure. The presence of these materials in all the consumption sectors creates a very important waste flow.

Managing this waste seems essential. Therefore, a European regulation has been put into place and is gradually being applied. Recycling methods and energy valorization are favored so as to reduce the quantities of waste taken to be landfilled. Those involved in recycling plan to equip the oldest incineration centers with recovery systems and energy distributions with the intention of preventing unvalorized materials from being destroyed.

In France, energy valorization represents nearly 70% of the collected plastic products output. 20% represents recycling and the other remaining 10% are incinerated.

Certain polymers are currently only present in certain valorization methods whereas other solutions might prove to be more interesting.

9.2.2. *Plastics: facts and figures*

The worldwide production of plastics, continually increasing, (Figure 9.1) has been multiplied by a factor of 5 in 30 years and was estimated at 169 million tons in 2003 [PLA 04]. France alone produces approximately 7 million tons.

Consumption in Western Europe is rising by nearly 40 million tons, with a large majority of thermoplastics.

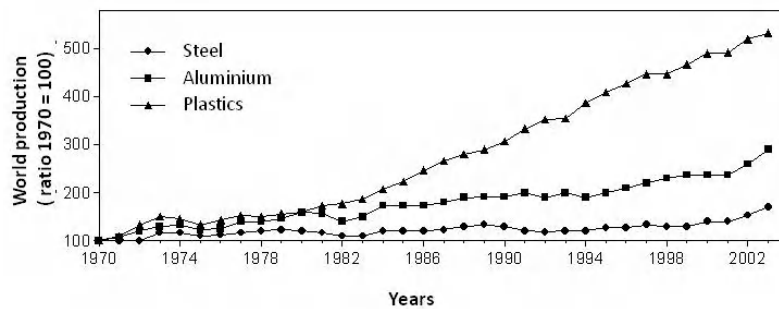


Figure 9.1. *Worldwide production – comparison between the evolution of plastics and other materials [PLA 04]*

France is one of the three highest consuming countries in Europe, approximately 5 million tons, with 39% as packaging, 23% in buildings and civic works, and 13% in transport.

This results in 21 million tons of plastic waste collected in Western Europe. In 2003, only 39% was valorized.

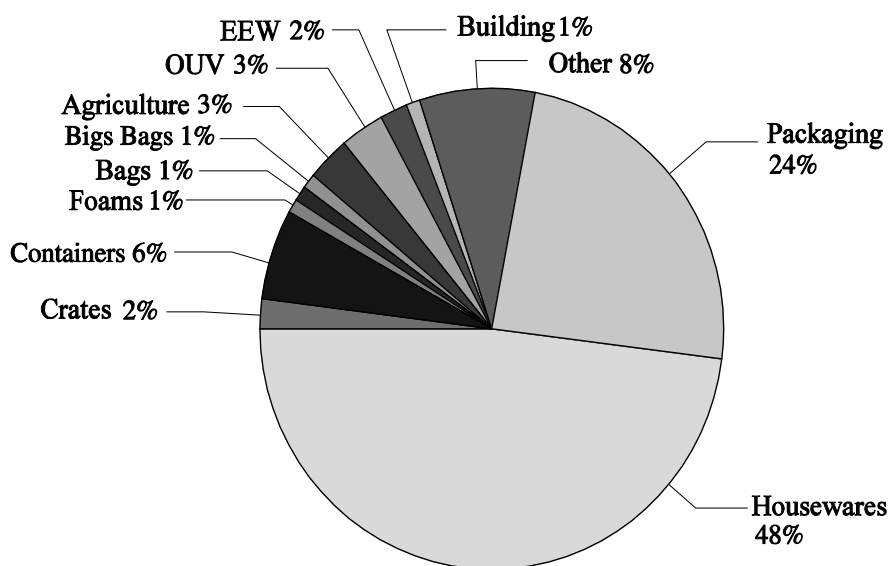


Figure 9.2. Pie chart of plastic waste in France (taken from Ademe) *OUV: out-of-use vehicle, *EEW: electric and electronic waste at the end of the lifetime

Regular and comparable data are requested from the Member States on the waste produced by economic activity and households, as well as their destruction and valorization. In France, the French Environmental Institute (IFEN) is responsible for collecting and processing the data on the environment and natural and technological hazards, and consequently, to develop the French response to statistical responses to waste.

This response, requested in 2006 for the first time, bearing upon 2004 and recently published, indicates that total waste *production rose to 414 million tons in 2004*. This figure includes data from *companies and households* but does not take into account agricultural waste, organic waste from food farmers and waste from tertiary activity.

A proportion of this waste (81%) is inert waste, mainly from buildings and civic works. 17% is household waste or similar (paper, plastic, wood, glass, textiles, etc.). The remaining 2% is dangerous waste which contains hazardous elements for both human health or the environment, which generally comes from industrial activities or buildings.

Waste processing aside, the IFEN estimates that *more than half the waste is disposed of by recycling or re-use.* This is especially the case for inert waste from buildings. It is a question of unpolluted mineral waste, which is unsuitable for any physical, chemical or biological evolution and not dangerous for human health or the environment (concretes, tiles and ceramics, bricks, glass waste, grounds and aggregates). Two thirds are recycled or reused as backfill, once it is transformed into aggregates after crushing in road sub-layers. The remaining third is stored, often in old carriers, which are filled with these materials.

Household waste has the lowest recycling rate: only 54% is recycled, 18% is incinerated and 28% is landfilled. Recycled waste mainly comes from selective sorting (paper, glass, packaging). Other waste which does not benefit from selective collection is incinerated or landfilled.

A portion of dangerous waste is also recycled (38%) but this waste is mainly incinerated (38%) or stored at a landfill (24%). Half of this waste comes from industrial activities, mainly the chemical, plastics and rubber industry, as well as the metallurgy industry. These are used up oils and other chemical waste, or even tarnished wood.

9.2.3. Legislation

Structures have been put into place in order to respond to French, then European, legislations. These particularly concern packaging and packaging waste by referring to directive 94/62/CE of 20th December 1994, modified by directive 2004/12/CE, and by referring to decree no.98-638 of 20th July 1998, relating to considering demands linked to the environment with regard to the design and manufacture of packaging [MIQ 99].

By these measures, the European Union is looking to bring together national measures regarding the management of packaging and packaging waste, in order to ensure a high level of environmental protection and to guarantee the working order of the inside market. Therefore, the Member States must put preventative measures into place for packaging waste formation, and they are encouraged to develop systems to re-use packaging.

Recovery, collection and valorization systems for valorizing packaging waste must be established in order to achieve the following goals: at the latest by the 31st December, 2008, between 55% and 80% of packaging waste will be recycled, including 60% for glass, paper and the cardboard; 50% for metals; 22.5% for plastics and 15% for wood [DIR 94], [DIR 04].

In France, the decree of 20th July, 1998, inverts the European directive 94/62/CE. The essential requirements are: minimalizing the use of substances which are dangerous to the environment, including a calculated limitation with regard to heavy metals. Moreover, characteristics of packaging re-use and valorization must be improved by following an eco-friendly design procedure.

9.2.4. Recycling and valorization channels

With the exception of recovered and processed industrial waste in production and channels of re-use (often packaging), the valorization methods are the following [MAN 00], [PLA 02].

9.2.4.1. Valorization by mechanical recycling

This mode of valorization consists of crushing plastics and regranulating them to produce a secondary raw material for new applications in new products. Some projects have been carried out on PET (polyethylene terephthalate) recycling [VER 06].

9.2.4.2. Valorization by recycling matter (or chemical recycling)

This brings together all the techniques which allow a return to monomers or the purification of polymers by dissolution.

9.2.4.3. Energy valorization

In this case, waste must be combustible and able to provide a sufficient calorific gain.

9.2.4.4. Valorization by composting and biological breakdown (organic methods)

Here, waste must be able to disintegrate during a biological process.

Waste which is not valorized by one of these modes is disposed of by incineration (without energy recovery systems) or taken to a landfill. This last solution is only possible for ultimate waste.

With the aim to valorize a maximum plastic waste, French communities have put several structures into place, on the level of household waste as well as industrial and commercial packaging [PLA 02].

In 2002, two thirds of collected plastic waste corresponded to household trash, including packaging and various domestic objects. The remaining third, coming from distribution, industry, electric products, cars, agriculture and buildings, is dealt with by specific channels.

The total mass of collected plastic waste is rising by more than 3,000 kilotons (Figure 9.3).

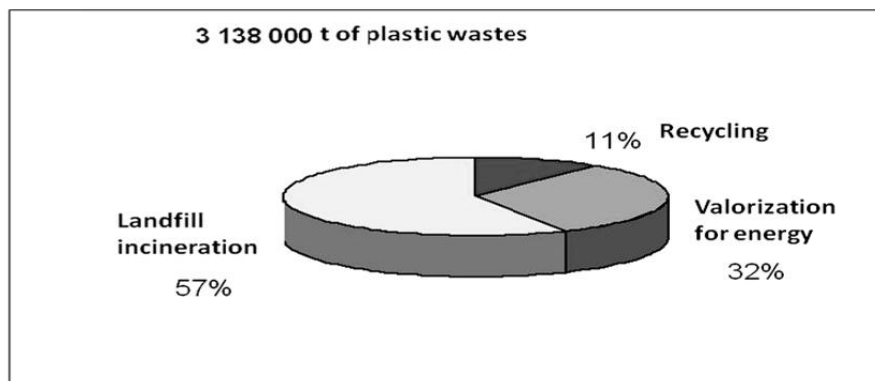


Figure 9.3. Processing methods in France (ADEME)

In spite of this organization, not all the waste is collected, and amongst the recovered plastics, not all of them are valorized.

9.2.5. Current proportion of recycling in waste disposal

In 2002, approximately 7 million tons of plastic waste out of nearly 20 million tons collected were valorized in the European Union. Recycling valorizes 13.6% of this waste, whereas 21.1% is disposed of by energy valorization; the rest is often incinerated without recovering energy.

In France, 1.3 million tons out of 3 million tons are valorized. The proportion of recycling represents a quarter of valorization, and 31.6% is disposed of by an energy channel [PLA 04].

Since 1993, the efforts made to valorize waste have been clear. Figure 9.4 shows data from PlasticsEurope [PLA 04]. The proportion of mechanical recycling progresses much quicker than energy valorization and chemical recycling.

Although the valorized quantities are progressing, waste tonnage also rises proportionately.

Studies have been carried out to increase the recycling rate of plastics, to avoid incineration and, of course, being landfilled.

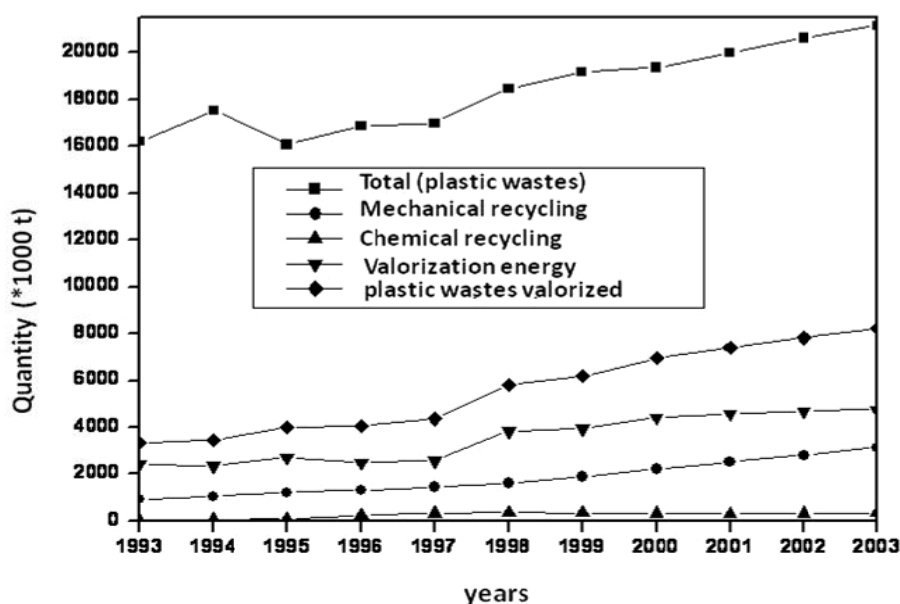


Figure 9.4. Valorization of plastic waste in Western Europe 1993-2003, according to [PLA 04]

Mechanical recycling is currently the most practiced, and efforts are being made to develop chemical recycling. Indeed, the method chemical valorization is only currently used for a small part of household waste or for production rejects [PLA 04, ADE 02, ADE 04].

The waste which benefits from the highest valorization rate is in agriculture, distribution and industry, and state refuse collectors. Cars, buildings, civic works and electronic and electric industries only valorize a small amount of their waste, essentially by using mechanical recycling.

9.3. Scientific aspects

The problems surrounding organic material waste cannot be completely disconnected from general problems surrounding “Materials and the environment”.

The awakening around such a question dates back to the end of the 1980s (Bruntland Report [BRU 87]) with the definition of “sustainable development”, which implied the notion of minimization, as much as for taking natural resources as for quantities of produced waste.

9.3.1. The concept of lifecycle

Everybody has heard, and continues to hear more and more, of the lifecycle of polymers. Each person imagines in his own way the motto “from cradle to grave”, concerning the different successive stages of polymers from this life. First of all, raw matter is obtained, where the majority comes from the petrochemical industry, and therefore are fossil resources. At this stage, we are touching on one of those debates which excite society: fossil resources and renewable resources. After this stage, we reach synthesis and then formulation. It is only from this point that we are able to speak of a “polymeric material” which will be used for a specific application, with the desired property for this application. Then, time gets to work and the matter itself begins to age, which leads to a loss in properties. The object then becomes unsuitable for the application, and therefore finds itself as “waste”. Up until the recent past, we hardly worried about this problem. But after 1987 and the Bruntland report [BRU 07] which defined the notion of sustainable development, it became necessary to settle the question of the future of material waste. Therefore, a new stage was added to the lifecycle: the “end of life” (EoL).

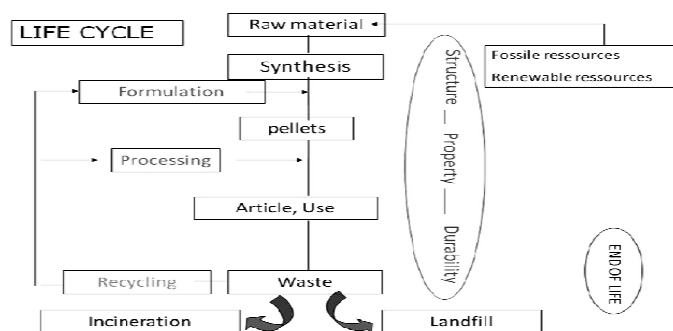


Figure 9.5. Representation of the lifecycle of polymeric materials and its fields of scientific studies

Therefore, while identifying each stage of the lifecycle, we realize that the scientific aspects concerned affect the science of materials and the particular field of relationships between “Structure-Property-Durability”. Concretely, this means that waste must be considered as special material. This refers to evolutive materials, because they present a certain level of initial ageing and are likely to evolve during later working operations. One of the main objectives will therefore be to limit the accumulation of the impacts of the processing operations specific to plastic waste recycling (Crushing, granulation, re-working, etc.). Stein [STE 92] was the first to publish a scientific article on “*Polymer Recycling: Opportunities and limitations*” in 1992. It distinguishes five thematic scientific fields:

- reduction at the source;
- incineration;
- bio or photo degradation;
- composting;
- recycling.

A second objective will be to take into account the concept of quality (not a hyper quality, as the objective is so difficult to reach). In the beginning, recycling tried to create tonnage. Quality was not important, provided that the processed quantity followed thereafter. Thus, the first applications always related to devalorized applications, known as *downgrading*. Very quickly, scientists realized that contrary to what they believed, it was necessary to *upgrade* the properties in order to respond to precise specifications for a given application (with the aim of substituting an expensive virgin matter by a less expensive recycled matter, but equipped with rather similar properties) [VIL 08].

9.3.2. Concept of adequacy, application duration/lifetime durability

Finally, the most recent progress now tends to integrate the concept of sustainability throughout the lifecycle. An objective, then, is to try to make the duration of applications compatible with the lifetime durability. For example, a polyethylene film used for packaging displays levels of durability which are often much longer than required for its actual use. Thus, each application for each use has its own time scale.

Let us add to this the concept of sustainable development which underlies the concept of removing the minimum raw material resources. This implies that a consideration of the renewal time of this raw material is a major criterion.

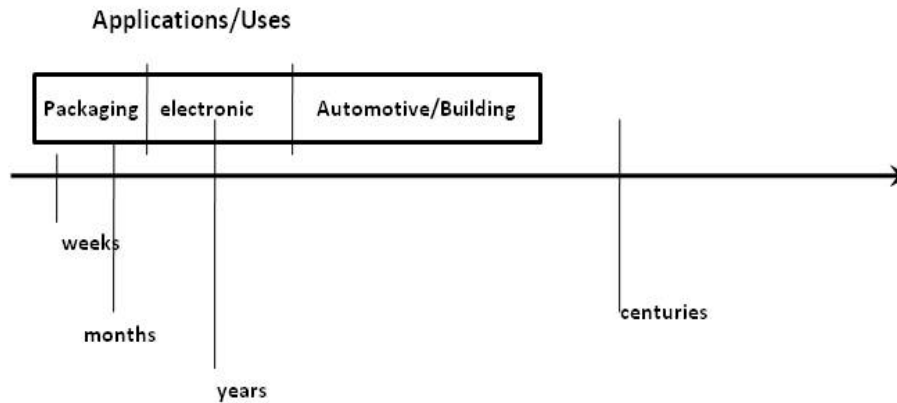


Figure 9.6. Size order of time scales for each application sector [VER 06]

From the previous reflection and on the basis of the principle that it is advisable to make the application duration correspond the best it can with the material's durability, it becomes important to divide such problems into two components: that of short-term durability and long-term durability. For long-term durability, there is no doubt that at the present time, only fossil resource matter can fulfill this demand. For short-term durability (lower than one year), polymers known as biodegradable, but especially those from natural and renewable resources (like polylactic acid, for example), begin to emerge.

9.4. The construction sector

The building and civic works sector is the second sector of material use after packaging, and before that, the car. However, only less than 1% of the quantity concerned is made up of organic materials. The strongest tonnages are achieved by large thermoplastic currents (polyvinyl chloride (PVC), polystyrene (PS), polyolefins, etc.) which fulfill the requirement of long-term durability needed for building materials [APP].

The materials used are found under different physical forms:

- coatings and flooring;
- tubing and pipes;
- insulation;

- profile;
- waterproofing membranes;
- windows;
- housing applications.

For floor coverings, we will normally find PVC, which is also present in window sections or shutters, waterproofing membranes or, finally, electric wires. High or low density polyethylene or polypropylene will essentially be found in tubing and pipes. Lastly, insulation materials will provide styrenics or polyurethanes either in compact form, or as expanded foams.

When a building is demolished, the collection of these materials used in different physical ways will be found in the waste deposits, if there is no selective sorting. Another problem arises with regard to the age of the recovered materials, since they are generally as old as the building! These first two aspects show that we are not dealing with a simple problem.

It is because of this fact that the environmental approach of the construction sector can and must cover two distinct and complementary forms:

- Favoring the recycling of the sector's internal waste. This implies a certain level of organization from a construction site, in particular on the level of sorting and collection (by polymers, physical form, colors, etc.). A good solution consists of promoting isofunction/isosector recycling. For example, PVC window sections are only oxidized and aged heterogeneously on the surface, some on a depth of approximately 50µm. It is sufficient to develop an extraction process from this superficial layer to find a quasi-“new” matter ... and in any case suitable to make another new window section with a durability of the same size as a virgin matter [BRA 04].

- Favoring the use of recycled polymers in the building sector [MAR]. On the basis of the principle that this sector is a large organic material consumer, this can constitute a viable outlet for second generation polymers on the condition of respecting precise specifications. For example, T. Grossetête [GRO 01] has shown that we could use polyolefins completely recycled from waste (battery containers, car bumpers) to produce an object out of recycled polypropylene presenting durabilities compatible with the building's requirements. F. Fraïsse [FRA 05] showed that we could achieve the same goal by using the waste of PET and polycarbonate packaging.

9.5. Conclusion

There is no doubt that the interaction between “polymers and the environment” is one of the major aspects of the problems concerning organic materials used in the construction sector. Buildings, large consumers of these materials, use impressive quantities of organic materials. This interaction may also substitute an important part of its own internal consumption by second generation materials as a result of recycling. One of the major points is, then, to be able to ensure the long-term durability needed in this sector. This can only be made possible by perfectly organized collection and sorting circuits.

The need for long-term durability makes resorting to fossil materials somewhat obligatory, as renewable matter is not, at the present time, capable of ensuring this criterion. Therefore, the concepts of sustainable development applied to materials in this sector make the concept of recyclability and recycling rather obligatory, particularly on the level of mechanical recycling. The implicated quantities in this sector make it possible to offer economically viable solutions for processing polymeric waste from other sectors. In terms of lifecycle analysis, two lifecycles with long-term durability (several decades) for each cycle have an undeniable environmental advantage.

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PART 3

Manufactured Products

Chapter 10

Geosynthetics and Waterproofing

10.1. Waterproofing in civil engineering

Waterproofing devices aim to reduce or prevent the movement of a fluid across a material or construction: the fluid concerned may be a liquid (water, oils), liquid waste (leachates) or a gas. Waterproofing properties in civil engineering may be obtained in two ways:

- either by building with materials which already possess this property, through their weak permeability level or by adding certain products to them. The construction will obtain a waterproofing property by its constitutive materials;
- or by putting waterproofing devices around the structures, so as to obtain waterproofing at surface level. The quality of waterproofing, then, depends on the choice of materials and devices.

Restoration of old constructions, in terms of restoring the waterproofing property, is generally carried out by adding surface devices or liner systems.

The types of works concerned are also very diverse:

- large civil engineering constructions (bridge decks, dams, underground structures, maritime constructions, canals);

- geotechnical constructions (foundations, retaining structures, embankments, earth dams);
- everyday buildings (roofing, terraces, pavements, under-tiling, basements, swimming pools, basins, etc.);
- transport infrastructures (roadways, railways);
- networks for distributing drinking water, waste water (underground pipeworks);
- water treatment plants, settling basins, storage basins, reservoirs;
- refineries, chemical plants;
- landfills, retention ponds.

Waterproofing devices have varied dimensions according to the dimensions of the constructions themselves. In the context of dams and waste storage sites, we notice the largest heights and biggest surfaces for these devices. As an example, Figure 10.1 shows a general view of a liner system device put into place for the dam at La Galaube [GAU 02], which required 23,000 m² of watertight surfaces for a maximum height of 43 m, and a slope of 1 for 2. Larger heights have been treated since, with up to 190 m for the concrete Miel Dam (Columbia).



Figure 10.1. Geomembrane-lined dam (40 m high geomembrane for La Galaube dam over the river Alzeau, France) [GAU 02]

Waterproofing requirements are not the same, seeing as we wish to protect infiltration constructions or protect the environment from contamination (earth and ground waters), or both. On the one hand, we do not want a liquid to penetrate into the construction, and on the other hand, we do not want it to disappear entirely. In terms of phenomenology, the problem is identical, but the liquids involved and the hydro-mechanical aspects are not strictly identical, depending on the context.

In general, the desired level of waterproofing is for a completely watertight construction (Figure 10.2). However, we can also set a level of acceptable leaks with regard to labor and environmental constraints, or regulations.

In light of the functions and the type of waterproofing needed, it is often possible to predict areas where the presence of liquids will be the most abundant and where stagnation is possible.



Figure 10.2. *Cut-and-cover tunnel at Constans, and waterproofing device (cover) on an underground structure (photo taken from SEMALY, [MAH 06])*

This chapter deals with liquid permeability and geotechnical constructions in particular. Waterproofing devices for bridges and buildings are not dealt with here.

10.2. Flow in civil engineering materials

10.2.1. *Equations of porous media mechanics*

Calculating flows in civil engineering materials largely relies on the mechanics of Newtonian fluids, transferred to the context of porous media. Newtonian fluids are defined by the following hypotheses:

- their behavior is isotropic;
- the pressure depends on two state variables (volume mass ρ and temperature T);
- the viscosity tensor is a linear function of the velocity gradient tensor, with coefficients which only depend on ρ and T .

Water and air are Newtonian fluids. The main equations are:

- the continuity equation which expresses the conservation of mass during fluid movements;
- the Navier-Stokes equations which translate the fundamental principle of dynamics ($F = m \gamma$) for viscous fluids with constant viscosity coefficients.
- the heat equation, which expresses heat conservation under the combined effect of its conductive and convective transport by the fluid, and other external exchanges;
- the equation of state for fluid which connects pressure to the two variables ρ and T . This equation can take various forms according to the fluids and the behavior context concerned. For examples, with regard to gasses, we can use the Boyle-Mariotte laws, or the Berthelot law.

Solving these equations provides the 6 unknowns: volume mass of fluid ρ , pressure of fluid p , temperature T and the 3 velocity vector components at any point (x,y,z) of space, and at any time t . Generally, this solution is extremely complex and requires powerful calculators. Additionally, these equations are not applicable as we are referring to porous medias, and because in practice we cannot present real velocity distributions, pressures and temperatures in all the pores located between soil, rock or concrete particles. Fluid mechanics equations are, then, replaced by equations based on the average volume values of the pores, of the quantities of moving fluids, etc. This approach implies that the results must not be analyzed on too small a scale, where physical phenomena are no longer described by their averages.

In geotechnics, for example, a fluid's velocity in a soil is defined in relation to a planar surface S crossed at any given moment by a certain quantity of water. The velocity across surface S is the ratio of flowrate q at surface area S : $v = q / S$. The flowrate is the volume of water which crosses surface S in one time unit. This speed is controlled according to the normal at surface S .

The classic description of saturated soil hydraulics uses concepts of hydraulic head $h(x,y,z,t)$ and hydraulic gradient vector $\vec{i}(x,y,z,t)$. This scalar function h is defined by the equation:

$$h = \frac{u}{\rho g} + z$$

where u is the fluid's pressure, ρ its volume mass, g the weight acceleration and z the altitude above a reference plane.

The hydraulic gradient vector is equal to the opposite of the gradient of hydraulic head h .

Fluid movement inside the pores is described by the experimental Darcy law (1856) which connects the flow velocity vector to the hydraulic gradient vector in a linear relation. Established for a water flow of clean, saturated sand, this law has been generalized for flows in other types of saturated soils, and is also used for flows in other fluids (oil, gas, air, etc.), either alone or mixed. For a 3D medium, the Darcy law is written as:

$$\vec{v} = \vec{k} \vec{i}$$

where k is the permeability tensor. When the orientation of the axes is unspecific, this tensor is symmetrical with 6 independent coefficients. In most natural soils, the main directions are 2 axes of natural stratification planes, and the perpendicular axis. With regard to these axes, the permeability tensor becomes diagonal. Moreover, these axes are often the 2 horizontal axes (where we usually have $k_{xx} = k_{yy}$), and the vertical axis. Lastly, some media are isotropic, in which case the permeability tensor is characterized by one unique scalar. The permeability tensor components are called permeability coefficients and have the same dimensions as the flow velocity.

For high hydraulic gradients, we observe through experiments that there is no longer any proportionality between the hydraulic gradient and the flow velocity. This divergence comes from the path taken by the fluid flow from a laminar system to a turbulent system. The behavior relationship is thus a parabolic function between

gradient $\vec{i}$ and velocity norm $\vec{v}$. In practice, away from highly permeable terrains and closer to water collecting constructions, flows always occur in a laminar system.

10.2.2. Permeability coefficients

Liquid flow, across construction materials and natural soils, is characterized by one or many permeability coefficients. These coefficients, obtained through experiments, are also called “hydraulic conductivities”. In isotropic cases (a hypothesis currently admitted for average values), Table 10.1 provides some permeability values relative to water for different materials found in civil engineering. In spite of low values, no material is truly watertight in the long term and there is no absolute waterproof structure. In geotechnics, the least permeable materials are clays.

Peat	10^{-5}	Gravel	$10^{-2} - 10^{-3}$	Schists	$10^{-10} - 10^{-15}$
Soft clay	10^{-9}	Basalt	10^{-14}	Healthy granite	$10^{-9} - 10^{-13}$
Hard clay	10^{-11}	Chalk	10^{-9}	Concrete	$10^{-13} - 10^{-15}$
Loose sand	10^{-4}	Hard limestone	$10^{-5} - 10^{-15}$	Steel	–
Dense sand	10^{-5}	Sandstone	$10^{-5} - 10^{-10}$	Waste	$10^{-4} - 10^{-7}$

Table 10.1. Water permeability coefficient for natural and artificial materials (m/s) (according to [MAG 04])

The permeability coefficient depends on three main factors:

- the volume and geometry of the area where the fluid circulates. Permeability generally increases with particle size;
- fluid properties (essentially its viscosity, which depends on temperature);
- the conditions of contact between fluid and particles, determined by the nature of the particles and their more or less important interaction with the fluid.

It is not possible to analyze the influence of these three factors separately, because pore geometry depends on the nature of the particles. This is, then, related to the conditions of contact between the fluid and the particles while the fluid’s viscosity influences the interaction conditions between the fluid and the particles. This difficulty has led us to firstly characterize the influence of viscosity, then to link the level of permeability of the particles and material’s pores. The permeability

coefficient k is reversely proportional to the fluid's viscosity η and can be written in the following way:

$$k = \frac{\rho g}{\eta} K$$

where k is a coefficient called “geometric permeability” or “intrinsic permeability”, and has a surface dimension. It is, however, often expressed in Darcy (10^{-12} m^2) or Darcy terms ($0.987 \cdot 10^{-12} \text{ m}^2$). Intrinsic permeability K concentrates all the influences other than fluid viscosity on flow in porous medias.

Much effort has been spent on researching relationships between the permeability coefficient and parameters representing porous environment particles and their spatial arrangement. The obtained formulae generally have a limited application field:

- the formula proposed by Hazen (1911): $k = C d_{10}^2$ where dimension d_{10} (corresponding to the maximum diameter of 10% of the smallest particles in the examined volume of soil) is expressed in millimeters, and k in m/s. This ratio is valid for sands with dimensions of d_{10} between 0.1 and 3 mm. Coefficient C varies between 0.004 and 0.012 with an average near to 0.01;

- a linear ratio between the void ratio e and the permeability coefficient logarithm ratio k : $e = e_0 + C_k \lg \frac{k}{k_0}$. For natural clays, the permeability variation rate C_k is worth approximately half the initial void ratio of soil;

- the Kozeny-Carman formula (1956), which is resultant of a theoretical representation of pores as tortuous conduits with small diameters:

$$k = \frac{\beta \rho g}{\eta} \frac{n^3}{(1+n)^2} \frac{1}{S_s^2}$$

where β is a coefficient without a dimension; ρ is the fluid's volume mass and η is its viscosity; n , the material's porosity and S_s the precise surface of the particles in the porous medium. This formula is indeed interesting, but in practice it is difficult to determine parameter β .

The permeability coefficient may be determined in laboratories or in situ (by using a triaxial apparatus, an oedometer, a permeameter, etc.). Laboratory data sometimes leads to great variations in the same material. The tendency to vary in this way highlights the fact that permeability depends on the nature, shape and connection of the pores. For these pores, the measurements carried out in situ show

generally higher values than those obtained in laboratories, due to discontinuities or heterogeneities which appear on the mass scale. However, in laboratories tests are carried out on a much smaller scale, which may tend to neglect the effect of these discontinuities.

For fine materials, the compaction effect on the permeability coefficient value is very important. Through controlled compaction, we may also obtain a given density and thickness, which give the desired permeability. Compaction is often used for foundations in order to improve mechanical properties of materials on site or those which are brought in.

In some applications, size Θ known as transmissivity is introduced; it is equal to the product of thickness e_c of the permeable layer by its permeability coefficient: $\Theta = k e_c$.

When we have a mixture of many fluids (gas, oil, water, for example) the relative permeability of a fluid is defined as the relationship between the measured permeability for the considered fluid saturation, and the permeability of the medium defined for one fluid only.

Dimensioning waterproofing structures bypasses knowledge of mechanical behavior and hydro-mechanical interaction. Or, more generally, it bypasses the interaction between solid particles and one or many fluids. This interaction greatly depends on the fluid properties. Traditional calculation hypotheses postulate the media saturated by the fluid. In reality, this is more complex and the porous media and geometrics are often unsaturated on a certain thickness. An accurate analysis must take this non-saturation into account.

The effect of water in soils is rather well known and the mechanical equations for unsaturated soils have been established, even if we are still far from carrying out numerical simulations on construction works due to the lack of reliable tests in situ, and the uncertainty on the initial state of a natural, unsaturated soil. For these reasons, dimensioning calculations in geotechnics most often consider the hypothesis of soils saturated with water.

The harmful character of infiltration fluids adds a level of complexity to predictable interactions between the waterproofing structure and, potentially, with the construction which needs to be protected. This harmful effect has been recommended, notably by the French association for tunnels and underground space (AFTES) [MAH 06], [AFT 06]. Section 10.3 is largely inspired by this publication.

10.3. Characteristics of infiltration liquids

Knowing a liquid's physicochemical characteristics, those likely to pass through a material or civil engineering material, is important for the design and dimensioning stage, but also for optimizing its management, estimating its sustainability and dealing with possible repairs.

The liquids involved in construction are very varied:

- ground water, rain, superficial waters;
- the sea;
- clean and dirty waters, from networks and industrial basins;
- aggressive liquids, leachates (waste storage sites, purification plants).

The aggressivity level of infiltration liquids in relation to construction materials or waterproofing devices is the essential physicochemical characteristic. This may result in short or long term harmful effects for the mechanical stability of the construction and for the environment:

- attacks by hydraulic binder-based materials: concrete, masonry joints, etc.;
- corrosion of metal elements;
- grout disturbance.

The aggressive characteristic may be demonstrated by the following tests:

- measuring the pH level (on site, if possible);
- the complete alkalimetric title (CAT);
- calcium level (Ca^{2+});
- dissolved salts;
- aggressivity index calculation;
- dose of suspended matter, chlorides, sulfates, magnesium, ammonium;
- oxydizability by in alkaline medium (present organic matter)
- ionic assessment;
- sulfides;
- bacterial or biological analyses;
- hydrocarbons, etc.

Once again, the context of the construction's environment and its functions condition the scale of physicochemical study. Table 10.2 gives an indicative example of the alert thresholds needed to slow down potential aggressivity problems.

Liquid type	Alert threshold
Aggressive water	
CO ₂ (aggressive)	> 15 mg/l
Langelier index	< 0
Riznar index	> 7
Sulfates (ion)	> 200 mg/l
Magnesium (ion)	> 300 mg/l
Ammonium (ion)	> 15 mg/l
pH	< 6.5
CAT (soft water)	< 1 meq/l
Chlorides	> 250 mg/l
Organic matters	
COD (Chemical oxygen demand)	> 10 mg/l
DBO ₅	> 6 mg/l
permanganate oxidizability (alkaline)	> 4 mg/l

Table 10.2. Alert thresholds for infiltration liquid aggressivity (according to [AFT 06])

Fillers in infiltration liquids may also indicate a certain level of deconstruction in soils and rocks, which may reveal a source of extra damage (settlements, crumbings, etc.).

10.4. Choice of waterproofing device

This choice is conditioned by the type of construction, the intended end use, the sustainability, the materials used, the hydro-geological environment of each work, the level of acceptable leaks, the chemical compatibility of various elements between them (geosynthetic components, stored products, surrounding supports and soils) and *in fine* by economic considerations.

The waterproofing design must take into account hydrostatic pressure, mechanical strains, the intended use and hazard analysis. For more complex constructions or those exposed to particular hazards, ideally the systems should be controllable, so as to ensure high performance throughout the construction's life.

Waterproofing devices vary according to the demands imposed by regulations or the main contractor, by environmental conditions and the type of construction. We may cite the following devices in a non-exhaustive list:

- clay barriers;
- bitumen concrete;
- concrete or metal tanking;
- watertight screens (grout curtains, diaphragm walls, sheet piled walls);
- geosynthetics (geomembranes, geosynthetic clay liners).

Within waterproofing processes, we also classify surface sealing processes.

The devices may be combined so as to ensure a better level of waterproofing. Double or even triple, waterproofing systems have also been designed. For example, we can use watertight geosynthetics systems such as:

- simple waterproofing: structures made from one of the following technical solutions:
 - natural or treated (with bentonite) material,
 - geomembranes,
 - geosynthetic clay liners;
- simple waterproofing composites: structures made from two simple juxtaposed waterproofing devices;
- double waterproofing: structure made from two simple waterproofing devices separated by a draining horizon allowing the collection of leaks;
- triple waterproofing: structure made up of two geomembranes which frame thick protective and waterproofing geosynthetics. Thick geosynthetics protect the second membrane from risks of damage. The risks of leaking then becomes extremely low, thanks to this long lasting protection.

This example already shows an outline of possible techniques offered by geosynthetic materials whose ease of manufacture, flexibility of use, the relative ease of implementation for large surfaces and the low costs all constitute essential positive attributes.

10.5. Advantages of geosynthetics

10.5.1. *Geosynthetic types*

Today, geosynthetics are those which are widely used to build geotechnical constructions. Easy to implement, they enable us to plan new technical and relatively economical solutions. Their characteristics generally involve flexibility, deformability and permeability/impermeability. These are products made as natural or synthetic polymer-based continuous fabric layers, used for the contact between two materials. The CFG (Comité Français de Géosynthétiques/French society for geosynthetics) divides these into six families:

- geomembranes and geofilms, thin structures, flexible, continuous with impermeable properties for liquids and gasses;
- geotextiles, permeable structures, woven, unwoven or knitted;
- geogrids, plane structures made of an open network of elements resistant to tension, connected to each other according to a regular pattern;
- geospacers, 3D polymeric structures, enabling us to maintain space between two materials, in particular for drainage;
- geocontainers, 3D structures for containment, stability and filler reinforcement;
- geocomposites, composite structures linking at least one of the previous geosynthetics materials to other devices or materials (clays, bitumens, etc.).

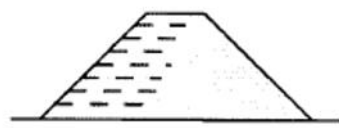
Geosynthetics therefore cover many types of manufactured goods whose specificities and performances widely vary according to their use in civil engineering sites and buildings.

10.5.2. *Geosynthetics and their function in constructions*

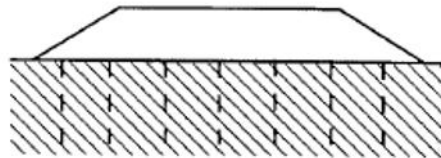
The diversity of geosynthetics enables them to fill many functions in civil engineering sites (Figure 10.3):

- separation: avoiding the mixture of two different materials;
- filtration: maintaining the soil subjected to hydrodynamic forces while ensuring fluid flow;
- drainage: collecting and evacuating fluids in the geosynthetic plane;
- reinforcement: improving the mechanical behavior of a soil mass by the capacity to resist geosynthetic tension;

- anti crack growth: increasing the construction's lifespan by limiting the effects of fatigue due to traffic and thermal and hydraulic shrinkage;
- protection: limiting or preventing disorders located in geotechnical constructions;
- anti-erosion: in fill bodies, dams or earth dams;
- waterproofing: minimizing fluid flow (liquids, gas) and products which are pollutant to the material or the construction which needs to be protected.



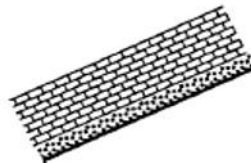
Drainage in embankment



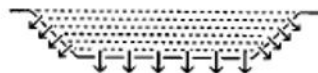
Drainage by vertical drains used to dissipate pore water pressures



Geosynthetic liner used as impermeable barrier to fluid



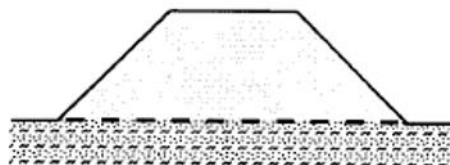
Geosynthetic liner used to guide flow water under drains



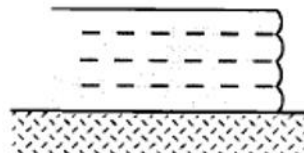
Filter allowing water to move



Geosynthetic used to separate two layers of soil that have different particle size distributions



Reinforcement of embankment on soft soil



Reinforcement of a wall with a vertical face

Figure 10.3. Examples of geosynthetics in soil masses [HAI 92]

These functions are the key elements of the geosynthetic structural design stage and make it possible to specify their characteristics [CFG 95]. This approach consists of indexing the functions provided by each component of a structure. In return, the component occupies the work and links these functions to the minimal characteristics that it must demonstrate. These minimal characteristics include:

- functional requirements to ensure the selected functions;
- requirements related to implementation;
- requirements related to durability.

Products	Characteristics	Ensured functions	Applications
Geotextiles woven non-woven knitted	Permeable materials made from fibers, wire, filaments, strips, woven or unwoven, out of polyester, polypropylene, polyamide, etc.	Separation. Filtration, drainage. Reinforcement. Geomembrane protection. Anti-erosion.	Tracks and roads. Railways. Waste storage. Fillers. Drainage system.
Geogrids	Permeable materials containing polymers or natural fibers presented as a sheet or band.	Reinforcement, mainly. Anti-erosion.	Support. Load distribution.
Geomembranes (thickness > 1 mm)	Materials or impermeable systems assembled by thermal welding.	Liner. Separation.	Hydraulic constructions, dams, undersoil works, waste storage, etc.
Geofilms (thickness < 1 mm)	Materials or impermeable systems containing polymers, assembled by thermal welding.	Liner. Separation.	Hydraulic constructions, dams, undersoil works, waste storage, etc.

Table 10.3. *Geosynthetic characteristics and application types (according to [FAY 96])*

Table 10.3 shows the characteristics of the products, their constitution, their functions and some applications. Generally, the number of functions which can be fulfilled by geosynthetics depends on its geometrical, physical and mechanical properties:

- *general characteristics* are provided by the manufacturer (natural fibers, wire, filaments, strips, polymer type, manufacturing method, weight, thickness, opening diameters, voluminal weight, roll length);

- the *identification parameters* are obtained by standardized laboratory tests. These include mechanical parameters (resistance and traction modulus, creep resistance, seam resistance, tear resistance, perforation resistance), sustainability parameters (abrasion resistant, sensitivity to ultraviolet rays and radiation, chemical and biological resistance, sensitivity to temperature) and hydraulic characteristics (permeability, flowrate). It should be noted however that these parameters should not be used directly in dimensioning because they are not representative of the real behavior in situ, since the majority of these tests are performed away from any soil containment;

- *soil/geosynthetic interaction parameters* are deduced from laboratory tests (traction test in a box under confinement pressure) and from studies on in situ behavior.

Geosynthetics are often used together with other techniques of improving natural materials and/or contributions, and are located, in fact, inside a “composite device” for improving the characteristics of a site, construction or building.

The products available for liner functions may also be classified according to their use and the polymers used to make them:

- membranes intended for waterproofing works of art (bridge decks, cut-and-cover methods) with a steel or concrete support;
- food quality membranes for waterproofing drinking water reservoirs. These are guaranteed not to interact with the liquid;
- bitumen membranes for waterproofing roofs and terraces.

In the rest of this chapter we will therefore define two groups:

- apparent geotextiles and products, characteristically permeable to fluids or where liner is not the main function (geotextiles, geogrids, geospacers, geocontainers, etc.);
- apparent geomembranes and products, whose main function is waterproofing against fluids (geosynthetic clay liners, geocomposites, etc.).

This regrouping is, then, carried out on the basis of liner properties which are covered in this chapter. Nevertheless, to be time efficient, a liner system must be protected at the same time by a reinforcement system and a drainage system. The

“waterproofing” function cannot therefore be presented without having previously demonstrated the “reinforcement and protection” and “drainage” functions.

10.5.3. Reinforcement and protection function of geosynthetics

10.5.3.1. Reinforcing geosynthetic constructions

The mechanical capacities of geosynthetics are primarily used to reinforce the soil masses and can be used to:

- increase the bearing capacity of a foundation. The capacity of reinforced soil depends on the width and the length of the geosynthetics, and on the depth at which it is buried. To be effective, this depth must intercept the fractured surface which would occur if there were no reinforcement. The number of geosynthetic layers considered is also an important factor for the foundation’s stability. This process may also improve the performances of roadways built on soft soil;
- increase the stability of embankments and slopes. Reinforcement is located at the bottom of the embankment or on horizontal beds in the embankment;
- create a work made of earth to bear large strains. Particular construction techniques for building such works have been developed by using geotextiles deposited in horizontal layers and shifted between two embankment layers;
- build supporting walls using soil masses reinforced by geosynthetic horizontal sheets. Several construction techniques have been developed over these last few years; they generally link concrete facings, to which reinforcements can either be attached, or not. Calculating these constructions also involves an additional parameter, the facing/reinforced soil interaction;
- repair or prevent slipping on slopes or natural soil. The link between geotextiles and geogrids may reduce repair costs and often proves to be an interesting solution.

10.5.3.2. Interaction mechanism between soil and a geosynthetic sheet

The fundamental mechanism of the interaction in reinforced soil is controlled by the mobilization of friction between the reinforcement and the soil. This friction depends on the characteristics of the soil’s shear resistance, but also on geosynthetic extensibility, the diameter of the interstices between fibers, the state of its surface, the effective normal stress applied and the unit weight of the earth. The interaction mechanism is thus characterized according to geosynthetic type:

- for *elements of low plate thickness*, the slip surface is easily determined and the friction coefficient is regarded as a constant for a given soil and a material

(containing the geosynthetic material). Bands or plates which are not very thick generate their tear strength entirely by their interfacial friction;

- for *non-woven geotextiles*, deformability and resistance increase with the confinement pressure exerted on the geotextile by the soil. On the one hand, this phenomenon results from the increase in friction pressure between fibers and, on the other hand, from the increasingly narrow overlap of the soil particles in contact, which, then, reject slippage [SCH 85];

- for *woven textiles*, the confinement effect is much less important, and it can be disregarded.

Two types of laboratory tests are used to characterize friction between a soil and a geosynthetic sheet:

- *extraction or anchorage tests*, which consists of placing an geotextile element (or another geosynthetic element) into the soil inside a box (Figure 10.4a);

- *direct shear tests*, in which the soil is put in a bigger half-box and rubs on the geotextile at the surface of the smaller half-box (Figure 10.4b).

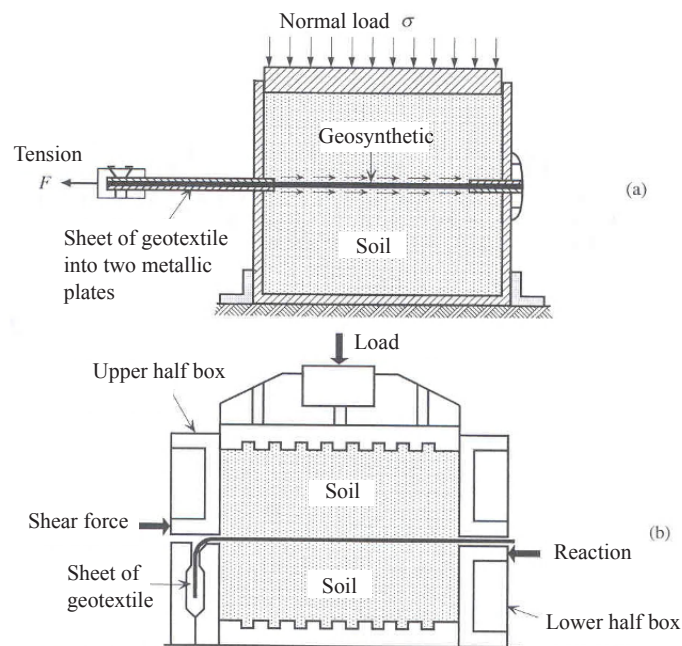


Figure 10.4. Test to characterize the interaction between a soil and a geotextile:
a) extraction test; b) direct shear test

Determining the friction angle at the soil/geotextile interface has been greatly researched, and current conclusions have allowed us to establish the following framework:

- for non-woven geotextiles, it seems that the angle at the interface of a rough surface with loose sand is smaller than the internal friction angle of the soil. For dense sand, it may be somewhat lower [HAL 78], [MYL 82];
- for woven geotextiles, extraction tests have shown that for dense sands, the interface angle is almost equal to the internal friction angle of soil [HOL 77];
- several studies ([COL 80], [GBA 91]) in Gourc, [GOU 93]) have shown that, for granular soils, the interface angle δ and the soil's friction angle φ tend to respect the inequality $\frac{\tan \delta}{\tan \varphi} > \frac{2}{3}$.

10.5.3.3. *Mechanical performances of reinforcement geosynthetics*

As their main function, reinforcing geosynthetics remove strains from traction setting, to generally limit soil extension strains. Geosynthetics used for protection must have good punching resistance. They must also present the following properties (according to [GOU 96]):

- a high enough resistance to traction so as not to break under imposed strains;
- significant interfacial friction with the soil under these imposed strains, so as to obtain rapid stabilization of the reinforced construction;
- a relatively low creep under imposed loads, so as to rapidly stabilize the reinforced construction;
- high punching resistance (as much for statics as for dynamics under shock effects).

Through these properties, geosynthetics are used to reinforce woven textiles, often with open meshes so as to obtain the best overlapping possible between the soil grains and the reinforcement material's texture, or geogrids for plastics.

Additionally, the possibility of controlling the resistance and the deformability of geotextiles (by manufacture) constitutes an important specificity for this mode of reinforcement. Geotextile fracture deformation may also vary from 15 to 80% (able to reach more than 100% for certain types of material). However, for soils, axial deformation by a triaxial apparatus on sheared sample fractures generally varies from between 0.5 and 10%. Generally, most membranes are able to bear strains which are higher than 5%. Table 10.4 presents some different mechanical properties of geotextiles and geogrids.

Geosynthetic type	Secant deformation modulus at $\varepsilon = 10\%$ (kN/m)	Tensile strength (kN/m)
Non-woven geotextiles	2 - 90	4 - 35
Woven geotextiles	50 - 1,000	15 - 350
Geogrids	50-700	9 - 90

Table 10.4. Mechanical properties of different geosynthetics ([CHR 84] and [JEW 84])

10.5.4. Hydraulic performances of geosynthetics

The hydraulic performances of geosynthetics, particularly geomembranes, are greatly reduced when mechanical strains damage their structure. The appearance of tears and holes strongly increases permeability and is the essential part of leak rates.

Constant attention to the dimensioning and implementation stage may decrease damage risks. Plans for quality and regular tests are useful tools to remedy such defects.

Theoretical permeability models have been proposed by Gourc *et al.* [GOU 82], Lombard and Rollin [LOM 86], Giroud *et al.* [GIR 02]. This model, which involves non-woven geotextiles, is based on the Kozeny-Carman formula:

$$k = \frac{1}{16} \frac{\beta \rho g}{\eta} \frac{(n_{gt})^3}{(1 - n_{gt})^2} (d_f)^2$$

where n_{gt} is the porosity of the non-woven geotextile and d_f the diameter of the geotextile's constitutive filament. Giroud *et al.* have advised a value of 0.1 for parameter β .

Permeability therefore depends on the diameter of fibers and the geotextile's porosity. The presence of soil particles in geotextiles reduces permeability, insofar as the size of the particles is sufficiently small.

In the study of geosynthetics and draining devices, the permittivity concept Ψ is often used instead of permeability. It is defined as the permeability coefficient quotient k by thickness e_c of the fabric layer which needs to be crossed: $\Psi = \frac{k}{e_c}$.

The thickness of the geosynthetic therefore plays an important role in its permeability coefficient value. As a consequence, mechanical compression which reduces the size of the pores and the thickness of the geosynthetic reduces permeability. Faure and Fry [FAU 04] have cited work from Palmeira [PAL 02] which shows a reduction in permeability according to the compression of the geotextiles impregnated with soil particles (Figure 10.5). The level of impregnation is characterized by factor λ :

$$\lambda = \frac{\text{particle mass}}{\text{fiber mass}}$$

We notice that permeability is reduced, but in relatively low proportions (by 1 to 5 times) in relation to the powers of 10 which characterize normal values.

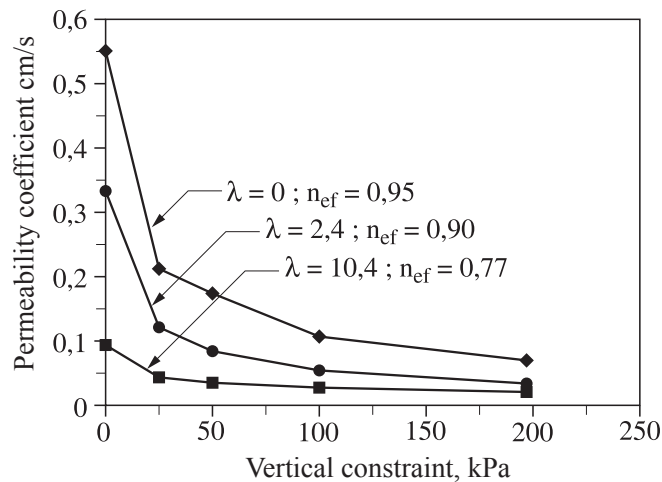


Figure 10.5. Reduction in permeability according to compression on geotextiles impregnated with particles. n_{ef} is the effective initial porosity before compression [PAL 02]

Tests determining the permeability of geotextiles have been standardized: norm NF G 38-016 (1983) and European norm NF EN ISO 11058 (1999).

10.5.5. Geosynthetic drainage functions

Fluids under geosynthetics or confined by a waterproofing system may exert hydraulic and chemical actions onto the geosynthetic material: sub-pressure, condensation, inflation, melting, gelling/ungelling cycles, dessication (drying/humidification cycles), etc. Fluid inflow may have external, natural causes (rain water, rusting, infiltration, sheet increase), accidental causes (outside pollution, leaks) or be the result of fermentation and decomposition of contained materials.

Under a geosynthetic material, fluids generally create sub-pressures which are likely to make the geosynthetic material rise. To avoid deformation, a drainage system must be set up: it may consist of a sand or gravel layer, of geotextiles, geogrids or drains (filter pipes). In particular, flat geotextiles have a substantial level of drainage and are able to convey consequent flowrates in their plane. Their thickness varies from a few millimeters to a few centimeters. If they are subjected to strong normal stresses, their drainage capacity may be notably reduced, due to compression in the geosynthetic material. Their transmissivity varies between 10^{-5} and 10^{-2} m²/s, according to product type. The plugging risk must be taken into account and prevent this phenomenon from decreasing drainage; a filtration device for the soil particles may therefore be put into place.

On a geosynthetic, stored liquids perform actions in terms of hydrostatic pressure and flow velocity, applied to the formation level (hydrostatic punching) or on the edges (viscous flow and friction). If the pressure is high enough, the geosynthetic may break and, consequentially, no longer ensure its waterproofing function. In this particular case, there is a coupling effect between the mechanical and waterproofing performance, which must be taken into account when dimensioning the device.

Functional requirements	Draining capacity Creep under compression
Requirements related to implementation	Tension Damage during construction
Requirements related to sustainability	Long-term drainage (plugging) Resistance to chemical degradation Thermal oxidation

Table 10.5. List of characterization tests for the behavior of geosynthetics drainage functions [CFG 95]

Dimensioning liquid drainage functions takes into the account the flowrate from outside the system (rain water, external leaks, etc.), of acceptable leak rates for acceptable storage and sub-pressures. Generally, geosynthetic characteristics must fulfill the requirements summarized in Table 10.5.

When there is both production and infiltration of a liquid, and biogas production, we must be able to predict a gas drainage system which must never be saturated with water.

10.6. Waterproofing functions of geosynthetics

10.6.1. *Geocomposite and geomembrane clay liners*

The “waterproofing” function is currently guaranteed by the two following families: geomembranes and geosynthetic clay liners. However, waterproofing systems may combine many functions to be truly useful and sustainable. For example, the construction of a waste storage site may connect a passive security barrier made of watertight materials (low permeability), an active security barrier made of high density geomembranes, a protective geotextile layer and a drainage layer made of leachates. Surface drainage reduces the quantity of liquids able to be infiltrated and ensures a waterproofing protection.

In this chapter, we will only be dealing with the case of waterproofing against liquids. Aspects related to gas waterproofing will not be dealt with: this excludes problems of radioactive storage, or storing CO₂ in old oil-bearing caves.

10.6.2. *Geomembranes*

Geomembranes are presented in the form of sheets of at least 1 mm in thickness and of variable width. They are generally conditioned in rolls and laid out on the building site to ensure waterproofing continuity. Products with a thickness lower than one millimeter are called geofilms. Two large families of geomembranes are distinguished, according to their composition:

- synthetic geomembranes, manufactured from synthetic polymers;
- bituminous geomembranes, manufactured from bitumens (without polymers or modified by polymers).

Generally, the characteristics of the geomembranes must fulfill the requirements summarized in Table 10.6. The tests cited are described in French and/or European norms.

Functional requirements	Thickness under specified pressure Permeability to water Eclatometry Tension Tension on assembly Friction Resistance to anchoring Permeability to chemicals Permeability to gases
Requirements related to implementation	Tension Damage to the construction Folding at low temperatures Stability at high temperatures Static and dynamic punching
Requirements related to sustainability	Resistance to chemical degradation Tension Hydraulic punching Static punching Creep under eclatometry Stress induced crack growth Carbon black (resistance, dispersion)

Table 10.6. *List of tests characterizing the behavior of geomembranes for waterproofing [CFG 95]*

10.6.3. Synthetic geomembranes

Polymeric geomembranes are varied because there is a large diversity within polymers which is likely to be used to manufacture them. These are classified into two broad families: plastomers and elastomers (CFG, 1995).

Plastomers (thermoplastic polymers) can be repeatedly softened by heat and hardened by the cold. The main plastomers used in manufacturing geomembranes are:

- plasticized polyvinyl chloride (pPVC);
- high density polyethylene (HDPE);
- chlorinated polyethylene (CPE);
- Ethylene copolymer modified bitumen (ECB).

Elastomers have the remarkable property of being able to quickly take back their original shape after loading/unloading cycles under stress (deformation reversibility). This property is obtained by vulcanization on site. The most widely used elastomers are:

- ethylene propylene diene monomer (EPDM);
- isobutylene isoprene copolymer (BUTYL);
- chlorosulfonated polyethylene (PECS).

The diversity of chemical natures and possible formulations may lead to varied characteristics of mechanical and physic chemical behavior. Table 10.7 generally indicates the properties of synthetic geomembranes.

	Synthetic Geomembranes	
	Elastomer	Plastomer
Behavior	Elastic	Plastic
Behavior under imposed stress	Elastic elongation function of stress The strain disappears with the stress (reversibility)	For a stress, higher than the flow threshold, strain partially irreversible after removing stress
Effect of heat	Low	Average. Possible softening

Table 10.7. *Synthetic geomembrane properties [CFG 95]*

The thickness of synthetic geomembranes varies in general from 1 to 3 mm. When they are composites, the additional materials have a thickness also in the range of a few millimeters.

In addition, geomembranes generally include additives in their composition, such as plasticizers, stabilizers, antioxidants and anti-UV agents in order to delay the material's ageing ([ROL 02] cited by [CAR 04]). In general, the commonly used anti-UV additive is carbon black, which then confers a black color onto the geomembranes. Using this additive means that the material can be subjected to high temperatures up to 60°C when the geomembranes are subjected to insolation. Expansion of the geomembranes may also cause large folds to appear under solar effects. This phenomenon particularly concerns PEHD geomembranes [CAR 04].

Variations in temperature also lead to geomembrane shrinkage and expansion, and therefore to stresses and strains, particularly in the assembly zones. High temperatures accelerate the ageing process and increase the material's creep. All the same, low temperatures (see gelling) may weaken geosynthetic structures. These phenomena must be taken into account and the exposed areas must be protected.

10.6.4. Bituminous geomembranes

Bituminous geomembranes are made by impregnating and/or coating various geotextiles with bituminous materials. The main materials used are:

- “blown” bitumens obtained by oxidization in bitumen refineries for direct distillation;
- bitumens modified by adding polymers. The polymers used are generally elastomers.

Bituminous geomembranes are often protected, meaning reinforced by armor at their core: woven or non-woven geotextiles in organic or mineral matter [CFG 95]. This armor ensures a good level of mechanical resistance. Their thickness is generally between 3 and 6 mm. Table 10.8 shows the properties of these membranes:

	Bituminous geomembranes	
	Blown bitumen	Bitumen modified by polymers
Behavior	Viscoplastic	Viscoelastic
Behavior under imposed stress	Same behavior as plastomers, with a different value for the threshold	Same behavior that elastomers, with elastic limit

Table 10.8. *Properties of bituminous geomembranes [CFG 95]*

10.6.5. Geosynthetic clay liners

A geosynthetic clay liner (GCL) is a product made as a sheet connecting geosynthetic materials to bentonite to guarantee waterproofing qualities. Waterproofing is ensured by saturation under the strains of the bentonite layer inserted between two geosynthetic materials, the pair being solidified by bonding, stitching or needle punching [NOR 06], [CGF 98]. In practice, hydration is carried out in soft water (watering, precipitation) before the construction is set to work or by transferring humidity through contact with the support structure or the protective structure.

GCL are used either can be used as a hydraulic barrier, or combined with a geomembrane to form a waterproofing system (at the foundation level load, for example). Inflation properties of bentonite are also the base properties of the waterproofing function.

Bentonite is a clay made of at least 60% montmorillonite (aluminum silicate, or hydrated magnesium), other minerals (quartz, mica, feldspath, pyrite) or other clay material fractions (illites, kaolinites). On a physicochemical level, the presence of certain cations Fe^{2+} or Mg^{2+} creates a load unbalance at the surface layers and cations such as Na^+ and Ca^{2+} may also be fixed on this surface [CFG 98]. The cation's characteristics greatly influence bentonitic properties and its inflation power. Some natural bentonites may swell up to 18 times their original volume in water. Chemical treatments such as polymer adjunction may also improve bentonite properties.

When bentonite is hydrated, it inflates and therefore the path travelled by the fluid particles becomes very complex, and very long. The “waterproofing” function is fully ensured when the bentonite is hydrated and contained (by a normal stress). The containment allows us to control the inflation; this decreases in a quasi-linear way with the logarithm of the normal applied stress. The water permeability values stated by the manufacturers are very low, between 10^{-10} and 10^{-12} m/s [SIL 04].

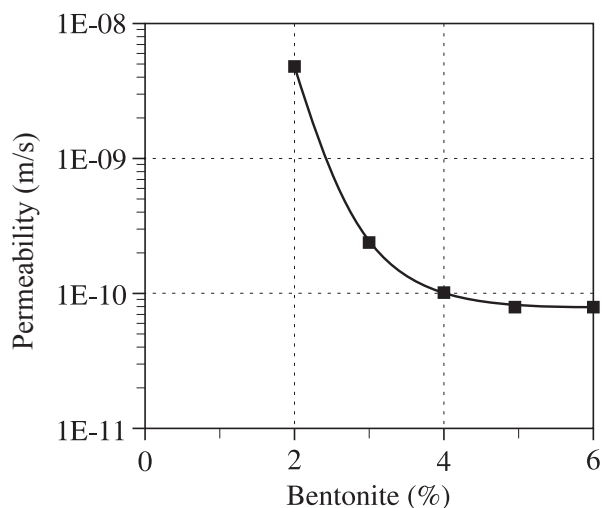


Figure 10.6. Influence of bentonite percentage on the permeability coefficient value ([DID 96], cited by [AIT 03])

Figure 10.6 shows the effect of the bentonite percentage on the permeability coefficient for a clay material. The hydraulic performance of geosynthetic clay liners is related to preserving bentonitic properties. Indeed, under mechanical or hydraulic effects, some of the bentonite may be swept away or deteriorated. There are generally three reasons for extruding bentonite:

- the inflation pressure of bentonite drives out some of its particles through the geotextile, especially if it has a low thickness. This phenomenon, however, remains limited;
- important hydraulic gradients may lead to bentonite erosion, particularly when there is a drainage mechanism established under the geosynthetic clay liner;
- folds in the geomembrane may favor bentonite migration, by no longer allowing for a good level of contact between the clay liner's components.

Thicker or reinforced geosynthetic materials are sufficient to minimize bentonite extrusion.

Additionally, a reduction in the water quantity, following bentonite dessication, greatly influences the permeability of liquids and gasses. This reduction may be irreversible if the fluid is chemically aggressive.

With regard to mechanical properties, once the bentonite is hydrated, it shows low resistance to punching. Stiffness J generally fluctuates between 50 and 200 kN/m for a maximum strain varying between 8 to 12 kN/m [OLI 06]. Table 10.9 summarizes the general properties of GCL and Table 10.10 displays the additional tests to be carried out alongside those shown in Table 10.6. The CFG specifies that the geosynthetic clay liner must not constitute a reinforcement element of the constructions; the design must not allow traction strains and important shear strains.

Behavior under imposed stress	Great flexibility and adaptation to the current soil strains. Low resistance to punching.
Hydrous behavior	Swelling under imbibition. Cracking under desiccation.

Table 10.9. *Geosynthetic clay liner (GCL) [CFG 98]*

Functional requirements	Swelling-shrinkage Auto-cicatrizization capacity
Requirements related to sustainability	Shear strength Sensitivity to gelling/ungelling cycles

Table 10.10. *Additional tests to characterize the behavior of geosynthetic clay liner [CFG 98]*

There are three types of geosynthetic clay liners which are distinguished by the treatment of the interface between geosynthetic and the bentonite [CFG 98]:

- structures made up of two geotextiles with a bentonite layer in between. The pair is maintained by water-soluble glue (Figure 10.7a);
- structures made of a geotextile carrier and cover, where the bentonite is kept in place by needle punching;
- sewn structures where the geotextile carrier and cover are connected by a stitching system or links through the bentonite (Figure 10.7c).

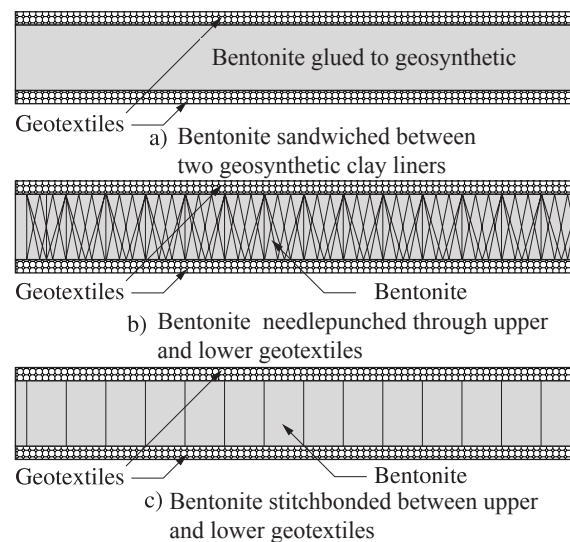


Figure 10.7. *Different types of geosynthetic clay liners [CFG 98]*

Geosynthetic clay liners also possess remarkable autosealing. By inflating, the bentonite may create a plug and limit localized leaks from accidental perforations or a defect with weak dimensions (a few millimeters) in the waterproofing structure [CFG 98].

10.7. Geosynthetics layering in construction

10.7.1. Assembling geosynthetic layers

Geosynthetic materials are delivered in rolls and form layers when they are laid out; their length is then limited and they must be welded to each other so as to cover

larger surfaces, particularly in waste storage sites. It is important to achieve good continuity between these layers to ensure uniform waterproofing on large surfaces.

The assembly process is delicate and requires care. Covering between strips must be wide enough to guarantee that it stays in place and is sustainable. This cover will vary according to the nature of the geosynthetic fabric: at least 5 cm for synthetic geomembranes, and from 125 to 40 cm for bituminous geomembranes [CFG 91].

For synthetic geomembranes, assembly is achieved by chemical welding (PVC, CPE), thermal welding (PVC, PEHD), solvent welding (PEC, pPVC), cold bonding (CPE). For bituminous geomembranes, assembly is carried out by thermal welding (Figure 10.8), hot bitumen bonding or bituminous bonding.



Figure 10.8. *Example of assembly by hot air welding [FOU 06]*

In these assembly zones, mechanical performances must be sufficient for the waterproofing property to last. Special care must be taken on site and checks must be effective. Tests consist of checking the waterproofing continuity and the mechanical resistance of the assembly zone. Tests can be either non-destructive (waterproofing continuity assessment) or destructive (mechanical resistance test).

The most frequently used non-destructive testing methods are [CFG 91], [GER 04]:

- visual inspection, which may detect folds, bubbles, blisters, partial welds, etc.;
- tests which involve passing a pointed instrument or a compressed air lance along the welded edge, which is sufficient to highlight the areas which have not been sufficiently welded;

- ultrasound method which provides an estimation of the geomembrane and weld thickness, and localizes areas of lower thicknesses which could create potential defects;
- vacuum bell jar method. The principle method entails wetting the weld surface with soapy water, applying the bell jar on top, and making a vacuum in the jar of 30 to 50 kPa. Immediately after, bubbles will appear under the bell-jar;
- adding hydraulic or pneumatic pressure from the central canal of a double weld. If there is low pressure, this denotes that there is a leak;
- electrical methods.

Destructive testing is carried out in situ or in a laboratory on samples taken from the assembly zone. Two types of laboratory tests are practiced [CFG 91]:

- a tension/shearing test is applied to a sample which is cut perpendicularly to the assembly zone and is subjected to simple traction (Figure 10.9a). The performance is understood when a break occurs in a part of the fabric at the assembly join level;
- a T-peel test consists of imposing a level of one-directional traction onto a rectangular geosynthetic sample, which is cut perpendicularly to the assembly zone. The strain is applied on a strip's free edge, on the surplus edge, or the welded side of the other strip (Figure 10.9b). The aim is to assess the weld resistance which is perpendicular to the assembly. A geomembrane's usual resistance to welding is in the order of 8 to 10 N/mm (per unit length of the assembly join), which acts as a very good resistant.

Building site tensiometers also allow us to measure tension/shearing resistance or T-peeling of welds [GER 04]. However, the results are not reliable yet and still do not allow us to make a conclusion on good quality welds.

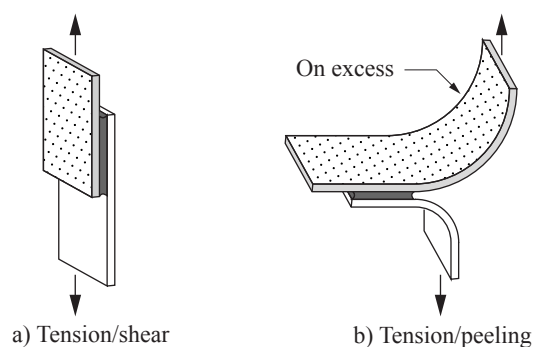


Figure 10.9. *Tension/shearing test and T-peel test [CFG 91]*

10.7.2. Connecting geosynthetic layers to constructions

Connecting a geosynthetic to part of a construction also creates sensitive areas which must be implemented with great care to ensure long lasting waterproofing. These areas are often subject to differential compression that the geosynthetic material must be able to bear without tearing. Constructions or parts of constructions concerned here are areas where liquids enter/exit, tunnels, slopes, embankments. Materials and connection supports are generally made out of concrete, masonry, metals, wood or plastics.

Waterproofing along the connection of a concrete construction is generally guaranteed by mechanical fixing (tightening by a stainless steel reglet) which includes two watertight bands located on both sides of the geosynthetic. For bituminous geomembranes, welding onto the support is also carried out. For geosynthetic clay liners, the fixing area is eventually covered by a material with watertight qualities (either as a paste or a powder).

In geotechnics, for basins, waste storage sites, natural slopes or excavations, the connection may also be achieved by simple techniques, such as ballasting (by gravity) or anchorage at the top and bottom of the slope (Figure 10.10). The importance here is to ensure a good level of contact between the geosynthetic fabric and the ground in situ.



Figure 10.10. Example showing geosynthetic fabric anchoring at a slope peak [MIL 06]

10.7.3. *Stability of geosynthetic fabrics on slopes*

The level of stability of a waterproofing system is largely influenced by the slope of the soil support, the normal strain which may be applied to it and the friction between subjacent/and or adjacent layers. For natural slopes or excavations, positioning the geosynthetic must be achieved with great care, so as not to produce serious problems. Effectively, according to the geometrical implantation and the interaction with supporting soil, geosynthetic materials may be put under tension by their own weight. If they are extended too much, their characteristics risk being degraded (tearing). Some non-woven geosynthetic materials may resist an extension of 30% and still manage to maintain their correct waterproofing qualities [HEN 06]. On the other hand, it is not recommended to use bentonitic geomembranes on slopes due to the bentonite's weak friction angle (in the order of 9 degrees, with a residual friction angle of around 5 degrees). Minimum reinforcement is necessary to ensure a sufficiently long term shear strength and to avoid breaking the waterproofing system. We should also study the possibility of a hydraulic gradient sweeping the bentonite across the slope or the occurrence of internal erosion.

Product performance and current installation techniques have allowed the realization of quasi-vertical waterproofing systems with geomembranes. Figure 10.11 shows an example of this kind of waterproofing [MIL 06].



Figure 10.11. *Using a geomembrane as a waterproofing system on a vertical wall [MIL 06]*

10.8. Product specificity and waterproofing systems

The main systems considered are the following:

- waterproofing device by geosynthetics (DEG);
- draining device by geosynthetics (DDG);
- waterproofing and draining device by geosynthetics (DEDG);
- waterproofing device by geosynthetic clay liners (DEGB).

Each system is made of one of many structures comprised of a mixture of natural material layers and geosynthetics. The function is to minimize the exchange of fluids (liquids and gasses) between the material or the protected construction, and the outside. The systems may be placed directly on the material which is to be protected (covering), enveloped (interior reservoir) or protected by other structures.

These devices are widely implemented in waste storage sites. The choice criteria between the devices make the following aspects intervene [CFG 91]:

- the level of acceptable leaks with regard to function demands and the environment;
- the site's geometry and geological, mechanical and hydraulic conditions;
- chemical compatibility between the device's elements and the infiltration fluids which need to be kept, stored products, surrounding land;
- cost.

10.8.1. Composition of geosynthetic waterproofing devices (DEG)

The possible methods of building these systems are described in Figures 10.12 and 10.13. The composite device may or not be protected on both sides: this protection is regulated for waterproofing waste storage sites. The protective structure (geotextiles) essentially needs to guarantee the original state of the waterproofing structure, notably when faced with mechanical strain (traction, compression, shear, punching). It must adapt and follow the support compression or the contained materials without being damaged.

Dimensioning methods of currently available DEG rely on:

- empirical formulae from experiment back analysis;
- laboratory tests (mechanical, hydraulic, chemical);
- respecting recommendations and existing regulation;
- the art of the engineer.

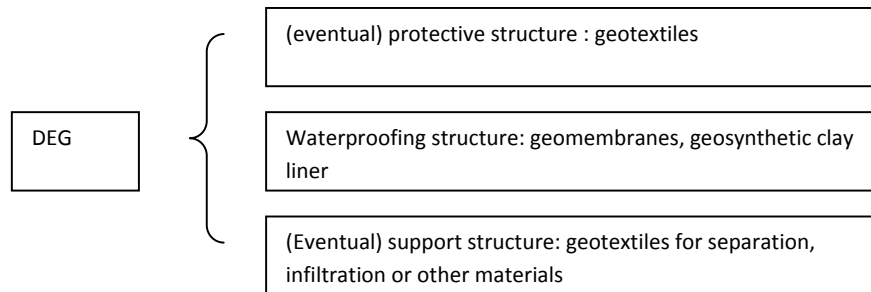


Figure 10.12. Principle of a geosynthetic waterproofing device (DEG)

The [CFG 91] recommend that: “the designer is led to choose strains which must be kept for dimensioning a DEG, according the site’s characteristics, the construction’s use, the chemical nature of the stored product and the creation, exploitation and maintenance conditions, all by taking into account locally available materials in economically acceptable conditions. There is, then, no unique solution for the structure of a DEG”.

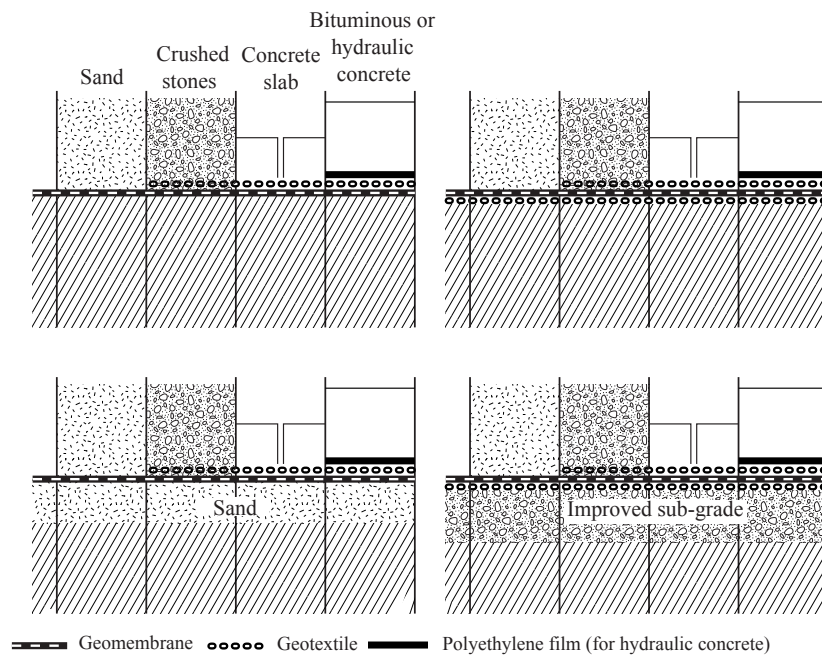


Figure 10.13. Possible configuration for a DEG [CFG 91]

Strains which may occur depend on applied stresses (resultant of the storage weight, of working loads), on irregularities in the support's structure (which is never perfectly planar), and on potential folds after implementation.

10.8.2. Composition of a draining system with geosynthetics (DDG)

A draining system with geosynthetics (DDG) ensures the collection and evacuation of liquids and gasses to the outside, which come naturally or which are the products of stored waste in a confined environment. DDG is also made up of three layered structures (Figure 10.14). Dimensioning this kind of structure takes into account the fluid flow which must be evacuated and the mechanical strains that the device must bear. We must also be vigilant with regard to the chemical compatibility of solid products with the fluids.

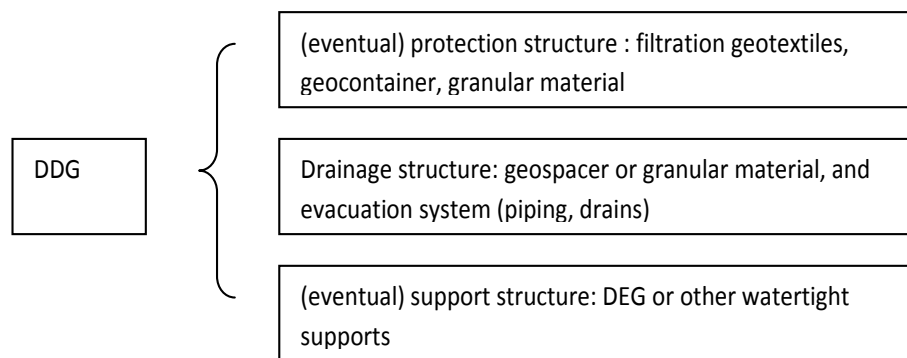


Figure 10.14. Principle of drainage structure by geosynthetics (DDG)

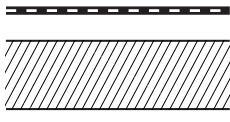
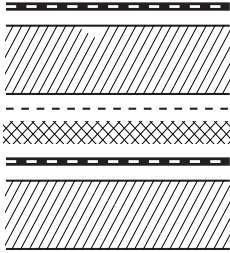
10.8.3. Composition of a waterproofing and drainage system with geosynthetics (DEDG)

Waterproofing and drainage devices by geosynthetics (DEDG) are generally made up of three elements:

- an eventual protection structure. This may be a protective geotextile, eventually connected with a layer of granular material;
- a waterproofing structure (geomembrane, geosynthetic clay liner, geomembrane and clay material);
- double waterproofing with a draining system in the environment);

– a possible support structure which gathers the elements located between the waterproofing structure and the surface which needs to be protected (ground, structure, building).

The drainage structure allows a reduction in the hydraulic load which could act on the geomembrane. The flow to be drained depends on pluviometry, infiltration capacity, and on the nature of materials located on or under the DEDG: in the first case, it is a question of storage, in the second case, it is a matter involving the supporting soil (either natural or artificial).

Combined waterproofing: Geomembrane and clays	Protective structure  Structure support
Double waterproofing with geomembranes	Protective structure  Structure support
Combined waterproofing with two geomembranes and clays	Protective structure  Structure support

Geomembrane  Geotextile  Geospacer  Related clay materials 

Table 10.11. *Examples of waterproofing structures [CFG 95]*

Table 10.11 gives some examples of geosynthetic based waterproofing structures.

10.8.4. Composition of a waterproofing device by geosynthetic clay liners (DEGB)

As for the previous devices, waterproofing devices by bentonitic geosynthetics (DEGB) is made up of three structures [CFG 98], (Figure 10.15):

- the support structure, a set of elements located between the formation level and the waterproofing structure;
- the waterproofing structure is made up of a geosynthetic fabric impregnated with bentonite;
- the containment/protection structure which must especially prevent damage to the GCL by mechanical strain or chemical aggression.

A waterproofing device by geosynthetic clay liners (DEGB) only works if the bentonite is hydrated with water and if a minimum overload is applied before hydration in order to control the bentonite's inflation. This containment is transmitted by the protection structure's intermediate and unavailable containment. The minimum stress is 5 kPa according to the CFG's recommendations in 1998.

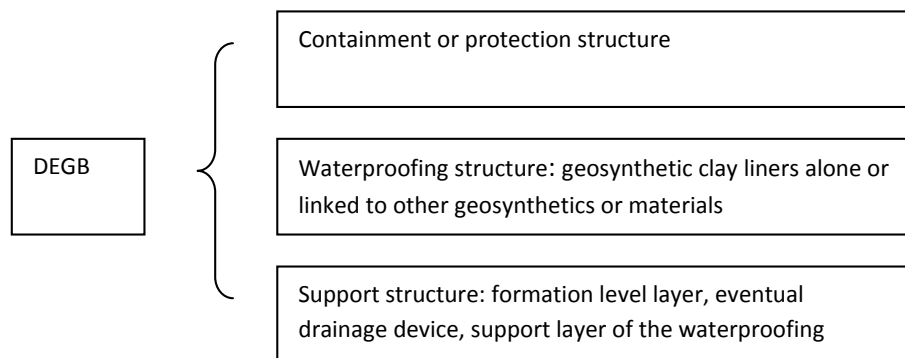


Figure 10.15. Principle of a waterproofing structure by geosynthetic clay liners (DEGB)

The level of chemical and mechanical protection of the DEGB is also a sustainability condition of the bentonite's properties, and therefore, the waterproofing structure. As an example, the permeability of a DEGB may evolve negatively for contact in a limescale environment (example cited by [CFG 98] recommendations).

10.8.5. Analysis and dimensioning of geosynthetic based structures

Currently, the analysis and dimensioning of waterproofing structures may be simulated by total and local approaches following roles played out by geosynthetic materials:

- for reinforcement, total approaches are based on limit equilibrium methods [DEL 86]. These methods calculate a safety coefficient and do not allow us to study the interaction between strains and nonlinear behavior of materials;
- for the reinforcement function, local approaches are based on numerical modeling by finite elements [VIL 02], discrete elements [CHA 03] or finite difference elements [LAL 98]. The advantage of such methods is to be able to take into account nonlinear behavior and soil structure interaction.
- for the waterproofing function, total approaches are based on liquid flow in an indeformable porous environment. The important aspect is essentially estimating flowrates or obtaining the interstitial pore pressure which is then inserted into a mechanical calculation for stability.

Although we can write equations on a local level, hydromechanical modeling, which involves coupling between fluid and solid behavior, still remains as a matter of research. The main limitation of accurately modeling these phenomena is describing, with a sufficient amount of realism, the paths travelled by fluid particles in the pores. Today, research is directed towards models inspired by those which exist for fractures in porous media which may be used to simulate flow in a waterproofing composite system [CAR 04]. The following paragraph describes the types of calculations which can be carried out to make a local approach for nonlinear behavior laws.

10.9. Numerical modeling

10.9.1. Mechanical behavior

Due to their manufacturing and fibrous nature, geosynthetic fabrics display a significant traction resistance, but only little resistance to bending. Under normal stresses, a geosynthetic fabric layer manifests a membrane effect and large strains may appear if the supporting material is degraded or has disappeared (karst, caving in). Finally, a geosynthetic fabric layer may be exceptionally subjected to compression, where the layer deforms into folds, which is very difficult to model. This aspect is disregarded in models which are used at the moment.

10.9.1.1. Geosynthetic material behavior

Three families of behavior laws are generally used to describe the mechanical behavior of geosynthetic materials [HAI 92], [HE 06], [VIL 02]:

- linear elasticity. Tension in the fabric layer is proportional to stress:

$$T = J \varepsilon$$

with T as the tension in the material; J the extension modulus and ε the geosynthetic strain. Modulus K is obtained by traction testing (Figure 10.16a);

- nonlinear elasticity (Figure 10.16b). Tension is connected to stress by a limited polynomial or hyperbolic relationship. Tension tends towards a fracture limit value;
- elasticity with hardening which describes irreversible behavior under stress from a certain strain threshold.

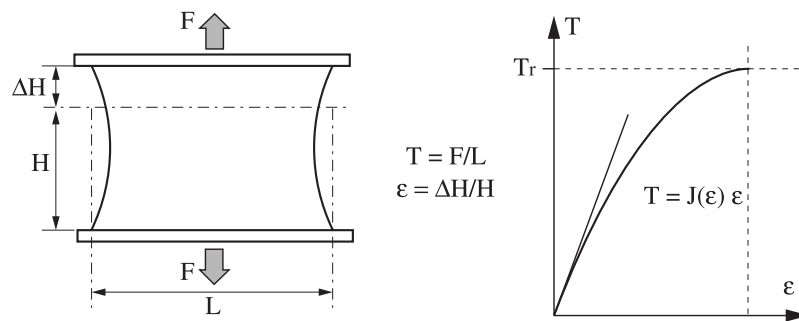


Figure 10.16. Traction test (EN ISO 10319) determination of extension modulus J [VIL 02]

10.9.1.2. Behavior of materials in contact with geosynthetics

Civil engineering and waste materials which may be in contact with geosynthetic materials are generally represented as deformable porous media. The behavior laws currently used are perfectly elastoplastic (Mohr-Coulomb criterion, Drucker-Prager criterion), elastoplastic with hardening or still elastoviscoplastic [VIL 02], [MES 99].

10.9.1.3. Interfaces between materials and geosynthetics

For 2D approaches, interfacial behavior is described in the normal and tangential direction. The contact law which is generally used is the Coulomb friction law which allows for a representation of slippage at the interfaces either with or without friction:

$$\tau = c + \sigma_n \tan \delta$$

where σ_n and τ are the normal and tangential stresses; c is interfacial cohesion and δ the interface friction angle (Figure 10.17). These mechanical characteristics are determined from adhesion tests or shear tests.

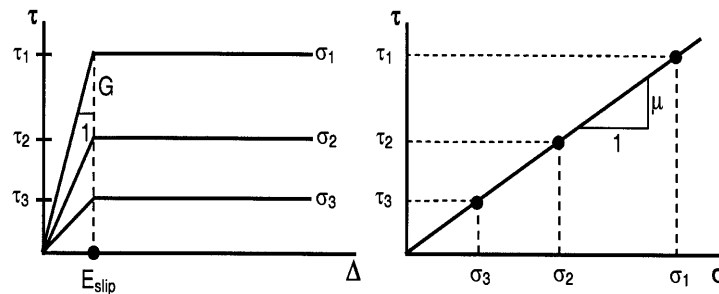


Figure 10.17. Mohr-Coulomb model for a soil/geosynthetic interface (according to [PER 05] quoted by [HE 06]). σ and τ are the normal and tangential stresses, Δ is the tangential displacement and μ the friction coefficient ($\mu = \tan \delta$)

Friction angles between the support and protection structures, and the geosynthetic materials are generally quite small. Where there is an interface between a geomembrane and waste, we must not forget that this interface is created away from a protection system, which prevents the geomembrane from degrading. Protective geotextiles avoid direct contact between the waste and geomembranes; modeling must therefore be more accurate in order to represent this reality.

10.9.2. Mechanical behavior modeling by finite elements

Finite element models may take into account the following aspects: construction phasage (position of the geosynthetic material or geocomposite structures, filling, position of the facing if it is for supporting), deformations of different materials, possible slippage at the interfaces, progressive friction movement, and consolidation development over time. Taking into account hydromechanical coupling (including the phenomenon of soil consolidation) is, however, a delicate matter, mainly due to the lack of accurate data and the considerable calculation time needed for coupling.

A rigorous analysis must also consider nonlinear behavior laws, related to large deformations and rotations but without large amounts of slippage, in order to correctly represent what happens in reality ([BUR 95], for example). Theoretical

models, then, turn out to be very complex, with multiple interactions, and are still too inaccurate to be used in current studies.

Nonetheless, it is indeed possible to carry out finite element models in plane stress for constructions comprised of geosynthetic materials by means of a few reasonable hypotheses on the reinforcement function. In 2D functions, geosynthetic materials may be simulated by bar, cable or beam finite elements and connected to interfacial elements (contact elements or a fine band of 2D surface elements). Civil engineering materials which are in contact with geosynthetic materials are described by 2D surface elements.

If the geosynthetic material is only supposed to take traction strains into its plane, it is often represented by 1D bar elements with two nodes, characterized by a rigidity level with insignificant flexure, and only working when extended. Bar element behavior is linear elastic, nonlinear elastic, elastoplastic or even still viscoplastic. For example, for a solid mass reinforced by geotextiles, each sheet has a corresponding bar element layer (Figure 10.18a).

If the geosynthetic material envelopes a part of the soil layer, the fabric layer may be represented by two of three bar interface elements (Figure 10.18b). The thickness of the soil layer depends on construction techniques and geotextile properties.

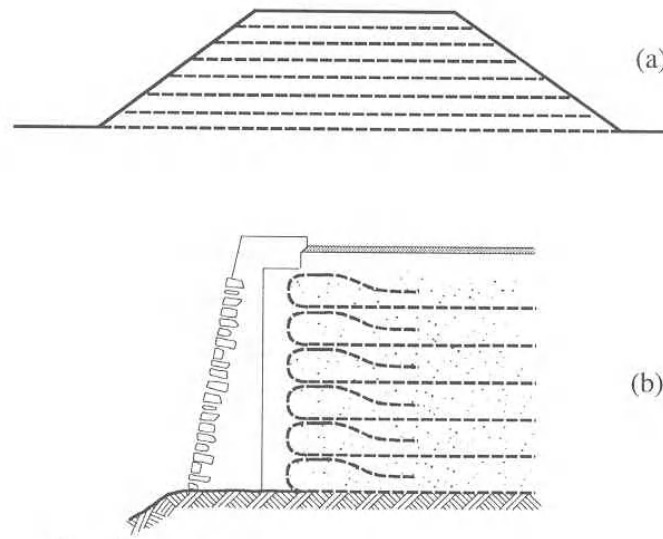


Figure 10.18. Geotextile fabric layer modeling: a) in a fill; b) in a supporting construction

Bar elements are very simple elements, but they do not allow for a complete description of the mechanical properties of geosynthetic materials; in particular, bar elements are unable to simulate membrane effects. For this reason, cable and beam elements, and thin layers of surface elements are often preferable.

If, in the calculation code used, bar, cable or beam elements are incompatible with numerical treatment of hydromechanical coupling, the geotextile can be assimilated to a layer of elements with a very slight solid mass (in the order of 20 times the real thickness of the geotextile, or around 10 cm). The geotextile's characteristics are then adjusted according to the retained thickness t_{eq} . Thus, on the basis of an equivalence between deformation constructions under traction, the strain modulus of the fictive material E_{eq} is obtained by the relation:

$$E_{eq} = \frac{t}{t_{eq}} E$$

where t is the geotextile's real thickness and E its real Young's modulus. This approach gives a reasonable number of nodes and elements, and regularizes numerical calculation by reducing the interval between soil rigidities and the geotextile [JOM 95].

The (soil/geosynthetic) interfaces are represented by contact elements or by compatibility conditions in the case of under-structuring. Modeling an interface includes three mixed nodes: two nodes belonging to materials located above and below (respectively) the geosynthetic material, and one node which is linked to the geosynthetic material. Friction is described by Coulomb's law.

If a concrete facing must also be taken into account (Figure 10.18b), this will be simulated by beam or solid mass elements.

In 3D analyses, the geotextile or geosynthetic fabric layers are represented by plate elements or fine layers of 3D mass elements.

In addition, with the aim of more accurately describing interfacial mechanical behavior, some authors have proposed to distinguish, in a plane model, two possible modes of interaction between the soil and a reinforcement:

- shearing mode (Figure 10.19a), whose parameters are determined in direct shearing tests;
- adhesion mode (Figure 10.19b) whose parameters are obtained by extraction or adhesion tests.

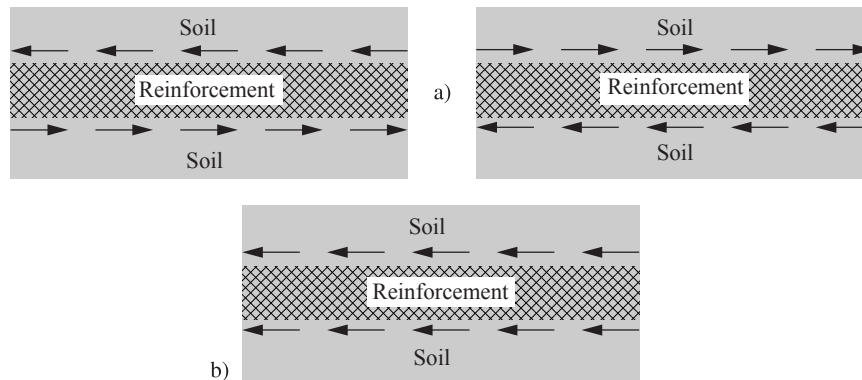


Figure 10.19. Interaction modes between the soil and a reinforcing geosynthetic material:
a) shearing; b) adhesion

Resistance and deformability parameters deduced from these two tests are different. For this reason, a relatively simple numerical solution may be implemented to detect the type of interaction (shearing or adhesion) from the sign of the shearing strains in each pair of nodes at both interfaces. Different friction laws are then activated in the finite element model. Outside of these laws, the Coulomb criterion and hyperbolic laws have also been used as a slippage threshold [CHA 93], [MES 99].

10.9.3. Numerical modeling of hydraulic behavior

An accurate approach of modeling the waterproofing function and estimating a leak rate would involve describing fluid flows (liquids and gasses), non-saturation phenomena, diffusion and transfer, and to consider defects or damage in the geosynthetic materials, and to take into account the interfaces between the geosynthetic materials and the surrounding soils, because flows may also occur on the level of the interfaces, etc. Of course, we are still far from being able to carry out these rather complex calculations and solving (under acceptable time conditions) nonlinear system equations which run from mathematical theory.

Nonetheless, numerical models which can be carried out with current information technology methods are divided into two approaches:

- The hydraulic approach of deformable, saturated porous media. This approach is more restricted but it only takes into account, in the current state of available knowledge, hydromechanical coupling in the sense of a Darcy flow, by disregarding aspects of diffusion. However, its advantage is simulating coupling and the

interaction between the solid's deformation and the fluid(s) flow(s) according to time.

– Hydraulic approach of saturated, indeformable porous media, which takes into account Darcy type flow, transfer phenomena and diffusion across a porous medium at the same time. However, there is no mechanical coupling. Interstitial pore pressure obtained in this way may then be introduced into mechanical calculations, to study stability under the effect of hydraulic forces, for example.

10.9.3.1. *Hydraulics of indeformable, unsaturated porous media*

Studying flow in unsaturated porous media induces the intervention of complex physical phenomena related to the polyphasic nature of these interactions. A fluid contained in porous media is characterized by the volume (water content, for example) that it holds in vacuums (porosity) and by its energetic state. The equilibrium of a liquid depends, then, on porosity, weight, dissolved salts and pressure in the gassy phase [MES 99], [COU 02].

In geotechnics, the most widely spread theoretical approach is based on relative suction and permeability curves according to water content (if the liquid is water). Suction is the difference between air and water pressures. The soil is considered to be a porous medium which is partially filled with water. The vacuums are occupied by water and air. The Darcy law is generalized for the case of unsaturated isotropic soil by the following relationship:

$$\vec{v} = k \vec{i} = k_r(\theta) k_{sat} \vec{i}$$

where k_r is the relative permeability coefficient and k_{sat} the saturation coefficient; θ is the water content.

Writing the preservation of interstitial fluid mass and the Darcy law leads to a differential equation, known as the Richards equation where the solution is achieved by using numerical methods. The finite element method is well adapted to solve this equation, but the solution requires iterative calculations which are time consuming. A lot of software is available for this solution and are used relatively often in engineering and in the field of environment. Calculations are carried out in either permanent or transitory regimes. Recent developments has been made with fractured porous media [CAR 04].

10.9.3.2. *Hydraulics of deformable, saturated porous media*

This approach presumes that the considered porous media are saturated and that the interaction in time is concentrated between the solid and liquid parts. Applying a

strain creates interstitial surpression which will dissipate in time while modifying the equilibriums in the solid and liquid parts. This phenomenon is called “soil consolidation”. In this approach, taking geosynthetics into account is both a matter of mechanics and hydraulics (permeability).

When in contact with a geosynthetic material, a fluid may pass through it or flow in its plane. We are therefore led to distinguish a normal and tangential permeability [HAI 92]:

- The normal permeability coefficient k_n (Figure 10.20). The fluid passes through the geosynthetic material in a normal direction to its plane. This property exists whatever the type of geosynthetic material. Generally, experts in the field prefer to characterize this property by permittivity Ψ , defined as the ratio between the normal permeability coefficient and the thickness of the fabric layer. The geosynthetic materials acts as a filter.

- The tangential or longitudinal permeability coefficient (Figure 10.21). The fluid runs in the geosynthetic material’s plane which acts as a drain. This property only exists with certain geosynthetic materials (non-woven), which must then be more permeable than the soil where the fluid comes from. For experts in this field, this property is expressed by transmissivity, defined as the product of the longitudinal permeability coefficient by the fabric layer’s thickness.

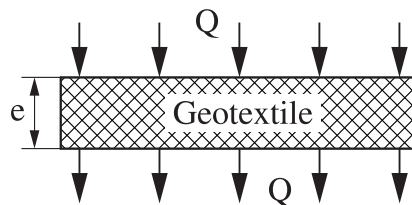


Figure 10.20. Model of the filtration function of a geosynthetic fabric (e is the thickness, Q the flowrate of the water through the fabric)



Figure 10.21. Model of the drainage function of a geosynthetic material (Q is the flow rate of the water across the material)

These properties allow us to describe the “filtration”, “waterproofing” and “drainage” properties in numerical modeling.

A hydromechanical coupling between the geosynthetic material’s permeability and the state of mechanical stresses is obvious because this interaction:

- prevents the filter in the material from being swept away by fluid flow across the particles in the drain that it protects (for example);
- allows the drain in the material to continue to work where the sand drain would have been sheared as a result of soil deformation;
- ensures that there will be no tearing in the material’s structure and that authorized permeability levels remain unchanged.

Another aspect of coupling is the effect of the normal stress on the permeability coefficient and the material’s thickness. This effect may lead to a drop in the draining capacity. A simple model consists of putting a hyperbolic relationship between the permeability coefficient and the normal stress. We can do the same between the material’s thickness and the normal stress [HAI 92].

Other hydromechanical effects are more delicate to take into account in numerical modeling according to the “drainage” function. It is a notable question of the filling phenomenon, which results in a decrease in permeability due to an increase in the number of soil particles in the geosynthetic’s pores.

10.10. Sustainability

According to civil engineering applications, the specified lifespans are highly varied. In buildings and civil engineering, current lifespans last for a few decades. This is no longer the same for constructions with a large influence on the environment. The most severe demands are related to waste storage site exploitations, for which a break in the waterproofing system could lead to catastrophic consequences. The demand for sustainability of geosynthetic materials may sometimes exceed a decade, with the exception of radioactive waste storage.

Knowledge of degradation phenomena in geosynthetic materials is therefore essential to ensure mechanical, hydraulic, thermal, and chemical sustainability. It is also equally as important to conclude by knowing the context of the civil engineering project and the working conditions of the construction. The device’s lifespan depends on its, more or less, large exposure to aggressive strains and possibly deployable protection devices.

When the use context is known, sustainability requirements are managed, on the one hand, during the selection of chemical based products, and on the other hand, in the detailed formulation of the product's components. Chemical additives are added to base resins so as to obtain the required qualities: the additive proportion represents 2 to 5% [BLO 06].

Among geosynthetic materials, polyethylene (PE) geomembranes are used widely today, and give excellent performances. The chemical compatibility and mechanical performances of these polymers are two key elements for a good level of sustainability under working conditions, working life and subjected loads. A lot of research has been, and continues, to be carried out. The main results obtained on polyethylenes are the following [BLO 06]:

- very high resistance to chemical aggression;
- low water and permeability;
- quasi-inexistent risk to microbiological degradation;
- virtually insoluble at temperatures lower than 60°C;
- insensitivity to acid attacks (exception of certain oxidizing acids), alkalines and saline solutions;
- high density polyethylenes (HDPE) are sensitive to crack growth under stress conditions (brittle breaks triggered by traction in the presence of a chemical agent fracture accelerator). This phenomenon may be reduced by selection base resin and by molecular weight distribution in order to increase micro-crack growth resistance;
- thermal oxidization for high temperatures and photo oxidization through UV may be reduced by additives, and thus achieve a satisfactory lifespan.

However, some products such as mineral oils, aromatic and aliphatic hydrocarbons may have an effect on the polyethylene during prolonged exposure and may lead to inflation, plasticization or fracturing.

The recognition of mechanical, thermal, physical and chemical environments, and a good implementation of geosynthetic materials are also two important factors for sustainability. Notably, attentive care must be taken for protective structures mentioned in preceding sections, as much as in the implementation as in later tests. From a practical point of view, it is impossible to determine a correlation between the properties of a geomembrane and its sustainability, due to the environment's vast variation over the years [BLO 06]. The scrupulous follow-up of norms and recommendations allow us to ensure good sustainability conditions.

In waste storage sites, the lifespan of a geomembrane in contact with a leachate may be estimated as a century, according to Australian research [PIE 04], when it is chemically inert in relation to leachates, and when the installation is achieved with care and controlled by respecting a plan for good quality [BOU 02].

A lot of research has been carried out over the last century to estimate product sustainability. There are still many questions without answer, particularly in the domain of chemical sustainability and the lack of waterproofing functions in stress combinations which are virtually impossible to envisage in an exhaustive way. Research continues all over the world so as to increase knowledge and the performance of the proposed products.

Lastly, a simple way of decreasing the number of defects and increasing geosynthetic material sustainability is to increase its thickness. This clearly has economic implications, but the question deserves to be asked in terms of sustainability and environmental safety.

10.11. Testing, exploitation, maintenance, repair

10.11.1. Levels of testing

French norms and the CFG recommendations outline in detail tests which must be carried out so as to ensure a good construction process and its capacity to fulfill its function (norm NFG 38-060; CFG 1991, 1995, 1998). These tests take place before the construction process has begun, on the worksite and after construction: on the one hand these tests deal with support, waterproofing and protective structures, and on the other, the construction and parts of the construction itself. Using test boards may also help to complete these tests.

Level of testing		Filtration	Reinforcement	Drainage	Protection	Waterproofing
	***		Traction			Thickness
	**	Filtrating opening Permittivity		Drainage capacity	Static and dynamic punching	Traction
	*	Traction Flexibility Perforation Thickness	Friction Perforation	Creep under compression Traction	Perforation Traction	Static and dynamic punching Inflation/shrinkage (GCL)

Table 10.12. Tests to control the quality of geosynthetics and level of testing [CFG 98]
(***: high frequency; **: average frequency; *: low frequency)
(GCL = geosynthetic clay liners)

Higher risk constructions (dams, canals, waste storage sites, etc.) will use auscultation and monitoring devices. For waste storage sites, many tests are performed according to potential risks. In situ and laboratory tests are also recommended, mechanical as well as hydraulic and physicochemical. Table 10.12 displays the tests which aim to control the quality of the geosynthetic materials used on a storage site. Testing frequency and the level of requirements clearly depend on the envisaged risks.

10.11.2. Evidence of loss of waterproofing

Loss of waterproofing in a construction will result in liquid infiltration, which will lead to interaction with the construction materials and the environment, and will gradually lead to visible degradation: appearance of water, loss of resistance in the structure, corrosion, etc.

In constructions and buildings, the appearance of crack growth and cracking in coating (facings, ceilings, etc.) constitutes an undesirable liquid index (stagnant liquid, or possible flows). The path followed by the liquid particles in a construction or building may be particularly complex, and specifically a leak may quickly be diffused.

The flowrate measurement is essential to estimate potential waste. Estimating hydrostatic pressure is also important for recalculating the mechanical stability of constructions (dams, underground constructions, retaining structures, diaphragm walls, storage areas, etc.) As an example, Table 10.13 gives the water inrush levels proposed by the classification in article 3.8 of the norm “Taux d’humidité dans les fissures” (Humidity Rate in Cracks) (NF EN 1504-5), quoted in recommendation from [AFT 2006].

Levels	Water inrush rates
0	Dry support
1	Humidity without flow
2	Light drop by drop ≤ 30 drops/minute/m ²
3	Consequential drop by drop > 30 drops/minute/m ²
4	Continuous flow at low rates ≤ 1 liter/minute/m ²
5	Continuous flow at important rates > 1 liter/minute/m ²
6	Continuous flow at high rate ≥ 20 liters/minute/m ²

Table 10.13. Definition of water inrush levels [AFT 06]

For geomembrane fabric layers, the loss of waterproofing essentially comes from defects due to short term installation constructions, and to long term hydromechanical strains, on the level of welds between strips, the strips themselves or even at the interface between the geomembranes and support soil. In particular, the non-planarity of the interface gives a low performance waterproofing device. For large surfaces as in waste storage sites, studies have estimated the average density of geomembranes defects to be around ten per hectare [SAI 06], [COL 95], [PEG 01]. These defects are potential weak points for the waterproofing system and likely places for flows to take place, such as folds and interfacial non-planarity.

Analytical formulae have been proposed to predict leak rates in waterproofing devices, including geosynthetic materials. These formulae result from theoretical calculations [ROW 98], [TOU 99], [CAR 05] or from empirical estimates [GIR 89], [TOU 06]. Theoretical developments have involved circular defects (revolution symmetry, circular or elliptic holes, for example) and longitudinal defects (plane strain, slots, folds). These defects are representative of surfaces which are generally between 1 cm² to many thousands of cm². The obtained formulae express the leak rate in the following general way:

$$Q = \beta (h_w)^n a^m (k_s)^p \left[1 + \alpha \left(\frac{h_w}{H_s} \right)^q \right]$$

where β , n , m , p and q are constants which essentially depend on the interface properties, the presence of folds and the defects' geometry; a is the defect surface area; k_s the hydraulic conductivity (or permeability coefficient); h_w the hydraulic load and H_s the soil thickness (see [CAR 04], [TOU 99] and [TOU 06]).

Many investigations have been carried out on the recognition of defects in geomembranes used in waste storage sites, meaning, on large surfaces [PIE 04]. The summary shows that:

- for problems involving punching or tearing, we must count (on average) between 15 and 20 defects per hectare. The important kind of defects is having a surface smaller than 500 mm² and appearing in the building phase of constructions (particularly by engines, heat effects, using aggregates in the associated drainage system, bad welding, etc.);
- for leak problems, an average of 5 defects per hectare have been noticed.

10.11.3. *Methods for detecting defects*

The number of defects may be reduced by a strict control process before, during and after the building site. The care taken to put the protection and drainage structure into place, and obtaining a good contact plane at the interfaces are both also factors which decrease the risk of defects in working life.

Testing for waterproofing may be carried out in many ways and use different techniques, amongst which:

- generally putting water into the construction over a few days, which allows us to measure leak rates;
- visual examination;
- mechanical tests with a blunted-end instrument (above all for welds);
- methods which use pressurized or depressurized air (vacuum bell-jar);
- ultrasound tests;
- fluid tracers (infrared spectrometry, pressurized colored liquids);
- infrared thermography;
- geoelectrical methods;
- conductive geomembranes. A conductive sub-layer is included into the geomembrane at the point of manufacture.

A recent publication by the CFG details these methodologies and their limits [CFG 03].

Geoelectric methods consist of detecting the fracture of the electric insulator generated by a defect, by putting water into the studied area by moving it there with an electrode. These methods are generally quick to use and provide large output for large surfaces to be evaluated.

For conductive geomembranes, these are subjected to a high potential energy in situ, and the leak is detected by making a conductor circulate above them. The advantage of this method is detecting defects after the drainage and protective structures have been put into place [PIE 04].

After construction, periodic tests may be organized so as to plan it into the waterproofing system design. For example, in waste storage sites or hydraulic constructions, conductive geomembranes and indicator coupons for materials and joints can be put into place in order to make construction drainage systems to reach

waterproofing devices. These periodic tests allow us to follow the ageing process of the devices and to anticipate their repair or renewal [GER 04].



Figure 10.22. *Leak detection device in the formation level of a waste storage site [CAQ 06].*

Each of these methods has its own advantages and limitations. To summarize, small defects, some site conditions, characteristics, and electric masks are general limitations. At any rate, it would be impossible to truly affirm the absence of defects in a waterproofing system. By just manipulating the tests, we can reduce leak risks by using an acceptable criterion, such as 180 liters/hectare/day for current waste storage sites [MAR 06].

10.11.4. Repairing constructions and autocatrization

Repair works can be costly. This is because, on the one hand, the techniques and products are expensive and must be obtained from specialist organizations, and on the other hand, because there are often maintenance and exploitation constraints during construction.

It is important to know the origin of the liquids: recognition (examining surface traces), flowrate, temperature, and conductivity measurements, chemical analyses.

According to how accessible they are (bottoms, covers, edges), the repair works may require more or less delicacy and correspond to three intervention types:

- temporary treatment. This involves blocking infiltration, particularly by grout injection, and the new position of temporary coatings;

- “perennial” surface treatment by adhesion or filling;
- “perennial” structural treatment by regenerating or replacing the waterproofing structures, treating cracks and tears (injections, fixings).

In each case, it is appropriate to pay attention the environmental compatibility of the devices used and to the maintenance of the construction and building's performance (particularly mechanical performance).

Geosynthetic clay liners manifest a certain advantage by their capacity for autocicatrizacion, resultant of bentonite inflation. This property is interesting to plug small, insignificant leaks, but if the said liquid is chemically aggressive, then the inflation capacity may be affected when it comes into contact, e.g. between leachates and bentonite. In the long term, this property is not exactly guaranteed. The norm AFNOR XP P84-708 states the tests required for determining inflation characteristics, water permeability and the hydraulic head limit for breaking down a geosynthetic clay liner where a hole with a fixed diameter is practiced. These tests allow us to estimate the capacity for autocicatrizacion [HEH 06].

10.12. Watertight barriers for waste storage sites

10.12.1. *Designing a waste storage site*

Designing a waste storage site is a complex and multidisciplinary operation, combining mechanical, hydraulic, thermal and chemical problems, with strict respect for enforced regulation:

- mechanical solicitations (settlement, rotation);
- chemical activity (more or less aggressive leachate production, from water percolation through waste, corrosion, oxidization, combustion);
- gas production from the fermentation of certain waste materials.

Enforced regulation imposes a limitation on the maximum number of exchanges in the environment (input and output of fluid on the storage site), organizes liquid evacuation (leachates) and emitted gasses, and ensures sustainability for many decades. Waterproofing devices thus have a fundamental role in the safety of waste storage sites. Regulation for this type of arrangement also enforces the creation of a double safety barrier (Figure 10.23, [AIT 03]):

- an active safety barrier, which ensures drainage and leachate collection. It is made from a waterproofing function (geomembrane) and a drainage function (natural materials, geotextiles);

– a passive safety barrier which must guarantee the installation's sustainability and the protection of the surrounding natural environment. The waterproofing function is provided by the very low permeability of the clayed material which constitutes the barrier. This permeability must be smaller than 10^{-9} m/s on variable depths according to waste type. The minimum imposed depth varies from 1 m for household waste to 5 m for special industrial waste. Clay material is either natural or brought in and compacted, with an eventual bentonite treatment to improve the waterproofing property.

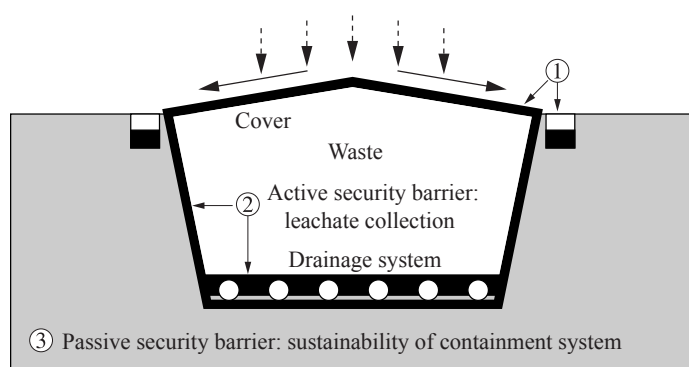


Figure 10.23. Construction principle for a waste storage site [AIT 03]

In terms of waterproofing, geomembranes is generally a good barrier in relation to ionic compounds, including metallic ions. The clay materials constitute a barrier which is often satisfactory to stop volatile organic compounds (benzene, toluene, xylene, etc.) [PIE 04]. The mineral barrier thickness conditions these waterproofing performances in the long term.

When the passive barrier in place does not have sufficient barriers, the clay materials may be replaced by means of accurate studies, or reinforced by geosynthetic clay liners [SAI 06]. The association between a mineral and synthetic waterproofing system is called “composite waterproofing”. The performance of this association depends on the state of the interface between the composite and the soil support, and also on the quality of the geosynthetics (few defects, reliable welds between the strips). Geomembranes may manifest defects due to manufacturing processes, or more often they will appear during positioning and assembly. Damage (tearing) may also occur in the long term.

The waterproofing function therefore must be protected so as to guarantee long term safety and avoid the appearance of cracks which may compromise the waterproofing quality. It must also be separated from the drainage function (French

law from 9th September 1997). From a design point of view, waterproofing properties involve (all at once):

- the foundation layer;
- edges or slopes;
- covering waste storage sites.

Following the position of geosynthetic materials in waste storage sites, the choice and dimensioning criteria will not be the same.

10.12.2. Foundation of a waste storage site

The foundation of a waste storage site must be able to ensure two essential functions [PIE 04]:

- underground protection in relation to pollutant infiltration, meaning the role of the barrier;
- evacuation of leachates towards the exterior, produced by waste and pollutant generators, meaning the role of drainage.

Chemical compatibility with stored waste and mechanical performances (particularly in relation to punching) are fundamental parameters for designing a waterproofing system at the bottom of the storage site. If the bottom is at an angle, friction and traction phenomena must also be taken into account.

The DEG support structure must provide an interface which offers maximum security between the waterproofing system and the foundation level. When the formation level is subject to gas or water inflows, an additional drainage device must also be envisaged in the support structure, or put a DDG system into place.

10.12.3. Waste storage site slope

For small slopes, stability calculations for the waterproofing system must be carried out because the waterproofing system may constitute a preferential slippage plane. Slopes in the waste storage sites are often quite straight and the waterproofing system will not be stable without anchorage mechanisms from top to bottom. Moreover, to improve stability and avoid large deformations, reinforcements may be added. It is largely inadvisable for the slope reinforcement function to be used as a geomembrane waterproofing device.

Nevertheless, geomembranes must have a strong load-carrying capacity for traction due to slopes, and be chemically resistant to leachates. Another frequent problem of instability is caused by the accumulation of biogasses under a geomembrane.

10.12.4. *Waste storage site covers*

According to the kind of waste, a cover on a waste storage site can be either permeable or impermeable, meaning that it either allows or does not allow water infiltration. From a dimensioning point of view, mechanical performance is essential, and sometimes more determining than chemical compatibility. Effectively, the cover must be adaptable to storage deformations and continue to ensure its protective role over the site: limiting infiltration in the waste mass and biogas emissions into the atmosphere. Geosynthetic materials can therefore be in contact with a biogas product, and chemical problems related to condensation under a watertight barrier must not be neglected. In addition, rain water may be infiltrated and exert pressure onto the cover; an additional drainage system is, then, recommended to reduce the flow into the waterproofing system. If the drainage system is not sufficient, water may gather and flow forces may appear, leading to risks of instability by sliding on the cover's slopes.

The cover may also bear vegetal earth layers, intended to promote the integration of the construction into the atmosphere.

10.12.5. *Using geosynthetic materials in waste storage sites*

For approximately 20 years, geosynthetic materials have been an interesting alternative to in situ or brought in and compacted clay materials, to fulfill waterproofing functions in waste storage sites. Their big advantage comes from manufacturing which gives them quasi-constant properties over large surfaces, in relation to natural or surplus materials which often remain heterogeneous in spite of compaction for large surfaces [SIL 04]. The risk of desiccating clay soils and therefore an increase in permeability by cracks is also reduced by using geosynthetic materials.

The CFG recommends a few basic rules to design DEDC materials used in waste storage sites (Figure 10.24):

- the waterproofing structure must only have a waterproofing function. It must not be mechanically strained;

- consequentially, the support and protection structures must be designed and dimensioned to continue mechanical strains;
- an effective drainage function is recommended to minimize water flow across the waterproofing structure.



Figure 10.24. *Example of waterproofing implementation on protective geotextile/drainage bands and connection the biogas collection network (waste storage site from Lescar [JAR 06])*

10.12.6. Numerical modeling of waste storage sites

Modeling the function of a waste storage site can be broken down into three parts:

- the waste;
- site itself which holds the waste;
- the natural surrounding soil mass.

These three elements may be modeled, as with porous media. In particular, a composite waterproofing system will also be considered as the link between three porous media: a clay material, a geosynthetic material and an interface between the two.

The most delicate aspect of this type of modeling comes from the heterogeneity of the “waste” material, its compaction, its implementation in block form which interact on each other, from the variable height of the waste under cover and finally from the difficulty of characterizing the behavior of this “material” for a mechanical type approach to continuous media.

Waste permeability varies from between 10^{-4} m/s for low confinement and 10^{-7} m/s or less, for confinements of around 300 kPa [AIT 03]. This permeability is difficult to estimate, because the waste is varied and heterogeneous; moreover, it evolves over time according to the decomposition and compaction of this waste. This parameter is a great source of uncertainty for numerical modeling.

In addition, the degradation of organic waste fractions is largely exothermal. Temperatures of around 60°C are currently being measured [CAR 04]. This important source of heat must be taken into account in the simulation as it triggers a thermal gradient in clay materials, which may lead to desiccation, cracks and therefore a drop in waterproofing performance.

10.13. Conclusions and perspectives

Despite many recommendations, experiment feedback and plans for quality, each construction or waterproofing system of a particular importance is unique. The performance of geosynthetic based waterproofing systems narrowly depends on the care taken during their construction: from the acceptance and testing of the products, the testing of the constructions, final acceptance and the exploitation phase. In light of people and the environment and the stakes involved, the tests will be more or less frequent, and more or less limiting.

In terms of research, many aspects still need to be explored, particularly in the context of sustainability and contaminant transfer across geosynthetic materials. Understanding these phenomena is a strongly environmental matter. Current research is inclined, on the one hand, towards improving the performance of existing products, and on the other hand, towards new generations of geosynthetic materials. Theoretical studies have also made significant progress over these last few years by providing leak rate estimates and by inserting crack growth into hydraulic calculations. However, different couplings between these thermal, hydrous, mechanical and chemical phenomena need to be formulated, and the truly 3D aspect of flow and deformation in these complex, sometimes cracked structures need to be taken into account; these structures which form the waterproofing systems used in civil engineering.

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10.15. More information

Geosynthetic characteristics are defined using test methods, most often standardized by norms on a French level (AFNOR), a European level (CEN) or international (ISO) level. For more information, we recommend that the reader consults the recommendations published by the CFG, by accessing their free website www.cfg.asso.fr.

Chapter 11

Waterproofing Buildings: The Point of View of an Expert

Going over the different solutions available to the builder to achieve a waterproofing property presents a challenge, as the domain covered by this concept is so vast. However, we will try to offer a summary of the families of technical solutions which are currently practiced, focusing particularly on some in particular, the main ones, the most used and effectively, those which use organic materials, which provide the subject of this entire work.

11.1. Introduction

If we were to consider waterproofing works in the different fields of construction, we must also try to consider, in terms of constructive reality:

- real estate (individual or collective rental, large administrative structures);
- industry, with its corrosion and various waste problems;
- civil engineering (roads – bridges, tunnels, manufacturers, energy plants), etc.

We should add to this that the issues associated with waterproofing are present in virtually every construction domain. We are able to come to this conclusion by the number of disasters observed during our careers: to just quote a few figures, out of 2,500 cases in 30 years, from the most important to the most modest, waterproofing issues are called into question in about 60% of these cases.

Chapter written by Gérard HÉMOND.

Detailing this experience allows us to say that these disasters are due to:

- design errors for 7% of cases (inappropriate materials and solutions);
- performance errors for 88% of cases (unqualified companies or wrong usage);
- the fact that works have been carried out by companies where this was not their trade (5%).

Today, waterproofing, contrary to what is often said and written about it, *no longer consists of solely preventing water from penetrating a constructed unit, but takes into account the parameters which can influence the life of the work*, in relation to the regulations and standards in force. It seems, then, that the simplest presentation of these defects comes from the presence of unwanted water.

With regard to general teaching around waterproofing, things do not seem any better. For decades, it was standard practice to use the gardens of Babylon, or worse, bitumen waterproofing on Noah's Ark, as a starting point for teaching about waterproofing. Today, we are obliged to admit that waterproofing alone – the act of using a barrier to prevent water from passing through – is not enough, that waterproofing and its support must be taken into account (or the support that it will be applied on), meaning all the life conditions of the constructed unit. Effectively, a waterproofing agent, as effective as it may be, when applied to a poor quality support will only give poor results. Therefore, the *waterproofing agent and its support* must be explored together, in order to give good results, while incorporating the other parameters into the analysis.

The total conclusion to these problems can be summarized by the following formula: “the combination of conforming support + adapted waterproofing solution + good application” makes it possible to find viable solutions to this difficult problem.

11.2. Initial analyses

Before imagining a waterproofing solution, we must, then, consider the entire constructed unit. This is unquestionable logic. Defining a waterproofing solution must take into account, in the most precise sense, everything in the building's environment, regardless of its characteristics.

We must not forget that construction materials can only offer a certain performance according to the nature of their physicochemical structures, these being the consequence of either chemical reactions occurring during implementation, or of a simple mix of different elements. At the moment when the problem is examined,

considering these structures is essential to be able to understand what has happened, and to predict what will happen.

Therefore, we must define in advance, as perfectly as possible, what the life conditions of the waterproofing will be, in the widest yet most precise meaning of the term.

It is appropriate here to recall that suppliers and the products they offer are at the designer's disposal (often an architect) but, importantly, not the other way round. This should be obvious to everybody. It is also obvious, in the case of civil engineering of structures or industrial constructions, that this role should be held, preferably, by a responsible civil engineer.

The parameters which have always seemed important to take into account are the following:

- geographical location;
- nature of the ground water against which the barrier is necessary;
- weather conditions, as for the building site as well as for the life of the work; pluviometry is important, but outside temperatures are equally so;
- working conditions: waterproofing a bridge deck does not have the same requirements as a roof terrace, especially because there is no decreasing performance classification or specific characteristics;
- total life conditions (long-term) of the constructed building.

In other words, the totality of the reflection intended to lead to the conception of a system or a waterproofing complex is very close to the work of a building physicist, who can plan all the parameters of the life of the constructed element, *before, during and after*.

According to this information, the list is not exhaustive. We can start by reflecting on the solution(s) which can be put into practice. Unfortunately, we have to add here that the economic parameter, generally quite far away from the technical parameter, is often important and frequently generates regrettable decisions.

We can add to this last remark by specifying that the detailed analysis of all the expertise quoted above allows us to say that in 90% of cases, an economy of 1 has triggered one, or several, disasters which represent an average spending of 16 (but with "peaks" from 500 to 1,000!).

There is one reality which must not be forgotten: water will always travel through the easiest pathway, and if we were to only seal off this first pathway

without dealing with the other circulation possibilities, the water would find a new pathway.

As a first conclusion, it is fundamentally important to know that, in order to be efficient, waterproofing must be total: waterproofing at 98% is not waterproofing, but is, in fact, a real absence of waterproofing.

11.3. Initial obligations

Whatever the classification of the building's "service", or the conceived work, many parameters must be taken into account, as we underlined previously. More specifically, it is a question of:

- thermal isolation and steam diffusion, to neutralize condensation phenomena;
- agreement between regulations and norms and what is conceivable (this is not always simple);
- the possible means or methods of testing;
- maintenance methods and processes (or follow-up) of the waterproofing complex, in relation to the guarantee period. Experience has taught us that it is recommendable to give the follow-up and management contract to the company who carried out the work.

11.4. Questions of definition

As surprising as it may seem, this difficult question of definition regularly comes up, when this point should not be subjected to any contestation. We have noticed that the terms *waterproofing* and *impermeability*, similar in terms of dictionary entry, do not mean the same thing in the construction industry. In fact, certain UTDs (Unified technical documentation) make a distinction between these two terms, and main contractors also. It is necessary, then, that the different groups listen to each other with regard to these definitions from the beginning.

To simplify this, we will say that *impermeability* consists of preventing water from penetrating to a certain degree of absorption after it permeates, whereas *waterproofing* is a real barrier for any water circulation. As *impermeable* clothing rejects "Kwai®" which completely prevents water from passing into the article but, on the other hand, promotes interior condensation. Let us add to this that we can consider a structure as being impermeable or even watertight though water passes through (but it is supplied) slower than it is evaporated! In this case, the disorder will only be noticed if we

cover the treated area and observe what is known as a “pressure-cooker” in construction sites.

In addition, in the case of civil engineering structures (tunnels, essentially) we can speak of *extrados* or *intrados* waterproofing. The two terms can be used on the same work according to the chosen solution (Figure 11.1).

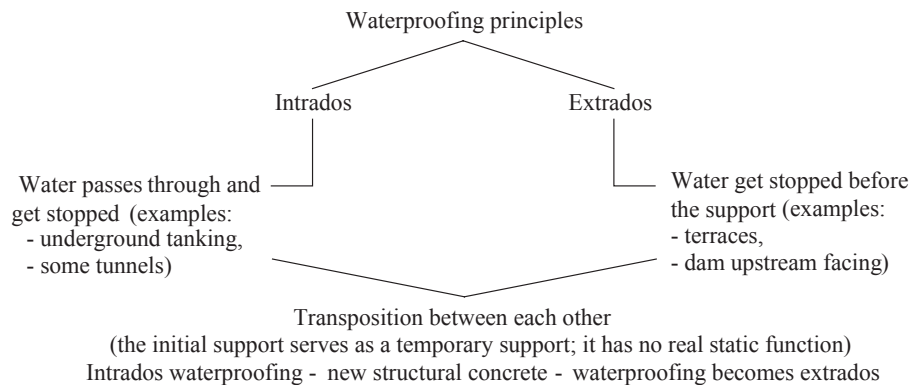
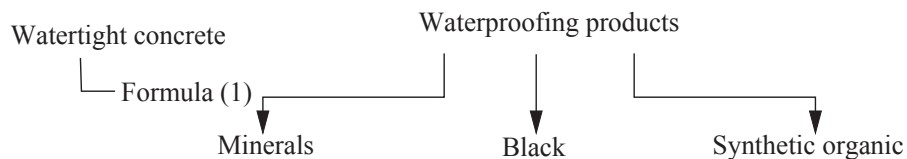


Figure 11.1. *Waterproofing principles*

11.5. Possible solutions

A general diagram (Figure 11.2) lets us show large families of usable products, being understood that the evolution of techniques means that we must take into account that the known performance of a product at a certain time can evolve (or be modified). This implies that updating technical files on products (internal documentation in offices) is important and proves to be very useful.



(1) Specific concrete formulas (including admixtures) with specific framework calculation

Figure 11.2. *Various waterproofing products*

11.5.1. Watertight concrete

11.5.1.1. Engineers' calculations

Civil engineers calculate concrete (essentially reinforced concrete) according to planned uses and loads, to allow the construction performance to meet demands (safety ratios included, provided by the norms and regulations in force). These calculations imply that cracks can (and must) appear, without it really being a problem for the structure. But, evidently, these cracks let water pass (rain water or other types), if they open too much, and this verges on a waterproofing problem.

Having been reminded of this precise fact, we can also make the choice of using another calculation method which makes it possible to predict whether the concrete is watertight, meaning, neutralizing risks of “cracking”. To do this, specific calculations and formulations must be planned, whose main elements are: the conception of appropriate concrete (therefore, modifying the current formulation of concrete), another method of reinforcement calculation (extra reinforcement networks – superior and inferior – for crack growth resistance) and executed perfectly with a supervision which is increased by the execution.

It must be clarified that this method requires consequential care, without so much as being guaranteed at 100%: the norms foresee crack formation as being “rather logical” but consider that waterproofing must be resolved, therefore regulated, separately.

11.5.1.2. Special joints during construction

There is the possibility of putting a rubber profile coated with fine gravel (these allow adhesion on new concrete) in to place, to ensure the join between the two parts being concreted together. This join greatly neutralizes the pathways of water (above all, water on the construction site). It is often completed by PE tubes with a small diameter (around 6-8 mm) which can be used to inject a product (in the great majority of cases with a polyurethane mono-component which reacts with water) to fill, if necessary, gaps in the mentioned profiles.

In the case of structures, we resort to prefabricated rubber joints, of particular shape (called waterstops), which ensure theoretical waterproofing between two concrete operations. All the same, they have a defect, in that they tend to not stay in place correctly during concreting (at great heights, for example), which partially neutralizes their effectiveness.

11.5.2. *Mineral products*

In this classification, which comes from the field of the present work, we will use as examples:

- *crystallization*, which consists of sealing superficial porosity of the concrete by applying hydraulic binder based grout;
- *cement coating* application, a technique which was mainly used for many decades but is currently losing speed;
- using certain *silicates*, combinations of silica SiO_2 , sodium oxide Na_2O whose ratio between the components is, for example, 3.2 and 3.3 for treating ground located beneath hydraulic dams.

11.5.3. *“Black” products*

These were quintessential waterproofing products used for centuries, where the main quality asked of them was to “prevent water from passing”. They came from several sources: natural deposits, pyrogenation from wood then coal, and finally oil distillation (bitumens). This last source, bitumen, is essentially that which is used today (see Chapter 16).

We distinguish three modes of use: the “warm roof” processes where the waterproofing is laid on thermal insulation (without an intermediate layer of air), “cold roof”, comprising of an external structure obtaining a level of waterproofing by an air knife, and finally, “reverse roof” where the waterproofing is applied onto the load-bearing structure, then covered by thermal insulation which must receive a mechanical protection.

The only important criterion consists of controlling the black waterproofing product’s adhesion to the carrier (classic bitumen or polymer bitumen) so that water circulation is prevented, by specifying that it is desirable for the installation to have a durability length of at least 10 to 15 years. Millions of m^2 of terraces have been created this way.

There are some variants in this domain where we accumulate insulation materials (such as expanded glass, a remarkable insulation material but which has no flexibility) with hot cast bitumen to ensure the join between the plates and the support, to finally be covered with the same bitumen. Other application can be used as examples, such as adhesive seaming of insulation plates with bitumen, in the making of cold chambers or other technical premises at low temperatures.

However, these products are often criticized for questions of safety (resistance to fire, chemical composition of the bitumen). This could lead to a significant reduction in their use.

However, there is one case in particular which is worthy of stopping for: natural asphalts.

This class of products presents thermoplastic behavior (with a viscoplastic dominant) which is necessary to implement this type of technical response on planar and flat supports (meaning no gradient, or the smallest possible) by the conjugated effect of time and temperature, to avoid that the current implemented thicknesses (4 cm in size) flows in the direction of the gradient in a few years, triggering fractures at the level of application connections.

Large surfaces of concrete (promenades, car parks, sports grounds, etc.) are still treated in this way today. We should add that this technical solution requires, before putting it into place, a preliminary waterproofing layer (often with polymeric or modified bitumen). On the other hand this complex, when made correctly, displays a life duration of around 25/30 years.

11.5.4. Organic and synthetic materials

11.5.4.1. Welded sheets

These sheets arrived on the market for the waterproofing treatment of roofs (terraces and similar) and they are essentially made out of PVC. Without going into detail on their composition or respective formulations, they presented, and still present today, a large disadvantage: the smallest hole of 1 mm can stop this “waterproofing” quality from being...waterproof.

Good solutions have been brought along by a diversion: this material (and therefore related technique) has been used in road civil engineering (tunnel construction) requiring large surfaces to be treated. This has led to the development of partitioning techniques which made it possible to localize the accidental phenomenon, therefore reducing the risk of an untreated perforation.

In civil engineering applications, evolutions on the level of methods of formulas have been put forward to fulfill certain requirements for the French Bridge and Roadway administration, without fundamentally changing the principle performances of these waterproofing sheets. Therefore, some improvements have been put into place:

- by introducing alveolar protection materials between the tunnel wall and the waterproofing;
- by using special plasticizers in the plastic sheet composition;
- by welding between sheets with controlled injected air between the two weld beads.

These techniques illustrate the definitions between *extrados* and *intrados* waterproofing presented in Figure 11.1.

11.5.4.2. *Polymers made on site*

The use of polymers in civil engineering is relatively recent with regard to the origin of concrete. The first large applications were carried out at the beginning of the 1960s, in the framework of repairs or construction work reassessments, before being envisaged for new works. We must specify that the application of pure polymers (formulations composed entirely of synthetic products) had been preceded by uses of these polymers in mixes with natural products (coal tar, pitches, bitumens) like “epoxy-pitches, polyurethane pitches”, etc.

If it is obvious that concrete represents the most high performance construction material with regard to the cost/performance ratio, it is no less certain that we cannot leave it such as it was built without running the risk of seeing it degrade over time. This is all the more necessary, recent analyzes have shown us, as this degradation is quicker today than it was 15-20 years ago, and *a fortiori* 50 years ago. This degradation is due, in most cases, to the action of the follow phenomena:

- Carbonation of the concrete, which transforms the cement lime into calcium carbonate. This modification leads to a change in the pH level (from 10.5/11 to 9) which no longer protects the armatures of the reinforced concrete from corrosion (passivation of steels brought about by the alkalinity of the concrete up to approximately pH 9.5).
- “Alkali-aggregate” reactions, where one of the origins is the exhaustion of rolled aggregate resources. Currently, we nearly only use crushed aggregates to make concrete. Before, we used rolled aggregated which had time to lose their alkaline ions, while, for crushed aggregates, this treatment due to time did not take place. For some “potentially reactive” aggregates, this state triggers a slow reaction, explained by the formation of expanding gels which provoke the localized destruction of the concrete.
- Washing-out action, spread by rain water (always acidic) in various forms: very dissolvent small rains, large storms probably with electric phenomena, snow possibly turning to ice, etc.

Before coming to polymers and their applications, we must remember the fundamental rules that we have cited for other domains.

First of all, it is not the products, the used polymers (in spite of the very high level of performance) which will resolve the weaknesses of certain supports in reinforced concrete. It is the combination of *conforming supports + adapted polymer formulation* which will allow a good result.

On the other hand, this first rule is only valid to the extent where the application of the chosen formula will be carried out in rules defined by the formulator, which must conform to the requirements of the regulations in force.

Let us remember about the application here that in the case where the implemented product must polymerize in situ, this phase must be completely controlled. In effect, the polymers, once formed (polymerized) present us with performances and characteristics which are the direct consequence of the molecular structure that we have succeeded in acquiring. This means that controlling the polymerization parameters (choice of reactive components, implementation temperature and mix quality of the two components) are determining in order to lead to an expected result.

The polymers used, and applied on site (while excluding prefabricated materials), belong to one of the categories below:

- epoxidic (reaction between an epoxy and an amine);
- polyurethane (reaction between a polyol and an isocyanate);
- polyester (polymerization reaction with a catalyst and accelerator);
- polysulfide rubber;
- silicone;
- acrylic in its various forms, mainly methylacrylate.

11.5.4.2.1. Epoxides (epoxy or epoxidic formulas, or epoxy resins)

Bicomposant products resulting from the reaction between a polymer generally containing two epoxide functions with a hardener containing at least 3 active H.

The base viscosities of these systems vary according to the base molecular structure and the molecular weight of the initial constitutive element. The formulations used in buildings and civil engineering today call upon mixes between resin based families, with the intention of taking advantages from both of them and reducing their respective disadvantages.

The biggest proportion of formulas used in civil engineering have a base of two types of resins (or maximum, three). In exchange, the used hardeners used are larger in number (40 types of known hardeners, without mentioning the many commercial references).

We must not forget that these systems are implemented on site and that, as a consequence, it is not possible to carry out the “baking” (acquiring a good cross-linkage by heating) of systems which would allow a sensitive increase in their performances (by a factor of 2). Today, experience shows us that few of these epoxidic formulas are used. Above all, we use systems of a mixed epoxy-pitch (or bitumen) type, but without taking the extent of what is carried out with polyurethanes.

We will note here that, in terms of vocabulary, an epoxidic system implements an epoxide resin and an amine hardener, and that the polymerized network obtained is always an “epoxy”, while there is no longer a free epoxide function if the reaction is complete.

11.5.4.2.2. Polyurethanes

A bicomposant polyurethane system implements a polymer with a base containing hydroxyl functions, called “polyol”, with a hardener containing isocyanate functions. Practically, these polyols are either polyesters, or polyethers, with alcohol endings (-OH).

The base products (polyols) obey certain less strict constraints in terms of their chemical structure than the other polymers, but today we can better control the total forms of these polymers. This means that we can decide the usage of a base polymer (according to a particular formulation) presenting a linear structure, giving the polymerized form a linear network. Using a polymer with a ramified base structure generates a ramified polymerized, or even cross-linked, network. The immediate consequence of this principle is found on the level of the performance of the product. A linear polymerized product will be more flexible than a greatly ramified product.

It will be noted here that, in terms of vocabulary, the base products called *polyurethanes* (while the urethane function is still not present) implement a *polyol* with an *isocyanate* hardener (or to be more precise, polyisocyanate), and that the acquired polymerized network is logically called a *polyurethane*.

The other polymers mentioned above (polysulfur – silicone – acrylic, etc) are less used, even if their specific effectiveness makes it possible to envisage a use for them. This makes it necessary to thoroughly examine the appropriateness between the planned applications and the performances required of the products. A specific

analysis is necessary, at the moment of study, to consider whether we need this type of formula.

11.5.5. Complementary products: expansion joints

Any constructed element, with some very rare exceptions, require planning expansion joints (concrete dilates as well as steel, but obviously on a different scale) and the inefficiency of an expansion joint verges on a waterproofing problem, cancelling out any waterproofing operation (on the whole surface, as good as it may be).

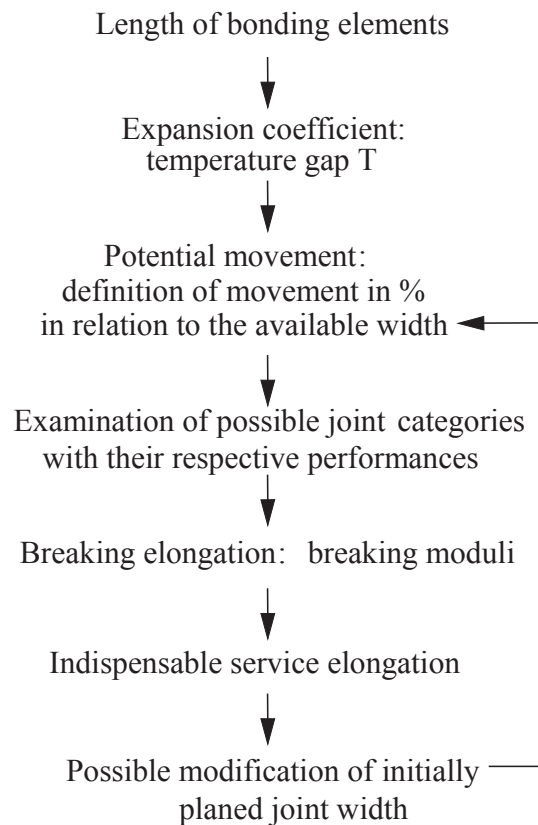


Figure 11.3. *Diagram of the dimensioning of an expansion joint*

Creating expansion joints is planned in a very precise way. They must be designed from the beginning of the project. This analysis must follow the diagram given in Figure 11.3, and starts by dimensioning the joint. In effect, it is a serious physical problem which must have fulfilled all its requirements so as not to trigger any disorders.

Water which circulates behind the joints will have to be collected at the bottom of a piedroit. If necessary, we will plan a thermal insulation material which prevents the water from freezing in the circulation pipes.

There are no joints with a base of polysulfuric rubber, even perfectly created, which can resist many MPa of sub-pressure. It is therefore a unit of “joint drainage + well-made joint” which will be implemented in order to acquire a effective and durable expansion joint.

One fundamental rule remains to be specified: the width of the joint must be at least equal to twice its thickness.

In the case of tunnels, the most important thing is the initial choice of the type of waterproofing. This choice is the consequence of the conjugation of unquestionable technical parameters and conditions of administrative and financial management of a project. This choice will condition the other polymer applications for the unit of construction works and town managements.

We will make a note here that *extrados* waterproofing construction works envisage ground waterproofing (once put into softened forms) by a waterproofing sheet (often PVC) on which the formed concrete will be flattened by flattening roller systems. In this case, waterproofing will logically be the first in contact with the ground water which must not, theoretically, circulate up to the concrete. In this technology, the joints must be treated with as much care as for the *intrados* solution.

It should be also specified that the concepts and definitions of “plasticity” and “elasticity” have considerable importance in this subject. The behavior and the durability of the long-term performances are completely related to these concepts.

In the majority of cases, it is necessary to envisage an expansion joint with “plastic” behavior, after having analyzed and defined the constraints which must be held. Then, the choice of the product and the company remain just as important.

Finally, it must be said that this chapter, in construction works, represents (at best) 1 to 2% of the amount of the workmanship, but this is a very important part (to not say more) of the success of waterproofing.

11.6. The future of these recent technologies

11.6.1. Products

The conversations between raw material suppliers, formulators and main contractors is often generated around a “circular” discussion, the bulk of which can be summarized by:

- the *main contractors* wish to be equipped with products of the highest performance and the most specifically adapted to their applications;
- the *formulators* ask that their needs are defined, with precision, so as to create formulas adapted to their needs;
- the *suppliers* cannot make raw materials in small quantities because the costs would be too high. Therefore, the existing products must be taken and “formulas” must be conceived from what already exists on the market.

We notice, however, that for a few years now, a constructive dialogue has been established between them.

11.6.2. Applicators

It is certain that when these new products (formulated polymers) appeared on the market, during the first applications, many errors occurred, consecutively, due to a lack of knowledge, practice and/or a lack of definition of techniques to be implemented.

These errors can be grouped into two categories:

- those due to a lack of knowledge of technical data with regard to the application (pot-life, polymerization time, bad mixes of two components, bad preparation of the support);
- those related to an insufficient analysis of the required performances or working conditions, which will commonly generate fractures in the implemented materials.

Today, application companies owe it to themselves to obtain an official qualification which requires them to train their staff, and to have practical knowledge of the used products, for example.

It is no less true that a lot of effort still needs to be made so that the seriousness of every moment is a reality of building sites.

Chapter 12

Elastomers and Rubbers used in Civil Engineering

12.1. Introduction

12.1.1. *Elastomers*

12.1.1.1. *General points*

In order to define this material that has very particular characteristics, the option chosen was to regard its extraordinary elasticity as the main mechanical characteristic of this product family and this is what especially interested civil engineering builders.

Elastomeric materials are products able to elongate up to at least 300% of their initial length and to take back their primitive shape spontaneously. Some synthetic resins or PVCs etc., are therefore not considered as such.

The typical material in this family is natural rubber but as we will see hereafter, other products that can elongate also exist, even if they are not manufactured the same way.

Chapter is written by Michel FRAGNET.

12.1.1.2. *Rubber and elastomers of the same chemical family*

Rubber was already known by the Mayans. It has been studied from the end of the 18th century and its use rose during the 19th century, especially due to the vulcanization technique developed, in US, by Goodyear [AFG 94], [MOU 03]. However its use was limited to fields that had nothing to do with civil engineering. Its high gas permeability, its poor behavior to oils and solvents and its sensitivity to ageing, which has to be compensated for by the use of additives, made it of little interest in this area.

These disadvantages, combined with the difficulty to meet demand (especially during World War II) as well as geopolitical factors led to the development of synthetic elastomers.

Development of the first synthetic elastomers began around the middle of the 20th century, but only achieved real success in the late 50s due to the development of polychloroprene (Neoprene®, Baypren® etc.). Since then, research enabled the perfection of polymer formulae belonging to this family, whose various grades are determined according to their intended use (e.g. dynamic properties, resistance to heat ageing or crystallization). The characteristics of these materials enabled the broadening of the mechanical properties of this product, while keeping rubber's interesting initial properties. As we will see in this chapter, this allowed them to be put to good use in the field of civil engineering.

So the main feature of rubber, its fundamental quality is its extraordinary elasticity which allows it to reconcile two conflicting characteristics: the form stability of solids and the high deformability of liquids [COL 48]. This property enables it to be elongated to several times its original length, without it expending any noticeable effort and without apparent damage. Therefore, rubber can be considered a true transitional material, a kind of bridge stretching from solid to liquid state.

Rubber's extendibility reaches approximately 800 to 1,000% elongation at breaking point compared to a few percent for metal.

We have to know that the manufacture of a rubber or an elastomeric product is the result of a compromise between various desirable and undesirable characteristics.

According to the nature and proportions of the ingredients added to the rubber mixture during the manufacture of the final product and the conditions of the vulcanization, material properties can be modified considerably. So we have not only to deal with one type of rubber but with several types, whose characteristics can vary enormously in a vast domain.

The ingredients to make rubber or vulcanizate (or vulcanized rubber) are extremely numerous (there exist over several thousand!) and various. However they can be grouped together in a few general categories:

- additives such as plasticizing agents aimed at facilitating placing;
- ingredients which are aimed at endowing the product being manufactured with the desired mechanical properties such as organic and mineral reinforcing fillers;
- chemicals which improve vulcanization conditions such as:
 - sulfur: vulcanizing agent,
 - vulcanizing accelerators,
 - activators such as zinc oxide; fatty acids;
- other ingredients are reinforcing fillers: carbon black (which is aimed at reinforcing mechanical properties such as tensile strength at break, resistance to tearing and abrasion) or elements necessary to the elaboration process such as zinc or magnesium carbonate, zinc or magnesium oxide, silica and some types of kaolin;
- fakes obtained by the polymerization of oils, aimed at improving suppleness;
- stearic acid, which facilitates incorporation of fillers and plasticizing agents by softening mixtures, thus making it easier to put in shape and giving a smoother final surface;
- fillers that reduce cost price by reducing rubber content without harming the desired characteristics:
 - inert fillers such as chalk, talc, sulfate of barium hydroxide or kaolin,
 - reclaimed rubber and/or rubber powder (see section 12.7);
- additives such as anti-oxidants that improve the ageing resistance of the product;
- finally: dyes, odorants, etc.

The amount of pure rubber in a product varies. For example it can be as low as 60% in tires and even less in certain products, without harming its properties.

The task of a rubber manufacturer is to determine the formula that best matches the use planned for the final product.

12.1.1.3. *The other types of elastomer*

Among the synthetic elastomers used in civil engineering we can name the following:

- the SBR (styrene and butadiene copolymer), which has properties very close to those of natural rubber;
- polybutadiene (BR) which has good abrasion resistance;
- butyl rubber (isobutylene and isoprene copolymer) characterized by its excellent gas impermeability;
- the EPDM rubber (ethylene-propylene-diene monomer) with a good resistance to ozone but a low resistance to creep under stress.

In addition to these synthetic elastomers that belong to the same chemical family as natural rubber, there are other elastomers such as the following:

- chlorosulphonated polyethylene (CSM) like Hypalon®;
- silicone elastomers which are inorganic matters formed by a silicon-oxygen chain in which groups fix onto the silicon atoms enabling the activation of the chains and/or linking them to one another;
- polyurethane elastomers (PUR). These are macromolecules characterized by the urethane group, obtained by polycondensation of a polyfunctional isocyanate with a polyfunctional alcohol;
- the SBS (styrene-butadiene-styrene copolymer) elastomers which have some characteristics of rubber at low temperature. That is why they are used in association with asphalt in order to improve the qualities of the binder which is a part of sealing coats and road bituminous mixes;
- etc.

12.1.2. *The products in question: field presentation*

The present chapter is limited to equipment with elastomers used on bridges, viaducts and similar structures in the road area.

It is quickly apparent that the main characteristics of elastomer (or rubber products) can be put to use effectively in bridge components. The qualities in question are:

- volume incompressibility of elastomer;
- significant elongation;
- good resistance to abrasion;
- water-tightness;
- vibratory insulation.

The first quality, volume incompressibility, proved to be very useful in the case of bearings. Moreover the shear modulus (relatively constant within the operating range of these products) of an elastomer being three times less than the elasticity modulus will have the following advantages:

- Using an elastomer of the same quality with a shearing force working on it, we have at our disposal softer springs than those working under compression.
- A sandwich (a layer of elastomer between two steel reinforcing plates) is far stiffer in the normal way than in the tangential way which enables good stability under normal forces without having to resort to guides or mechanical linkage systems that might harm its function.

In the expansion joints area, elastic qualities of pieces which have to follow the opening/closing movement of an expansion joint are an asset in order to prevent run-off water through the joint.

In the same way, resistance to abrasion is an important criterion for these expansion joints as they are subjected to traffic influence through vehicle wheels. Moreover they have a significant role in surface coating and lessening of vibration transmission.

Finally their behavior to water is a characteristic which interested designers of bridges and of their equipments within the frame of anything concerning watertightness and all individual points referring to it.

The manufacture of the final products is based on casting various shapes:

- we lay sheets prepared by calendaring into a mould having the shape of the final product in which the material is subjected to compression,
- after forming a kind of “sausage”, the latter is either extruded through a draw plate or injected into a mould which gives the desired shape to the final product.

Other manufacturing techniques like dissolved latex, soak, etc. are not used in bridge equipment area.

12.1.3. Terminology and vocabulary peculiar to this field

The field of elastomers calls on specific vocabulary and terminology as the behavior of this material is specific in itself.

Steel's tensile and elongation properties, i.e. its basic characteristics, are necessary when studying steel elements and their value has a direct influence on the

performances in service of these pieces. In the case of elastomers, traction and elongation resistance of rubber has little or no direct influence on its behavior in service [DUP 63].

The term “steel modulus” expresses the slope of the linear part of the traction-elongation curve. For an elastomer, it expresses the stress needed to reach a given elongation. So the tensile stress needed to obtain a 300% elongation is a modulus at 300% and the latter cannot correspond to another value of elongation.

On the other hand, these elastomers are hydrocarbons which are subjected to various influences (temperature, UV-radiation, ozone, fluids, etc.) which will cause ageing and modify their characteristics. Therefore, one has to distinguish initial characteristics from those after ageing.

All fundamental physical properties of elastomers, in particular the Young’s modulus, not only closely depend on exerted tensions but also on factors such as deformation speed and frequency, on temperature during the test, stress speed etc.

Apart from these important aspects relating to the material characteristics, there is also a peculiar terminology for tests, characteristics, flaws, behavior and so on [AFN 04] [SET 06].

12.2. Bearings

12.2.1. Role and functions of bearings

It is probably in this field above all others that elastomers showed how interesting their characteristics and qualities are. A bridge bearing is generally:

- an element of the structure linking the deck and the supports.
- a piece of equipment transmitting stresses between an element and its support while allowing a certain degree of freedom.

Please note that if there is no possibility of movement, then this relates to a restraint and not a bearing.

The quality of their structure is essential: in case of any flaw on this product the whole structure may be endangered. This is the reason why bearings are subject to a ten-year constructor’s warranty like the rest of the structure. To fulfill these functions, different types of products are available, some of them containing no elastomer [AFN 04].

The cost for their manufacturing is almost insignificant – 0.65% of the whole structure costs – which may be a reason for the presence of flaws. On the other hand their replacement, which requires that the structure be lifted up with jacks, brings about maintenance costs that are far from insignificant: about 4 to 7% of the funds dedicated to bridge maintenance. Hence the importance of choosing quality products with ideal proportions and ensuring their correct placement.

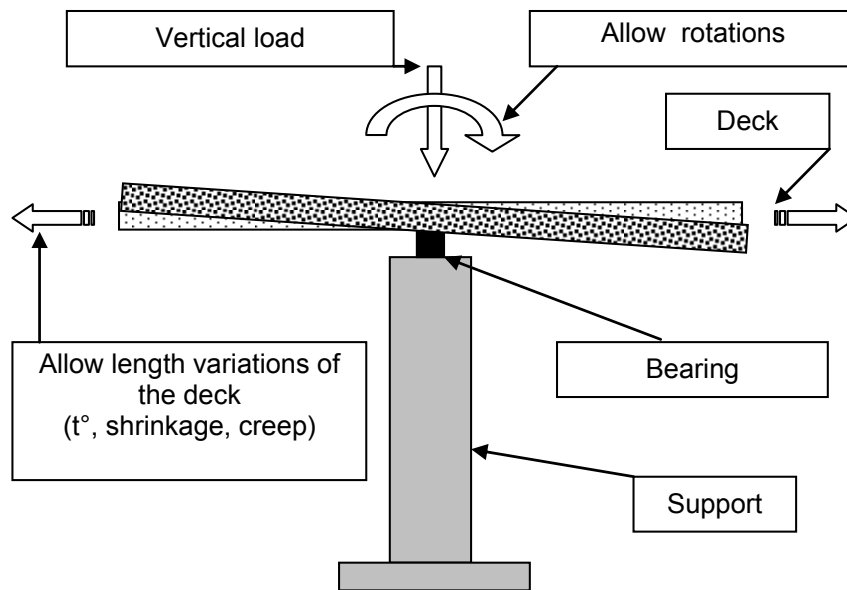


Figure 12.1. *Functions of a bearing*

12.2.2. Historical background

The first attempts to use elastomer layers in the field of bridge bearings date back to the 1930s. At the beginning, merely elastomer layers were used. Afterwards systems with elastomer layers combined with reinforcing steel plates came to be used as well. It was only at the beginning of the 1960s that laminated elastomeric bearings with steel plates bound to the elastomer layers by vulcanization were developed and began to be widely used.

It was also during the 1960s that it occurred to take advantage of one of the properties of elastomer – namely its ability to reconcile form stability and deformability, such as a liquid – to use it as a fluid enclosed in a pot [SET 07]. This led to the invention of pot bearings that developed during the 1970s.

12.2.3. Laminated or strip elastomeric bearings

12.2.3.1. General working principles

These devices put a specificity of elastomer into practice namely its volume incompressibility.

A laminated elastomeric bearing is a “block of vulcanized elastomer reinforced inside with one or several steel plates which have been bonded chemically (adhesion) during vulcanization (...). Elastomer is a macromolecular material which takes back approximately its initial shape and dimensions after undergoing a significant deformation under the effect of a small stress variation” [AFN 04-3].

12.2.3.2. Principles of performance verifications

Dimension principles are set in the [AFN 04-3] standard. They can be summed up as follows:

- limitation of distortion due to vertical loads, to horizontal stresses and displacements as well as deck rotation (see Figure 12.2);
- steel reinforcing plate thickness depending on the vertical stress submitted and on the elastomer layers;
- stability by rotation;
- stability by buck;
- stability by slippage;
- limitation of lift up.

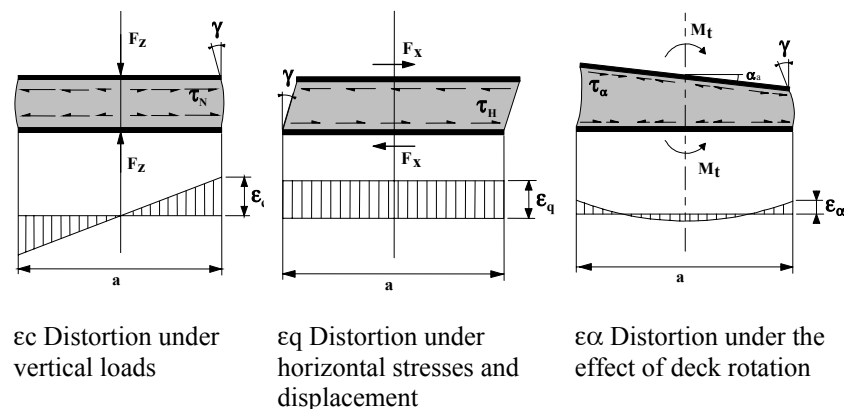


Figure 12.2. Limitation of distortions

Because of rubber's high deformability, deformations by crushing (under compression stress) occur at an almost constant volume of rubber and create complex tensions among which shearing forces are predominant. The high elasticity of rubber, which works like a compression spring, is only available insofar as rubber can spread crosswise freely. The importance of the role of lubricated surfaces on flow tables was demonstrated: the deformation undergone by the gum is roughly identical in all sections of the test piece, even in the vicinity of the tables. In case of bonding on the tables, the test piece is subjected to a maximal deformation in the median section whereas the areas which are the closest to the tables behave like rigid bodies. This was one of the reasons that led to bearing block systems with steel plates not being bonded to the elastomer layers behaving in the wrong way. One could observe that, on this type of bearings, some layers had been deformed crosswise as a result of lubrication simply due to water (flow of water or condensation on steel plates).

The limit of this process is permanent deformation by upsetting: this type of bearing should not be used when the crushing rate might reach 20% if we want to avoid annoying slow collapse in the long term. And if we want to assess the flow rate, long-term tests have to be carried out (at least 1 year).

The shear modulus of elastomer being three times less than the elasticity modulus will result in a sandwich (an elastomer layer between two steel reinforcing plates) being much stiffer in the normal way than in the tangential way which enables good stability under normal forces without resorting to guides or mechanical linkage systems that might be technically harmful.

12.2.3.3. *The various products available*

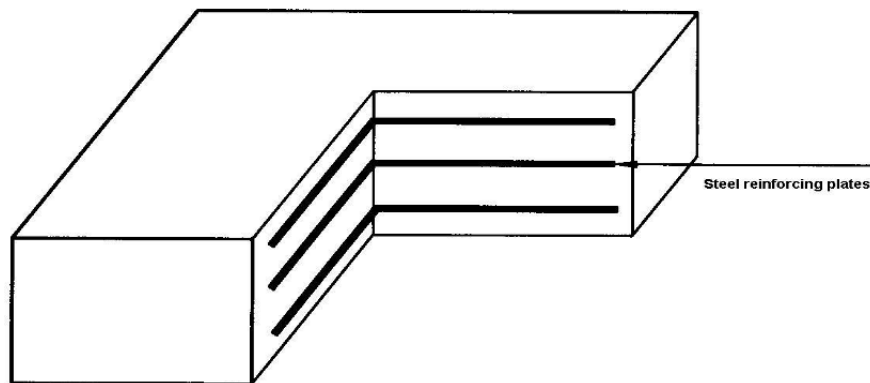


Figure 12.3. *How a laminated elastomeric bearing is typically made up*

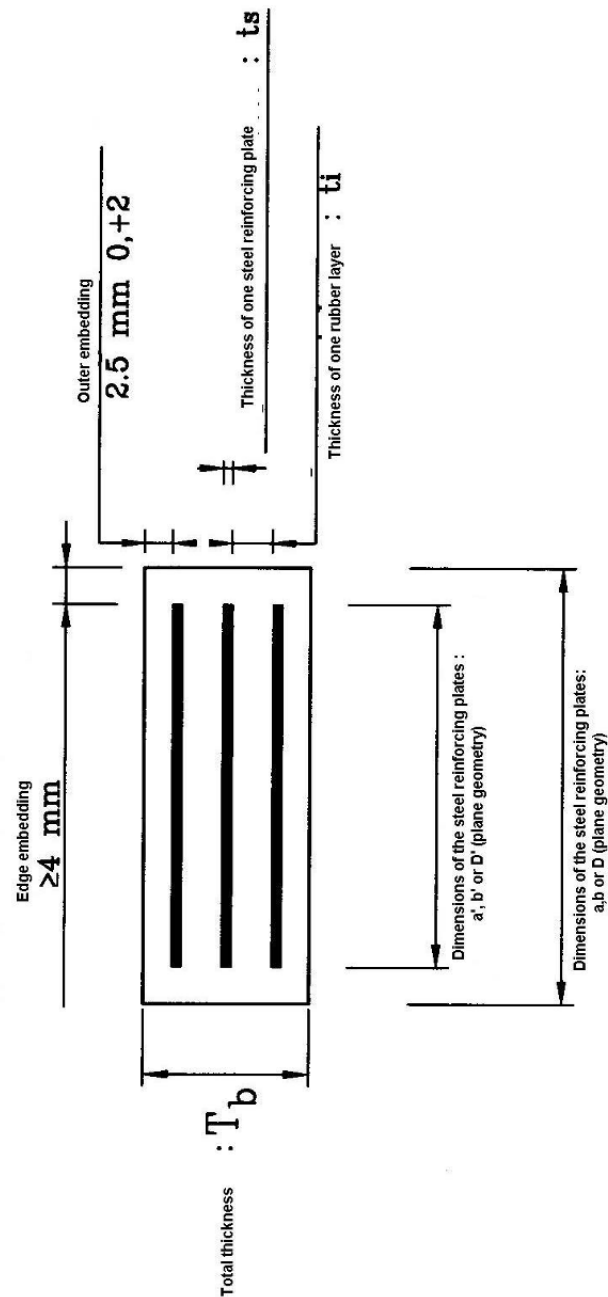


Figure 12.4. How a B-type bearing device is typically made up according to [AFN 04-3] standard

12.2.3.4. *Method of elaboration, manufacturing principle*

12.2.3.4.1. Mixing

This operation consists of the mixing of the fillers and the various additives of the chosen formula with a basic elastomer. Two different types of mixers may be used:

- Open mixers shear the matter, while mixing is in progress, between two parallel cylinders rotating at different speeds and which can be heated or cooled as required.
- Internal mixers are designed differently; the materials are confined to a chamber that is equipped with rotors and subject to the action of a piston.

The order of introduction of the various components, which is important, depends on the chosen formula and mixer type. In general, the vulcanizing agent or agents are added last.

12.2.3.4.2. Calendering

The various blanks corresponding to the chosen casting technique are fabricated either by extrusion or by calendering. Calendering consists of rolling the mixture between two cylinders in order to get a sheet with a constant thickness which is a sub multiple of the thickness of each individual layer, in the case of laminated elastomeric bearings. This operation is quite delicate as it must guarantee a constant thickness to ensure respect for tolerances of steel reinforcing plate placement into the final product. This constancy in the desired thickness is obtained by using a calendar with 3 or 4 cylinders with an adjustable distance between the axes. Emerging from the calender, the sheet is rolled onto a protective layer (i.e. a polyan plastic film) to prevent all sheets from sticking together during storage. At room temperature, the sheets should be stored for a limited time (as a rule less than 72 hours).

12.2.3.4.3. Making

Prior to this operation, the plates made of steel sheets are cut, granulated and coated with an adhesive.

The preparations for casting are cut out of calendered sheets sharing the dimensions of the bearing device by means of guillotine shears, a guillotine or a punch. The bearing is then fabricated by piling up rubber layers and steel reinforcing plates successively to obtain the desired composition.

During the making, the weight is adjusted by filling material to guarantee the good filling of the mould, essential for correct vulcanization, but while ensuring the steel reinforcing plates are kept at the right place.

12.2.3.4.4. Casting under compression

Once the bearing device, which at this stage can be likened to a “millefeuille” cake, has been fabricated, it is introduced into a metallic mould (which has been coated with release agents beforehand) sharing the dimensions of the final product.

After putting on the top, the mould is placed between the heating plates of a press with a capacity corresponding to an internal pressure of 5 to 10 MPa and with a regulated temperature between 150 and 200°C. The perfect control of these parameters is essential for a good vulcanization. The duration of the vulcanization process depends on the thickness of the element to be vulcanized. The products are then removed from the cast, de-burred and checked.

12.2.3.5. *Advantages and limits. Durability*

The main advantages are high suppleness and resistance capacity above what is actually needed. Although the calculations are made at Ultimate Limit State (ULS) on the basis of a coefficient of 1.35 compared to the Serviceability Limit State (SLS), it appears that these products offer possibilities of up to more than three times those of SLS.

The following text from a version of the [AFN 04] standard makes this resistance capacity clear: “Elastomeric bearings are dimensioned so that they can work properly at values lower than the ultimate strength of the materials they are made of, in order to take the effects of rubber fatigue into account. Bearings can consequently stand accidental excess load and deformations considerably more important than those of the calculation values without breaking. Experience shows that even when compression loads are sufficient to break steel plates, the bearing stands the load yet”.

The design and appearance of this type of bearing seem simple which was one of the reasons of damage in service, as it was all too often installed incorrectly or neglecting certain important aspects. Moreover the first types designed by French engineers mostly called on devices made of external steel reinforcing plates or with open air sections of steel reinforcing plates. Such arrangements of the plates led to sometime serious steel corrosion causing partial or total disappearance of the plate and thus modifying the product’s functioning.

The new devices with fully embedded plates no longer present this inconvenience. If bearings are correctly installed on concrete plinth, thus preventing

them from lying in a pool of water that might come from a leak in the expansion joint watertightness, one can assess the durability of these products as very high. This last point, which has been dealt with a lot in the [AFG 94] reference, was confirmed by the recent study conclusions which can be summed up as follows:

“If one assumes that the products had characteristics complying with the Technical Guide N°4 from the manufacturing on, one can conclude that:

- the ultimate elongation tends to decrease by ageing;
- on the other hand, the evolution of tensile strength at break is not shown;
- the IRHD hardness (International Rubber Hardness Degree) tends to increase, which corroborates the observations on the evolution of the G modulus in other studies... (there exists a relation between elastomer hardness and the value of the G modulus.);
- the evolution of the characteristics after heat tests denotes an insufficient core baking during manufacture” [SET 05].

Of course, durability also depends on a formulation adapted to the context. For example in countries where termites delight in this organic matter based product, it is important to allow for an anti-termite additive. Regarding oils, elastomer's behavior is relatively mediocre [COL 48] and the following arrangement should be planned on the bearing in order to avoid a possible contamination: placing on a concrete plinth.

There is no denying that the coming of this product was an important evolution in the area of bridge bearings as it brought simplicity, suppleness in the functioning of the structure, reliability, low costs and durability on this important device on a bridge. These advantages were acknowledged and appreciated very quickly and there exists almost no competing product for structures with a vertical load lower than 20 MN.

The French national market for this type of bearings is about 50 to 60 m³ per year.

12.2.4. Elastomeric pot bearings

12.2.4.1. General operating principal

This bearing type uses another particularity of elastomer which is its deformability that makes it similar to liquid (see section 12.1.1.2 and 12.2.2 above). In this case the elastomer block is enclosed in a pot.

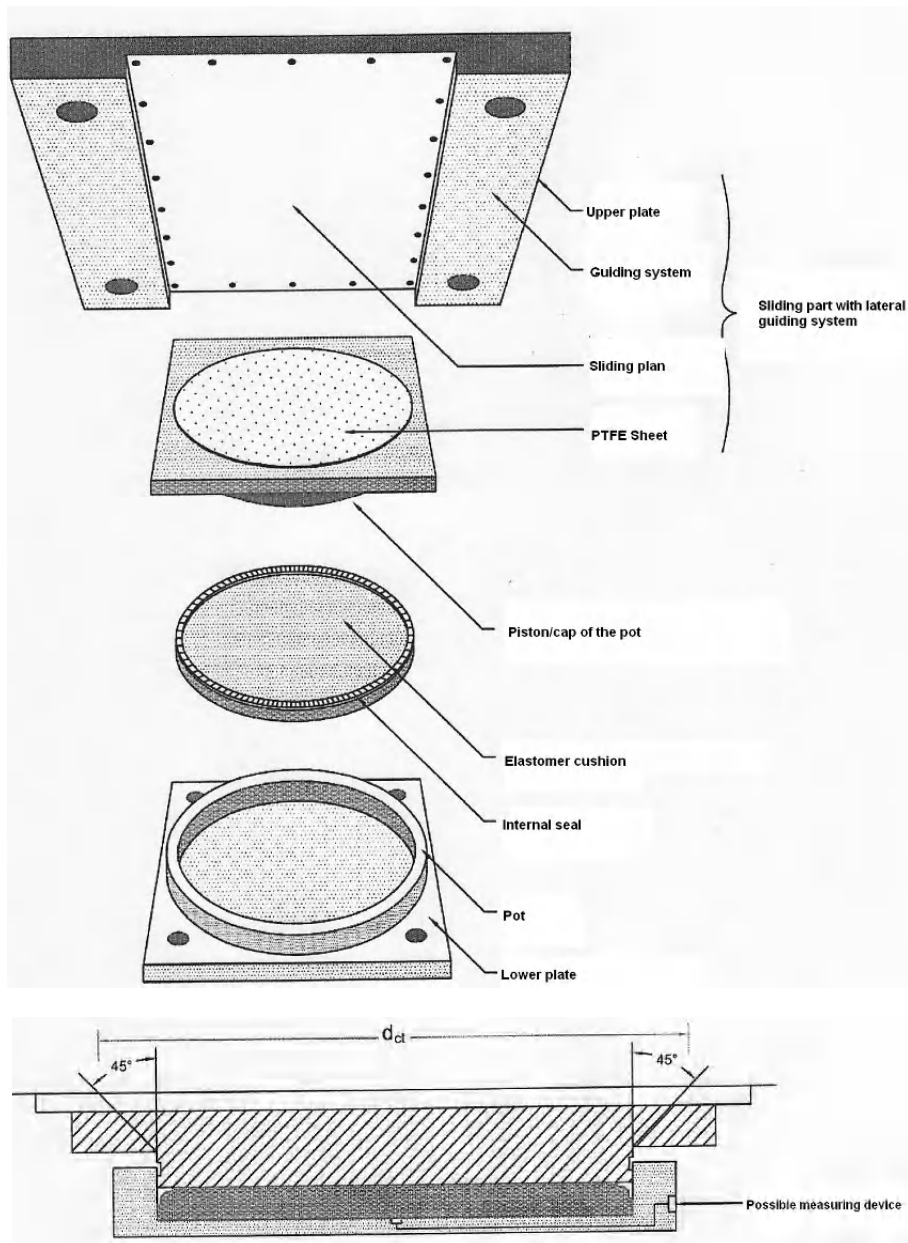


Figure 12.5. *Diagram of the various elements of a pot bearing*

The principle of a pot bearing (PB) consists of a cylindrical elastomer cushion enclosed in a pot and being subjected to a load through a piston forming the cap of the pot. The elastomer can only deform at a constant volume which enables it to transmit heavy loads and allows rotation imposed by the structure. A pot bearing is thus made of three main parts which can each receive particular equipment. These three parts, which offer the three degrees of freedom in rotation, may be supplemented with a fourth one aiming at ensuring one or two additional degrees of freedom in movement. Although the principle of a fourth part is usually adapted to the context of pot bearings, it can also be found in other types of bearings [SET 07].

12.2.4.2. *Principles of performance verifications*

The [AFN 04-5] standard specifies the principles of performance verifications that this type of bearing must meet. We can define them as follows:

- verifications under vertical stress:
 - pressure in the PTFE – polytetrafluoroethylene or Teflon[®] – sliding material (in the case of sliding pot bearings),
 - pressure in rubber;
- longitudinal horizontal stress for sliding pot bearings. Notion of “start of sliding”;
- longitudinal horizontal stress for fixed pot bearings;
- linear variations with friction coefficients;
- braking;
- other verifications: rotations, metallic elements, slide plates, etc.

12.2.4.3. *The various products*

There are almost no fundamental variants of the concept shown on the cross-section Figure 12.5. Sliding elements, measuring devices and so on are added to the basic product to ensure adaptation to other functional contexts or to widen the field of use.

12.2.4.4. *Method of elaboration and manufacture*

The metal parts are manufactured in a factory like any other metal part. The elastomeric part is elaborated as described in section 12.3.4 and the formulation is adapted to this field of use. Depending on the manufacturers, the elastomeric part may be natural rubber or synthetic elastomer (mainly Neoprene[®]).

12.2.4.5. *Advantages and limits: durability*

Pot Bearings (PB) are the bearing type used most after Laminated Elastomeric Bearings (LEB). This ranking is due to their principle of enabling high vertical loads combined with small overall dimensions, especially low thickness. Another advantage is their simple design which allows streamline of manufacture [SET 07].

On the other hand, the rotational capacity is limited by the capacities of the elastomer cushion and by the free play of the piston movement in the pot. Moreover, most of the flaws on pot bearings concern this point but one has to put this into perspective considering the number of structures equipped with this model around the world.

Taken as whole, their durability is still satisfactory and incidents related to faulty placement are rare, mainly because this product is heavy and its handling is complex, leading to significant consideration by placement teams before implementation. Please see standard [AFN 92].

12.2.5. *Bearings with polyurethane discs*

During recent years a new concept appeared on the basis of a patent that probably dates back to 1974. It consists of removing the pot of the pot bearings and keeping only the cushion which is in this case a disc of a sort of plastic (seemingly a urethane polyester) [SAN 06] (see Figure 12.6). As far as rotation is concerned, the capacity remains close to that of a pot bearing but it seems that immediate settlement under load is not controlled. However, the acceptable stress under load remains low compared to our regulations [SET 07], [AFN 04].

The field of use of this device, far cheaper than pot bearings, should find its place between those of laminated elastomeric bearings and pot bearings.

12.3. Expansion joints

12.3.1. *Role and function of a road bridge expansion joint*

Because of the changes in the length of the structure thus moving from the structure elements at its side, devices have to be installed at the ends of a bridge. They will fulfill:

- the following two functions:
 - allow freedom of dilatation and movement of the bridge,
 - withstand traffic and provide road surface continuity;

- and the following two conditions:
- ensure good watertightness or water drainage,
- not be a source of noise or vibration.

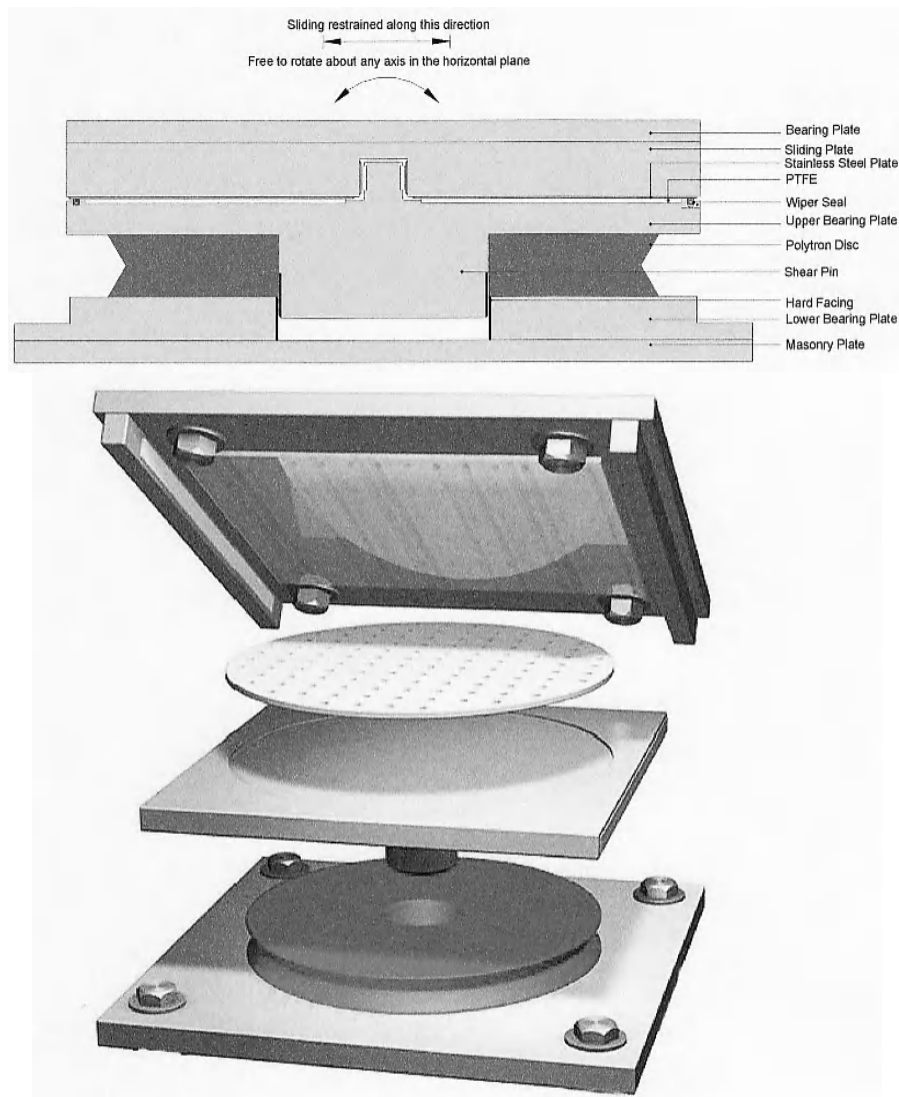


Figure 12.6. Diagram of the structure of a disc bearing [SAN 06]

When reading these elements, we can understand why expansion joint designers became quickly interested in the intrinsic characteristics of elastomers, able to answer their questions:

- It can elongate considerably, reaching lengths much higher than its original one and without any noticeable strain and apparent damage (see section 12.1.1.2).

- *Watertightness* of this material. This is an invaluable characteristic when combined with the previous one dealing with deformability. Besides watertightness, a good resistance to water is also necessary. In this case one should take this into account while setting the formulation as this characteristic essentially depends on the composition of the mixture, not on the basic elastomer; the use of water-soluble or hydrophilic ingredients must be avoided. We should bear in mind that, if water lets rubber swell, absorption is slow and low (about a few percent points maximum), which is also favorable.

- Excellent *abrasion resistance* of elastomers. There again the formulation is important: in order to have good abrasion resistance against rough surfaces (tires), relatively rigid mixtures with much carbon black and vulcanized with a vigorous vulcanizing accelerator are necessary. Note that to have good abrasion resistance in order to withstand fine particles (such as sand or grit), the use of soft vulcanizate is required [COL 48].

- Finally the role of elastomer consisting in *cushioning vibrations* seemed relevant in this field of use in order to prevent impacts caused by traffic from being transmitted to the structure and to prevent resonance in the latter with amplifying effects that may irritate people living in the neighborhood of such structures.

In addition to these characteristics, the fact that it was possible to manufacture complex forms by casting or extrusion and to obtain metal-elastomer combinations was a significant asset. Moreover one turned the opportunity to regularize this feature in all steel parts by ensuring corrosion protection of those pieces sensitive to many kinds of adverse conditions in the area of the road (de-icing salts, pollution, etc.).

In conclusion, elastomer is indeed an answer to the functions as well as conditions a joint has to fulfill.

The first road bridge expansion joint models that used elastomer were the FT joints elaborated in 1958 for a road diversion from the commune of Fontenay Trésigny but their development really started around 1966 (that is to say along with the development of the elastomer industry).

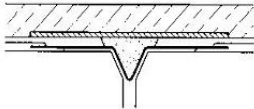
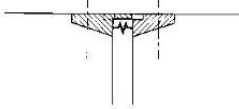
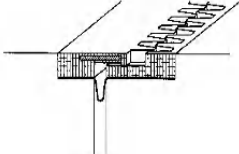
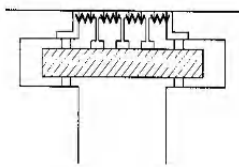
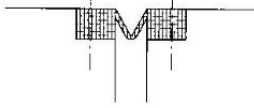
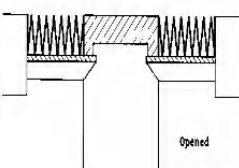
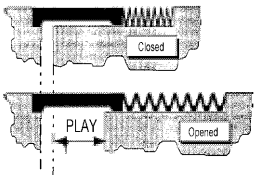
Joint family	Functioning principle	Joint family	Functioning Principle
Buried expansion joint		Cantilever expansion joint	
Flexible expansion joint		Supported expansion joint with elements sliding on a stand and a comb	
Nosing expansion joint		Modular expansion joint With supporting beam	
Mat expansion joint by deformation of a mat	 Opened	Modular expansion joint With cantilever support	 Opened
Mat expansion joint with a "spring"			

Table 12.1. The various joint families

12.3.2. The various product families

The advantages of elastomer were acknowledged very quickly so that joints containing little or no elastomer at all are almost nonexistent. As a matter of fact elastomer is used in one form or another in many applications: as additive to bitumen (SBS polymer, rubber powder, etc.), sealing profile, shear pad, deformable mass, corrosion protection, sealing and runoff water drainage bar etc.

The various joint models have been grouped in several families, within the framework of European work for CE-marking on road bridge expansion joints, according to their functioning principle, which can be summed up in Table 12.1.

Table 12.2 shows in a very simplified way the field of use of each family depending on the movement capacity.

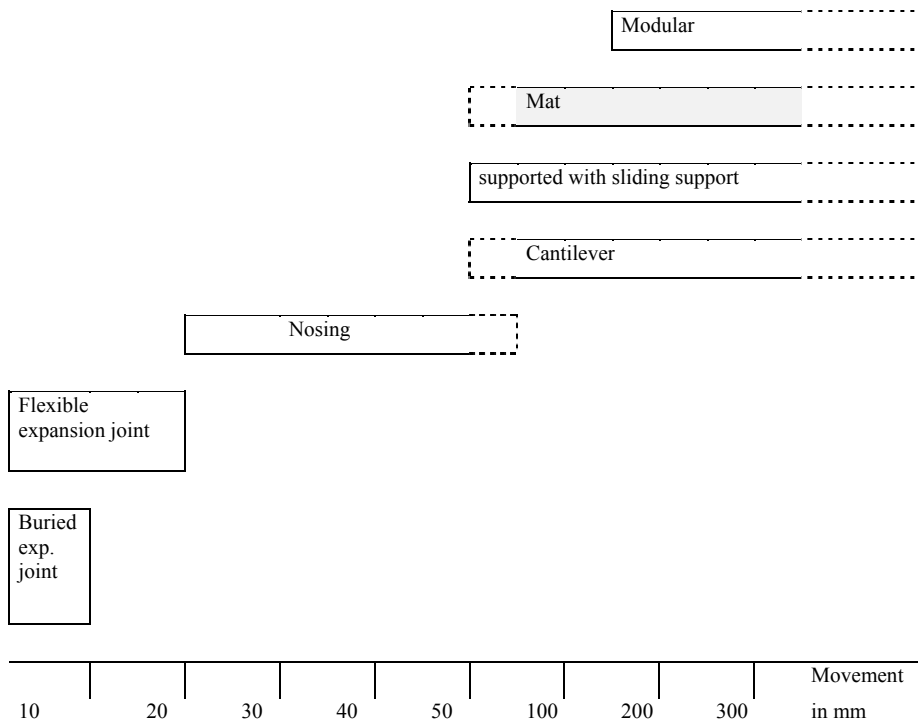


Table 12.2. Field of use of the various joint families depending on the movement capacity

12.3.3. Method of elaboration, manufacturing principle

Sealing profiles, which are inserted by force between the metal profiles by catching (or by engagement) into an adapted sealing groove are fabricated by extrusion (see section 12.3.1.2) to sections of at least 25 m each. It is conceivable to fabricate sections with higher lengths in order to avoid the construction of a junction on site, which would be synonymous with time wasting and virtually guarantees imperfections (Figure 12.7).

If not done this way, fabrication is made by casting (Figure 12.8) and elastomer lends itself well to a great variety of forms providing many solutions to the problems in question, as we can see in Table 12.1.

For some of the products gained by casting, in particular for the one illustrated on Figure 12.8, elastomer intervenes in the movement function by plot distortion, then as impact noise reducer and contributes to abrasion resistance at the surface, and finally as corrosion protection on the external faces of metal parts. Sometimes the surface subjected to abrasion may be formulated for this function and thus different from the parts subjected to shearing by distortion.

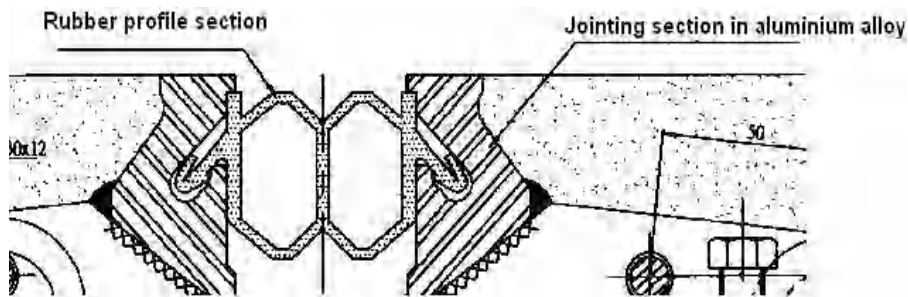


Figure 12.7. Example of a placement by engagement
(Joint Model GTA R30/R50, with the kind permission of RCA)

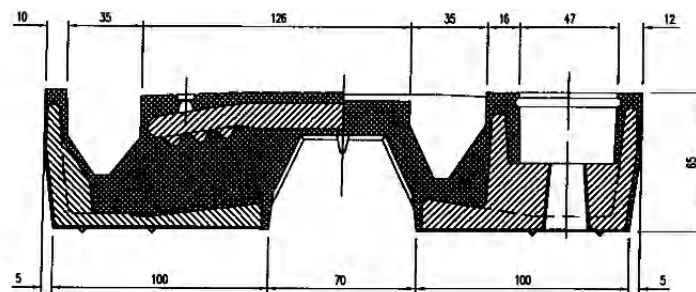


Figure 12.8. Example of fabrication by casting
(joint model M100, with the kind permission of Freyssinet)

12.3.4. Advantages and limitations: durability

Elastomer turns out to be an irreplaceable material in the road bridge expansion joint area. However the elaboration of the forms (i.e. for the correct fixation of the

elastomeric profile into its housing, or to make it possible for a profile to compress while keeping an adequate shape), of the formulae to meet requirements that might be sometimes contradictory (abrasion resistance and low stress under shear), of good behavior to service conditions, the search for a satisfactory corrosion protection, etc., are the reasons why designers and rubber producers sometimes have difficulties in bringing fully satisfactory answers and are forced to make compromises.

Not only service conditions, particularly road traffic (the influence of vehicles' wheels especially heavy goods vehicles, braking, etc.) but also the products we can find on the road track (ozone, de-icing salts, engine discharge, industrial effluents, etc.) make the situation complicated and are the reasons why there is room for improvement in the field of joint resistance in general, and not only for an elastomer. We have to know that, if this equipment costs around 1% of the investment cost of a whole bridge, its maintenance takes close to 8 to 9% of the credits for bridge maintenance, not to mention discomfort for drivers during maintenance work and the risk of an accident in case a piece happens to break when cars are passing (which is not an everyday occurrence).

That being so, despite these disadvantages, elastomer is still, for the time being, a preferred material and is unavoidable in road bridge expansion joints design.

To give some idea of the importance of the market, one has to know that around 21 km of expansion joints for road bridges are installed every year. Around $\frac{3}{4}$ of these are flexible expansion joints or buried expansion joints (see Table 12.2) and about 80% of the last $\frac{1}{4}$ deals with joints whose movement capacity does not exceed 8 cm.

There also exist joints for railway bridges with ballast but the market for these remains confidential despite the development of high-speed lines.

12.4. Sealing joints

In this rather small domain, elastomer brings its qualities such as watertightness, compression resistance and ageing resistance for the sealing between two parts in a structure. The techniques used are not peculiar to civil engineering and come from the building area.

When sealing between concrete cornice elements is to be ensured by a joint that will be poured in situ, an elastomer is used, mainly polyurethane in the form of mastic.

Whether to ensure sealing between elements of drainage pipes on a bridge or for a gutter-shaped drain in a gutter cornice, prefabricated elastomer joints are used. These are mostly modified ethylene-propylene-diene (EPDM rubber) that are standard and in this case the joint is shaped to match the form of the drain (Figures 12.9 and 12.10). The elastomer type is also adapted to the nature of the transported effluents: when a hydrocarbon is present, a nitrile elastomer should be used.

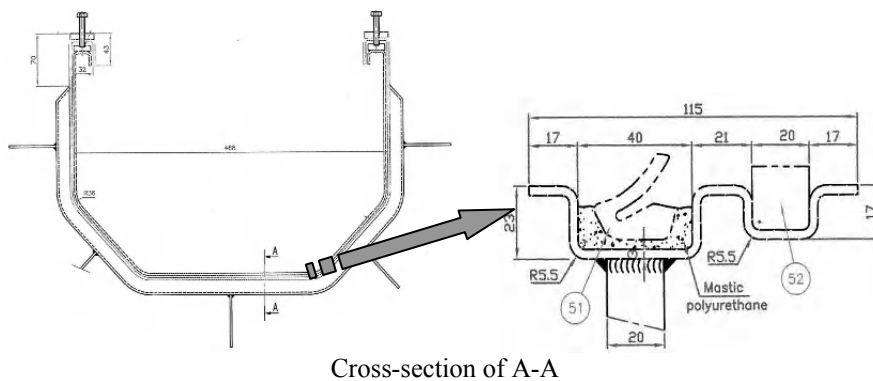


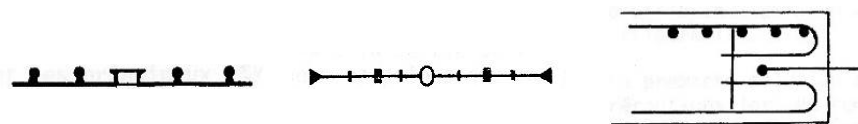
Figure 12.9. A cross-section of a sealing joint in the cornice gutter to be seen on the left view (RCA document)



Figure 12.10. Example of a joint of a rain water discharge drain (with the kind permission of Pont à Mousson SA)

In the case of retaining walls made of reinforced concrete, the presence of cuts is technically essential (differential settlement, uncontrolled cracking induced by shrinkage, thermal expansion, etc.). Depending on the site and its purpose, particularly when structures are under the water table level, it is essential to avoid stains in facing walls caused by water. To that end sealing strips will be put into place in the joints. Their shape will vary according to the way they will be placed into the section of the wall, the pressures to which they are submitted and the range

of expansion movements (at a wall level). The durability and elasticity of elastomer make it, in this area, preferable to its competitor: PVC.



Example of a sealing strip implemented on the bottom of a shutter. There exist models for which expansion is not possible.

Example of a sealing strip embedded in concrete. The shape of the central part is adapted to the expansion capacity.

Principle of implementation of a sealing strip embedded in concrete.

Figure 12.11. *Examples of sealing strips*

12.5. Bridges deck waterproofing

12.5.1. Role and function of a waterproofing

Civil engineering structures are sensitive to the action of water as it can either dissolve certain concrete constituents or corrode reinforcement elements (concrete reinforcement or prestressing cables). For a long time, designers of bridges and other civil engineering structures (cut and covers, tunnels, etc.) have added a water-proof barrier between the outside world and the structure in order to provide protection against these conditions.

12.5.2. The various family products. Method of elaboration and fabrication

Although the oldest waterproofing technique still being used remains asphalt, bridge designers have nevertheless tried to put the advantages of elastomers, principally watertightness and durability, to good use. However, difficulties of adaptation to the context of functioning as a bridge waterproofing (support of the traffic, braking loads transfer, etc.) slowed down their development over a long period of time. One can hold up as an example the failures of ready-made butyl membranes for which bonding on concrete was a problem and on which bituminous mixes did not adhere! These membranes are well adapted to tunnels, retaining basins, etc. (see Chapter 10) but for bridge waterproofing, elastomers are used in the following forms:

- as a polyurethane resin (PUR) in liquid waterproofing systems. In this case, fabrication is carried out on site by mixing the two parts making up this material at the time of spraying on the concrete support.

- as a bitumen-improving polymer. It is principally the SBS polymer that goes into the formulation of modified bitumen (BmP¹) intended for ready-made bitumen sheets and processes by high cadence means. These polymers enabled a better behavior of bitumen at low temperatures in service and to fatigue.

12.5.3. *Advantages and limits: durability*

Polyurethane-based bridge waterproofings perform satisfactorily concerning water-tightness. In particular their ageing resistance, their elasticity at fissuring at low temperatures, their resistance to weathering etc., are valued.

On the other hand, the main difficulty remains the junction with the upper layers wearing course. In order to transfer traffic loads which mainly translates into shearing between the two surfaces, a hitch up system has to be put in place but it is still not perfect, due to the lack of affinity between polyurethane after it has been polymerized and the bituminous mix. This leads particularly to compactness failures at the surface of waterproofing. In the presence of water, these may reduce the lifetime of the mix lying over the waterproofing layer.

Moreover the high cost of this type of waterproofing is, at the present time, a real curb on its development.

Finally, laying this coat at end-of-life, to change the waterproofing type or during surfacing course repair, turns out to be particularly difficult and very expensive anyway.

Concerning geosynthetic barriers, the choice between elastomer and modified bitumen will be made according to technical criteria depending on the site: simplicity and difficult placing, gas welding easier than welding of synthetic geosynthetic barriers, good resistance to perforation, ease of repair of elastomers. On the other hand, the price and a decreased resistance to hydrocarbons are more in favor of modified bitumen.

Polyurethane resins represent hardly 10% of the national market for waterproofing of new bridges (400 to 500,000 m² of waterproofing every year) and about 55% of the market concerns systems made of sheets or devices using modified bitumen. However, the part of elastomer for the latter is low.

¹ BmP: bitumen modified by polymer

12.6. Anti-seismic devices

Elastomers are to be found in this particular domain of rapid dynamic actions, earthquakes, and has by extension application in the area of road restraint systems. These are fields of application of the following characteristics of elastomers:

- suppleness in a direction corresponding to the horizontal plane and
- filtering of vibration frequencies.

To ensure insulation, elements are installed between the cause of the vibrations and its support. These elements are flexible enough to enable transmission possibilities as low as possible at the nominal operating speed by decreasing the system's own frequency. One can also install damping elements which lower the response in the whole system.

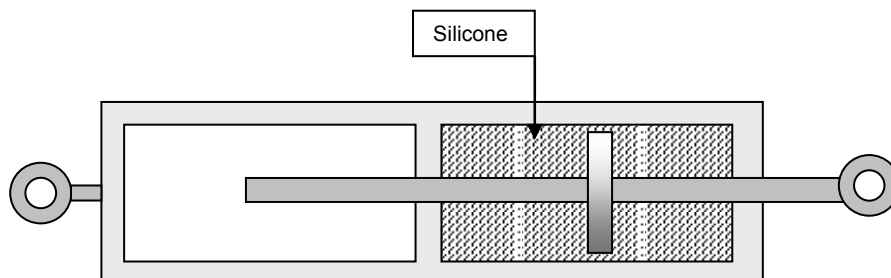


Figure 12.12. *Earthquake damping device using the properties of silicone*

This filtering, which is commonly called anti-seismic insulation, thus consists of putting between the soil and the structure, at foundation level, elements or systems decreasing the frequency in the soil-foundation-structure set to be insulated. It is obtained by using bearings similar to those used for bridges. As such devices are only supple in the horizontal and not in the vertical way, only the horizontal movement is filtered; the effect for the vertical seism remains almost unchanged. It is rarely a problem for the structures anyway.

This filtering is partial as the seismic frequency range may sometimes be very low (0.1 Hz); such low frequencies would require resort to extremely supple and relatively unstable devices. One merely decreases considerably the frequency (between 0.5 and 1 Hz in most cases) which enables to divide by 2 or 3, or even more, the accelerations transmitted to the structure, compared to a traditional foundation [AFG 94].

Another characteristic of elastomers which has been exploited within this domain is related to the intermediate state between the solid and the liquid state. Elastomer (a silicone material) is used in dampers made of one cylinder in which a piston circulates in a mass of elastomer of an adapted formulation. This elastomer behaves like a very viscous liquid and brakes the movement of the piston thus providing a damping effect (Figure 12.12). This principle has been used in various forms to ensure structural resistance to earthquakes.

This is also how the impact transmitter device “Transpec®” works. It is intended for safety barriers where they cross a bridge expansion joint and aims to jam the movement of barrier profiles at the time of an impact onto the road restraint system in order to ensure the mechanical continuity of the safety barrier, while allowing the slower movements due to thermal effects. Unlike previous systems in which elastomer is directly submitted to the stress within the piston, the Transpec® device (Freyssinet patent) uses elastomer as trigger by acting onto the anchorage keys of a prestressing wire strand. The blocking forces may then be noticeably more significant despite a far lower volume of elastomer.

12.7. General reflections on sustainable development

If, at the very beginning, the basic constituent of an elastomer is a matter harvested in nature and recyclable, its multiple transformations to reach the state of end product lead to relatively stable chemical formulas. There is relatively little release of by-products in the environment. The same goes for synthetic elastomers.

The production of an elastomer requires a lot of energy. For information, 4 to 5 kW.h are necessary to fabricate one cubic decimeter of bearing. This does not include the energy for the fabrication of the various constituents of the formula.

From this point of view, this is not a very favorable product in terms of greenhouse gas emissions! But it is clear that the advantages of this product make it difficult to do without and that only the efforts of the manufacturers will lead to energy-saving methods of fabrication.

The elastomers described in this chapter are used within a relatively limited working range compared to the potential of these materials. Thereby, they are not sensitive to fatigue and have a satisfactory durability. Moreover, their resistance to weathering or to the products to be found in the surroundings of the structures concerned is excellent on condition that their formulation is carefully prepared and adapted. This is confirmed by the experience of almost half a century of use in this domain.

There remains the question of the management of the elastomer parts at the end of their life cycle, in all products containing some. It is obvious that this material is very difficult to recycle, as one can see in the case of car tires. The solution consisting of burning it in ovens to produce energy, has been contemplated because rubber is an organic material which is moreover made up of carbon black and thus eminently combustible. This is however limited and must go with costly and delicate precautions as this burning releases chlorine that is particularly toxic.

Moreover, it is difficult to extract the “elastomer” part of the products made up of metal inserts adhering on it. Despite these difficulties, there exist two main principles for recovering elastomer:

- *Rubber powder*. The elastomer part is transformed into powder by crushing in adapted devices. This powder may then be used as filler in an elastomer formulation (see section 12.1.1.2). It may also be inserted in a bitumen formulation in order to improve some of its characteristics at an affordable price (bituminous mixes or bitumen used in certain types of expansion joints such as flexible expansion joints. There also exist other applications outside the field of civil engineering.

- *Regenerate action*. This consists of breaking the elastomeric bonds by means of chemical processes. One can then use the regenerated product in a rubber formula by mixing it with a non-vulcanized one.

Even so, it is still difficult to recycle this material in its final state. If it is not considered as a polluting agent, it is still cumbersome waste!

12.8. Conclusions

As a conclusion to this chapter, we can consider that the qualities of elastomers made it possible to bring technically neat solutions at quite affordable costs for the taxpayer to this equipment area where the questions of watertightness, follow-up of expansion movements, vibration filtering, etc., are recurrent.

The amount of elastomer being used and the developments made over the last decades are the result of its advantages.

12.9. Acknowledgements

The author is keen to warmly thank M. J. Vorin, Manager of the SNAC (one of the main French rubber bearing manufacturing companies) for his invaluable advice and his help in the writing of this chapter.

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PART 4

Composite Materials, Tensile Structures,
Textile Architecture and Timber

Chapter 13

Composite Materials and Construction

13.1. Introduction

Transport, industry or sport and leisure domains have already been using composite materials for a number of years in order to drive the concepts and performances of many different systems forwards. These sectors have given their letters patent to these new engineering materials, by associating them with high-tech fields of space or with competition.

In this chapter, we are essentially interested in showing the composites reserved for domains which require mechanical performances of structures, putting aside reinforced plastics known as “large diffusion” plastics (facades, panels, etc.). Because these “high performance” materials are capable of bringing a real significant added value through innovation, it is only possible to see them integrated and accepted in this economic sector where they are hardly present today. This is due to the nature, the volume, the costs, the customs and the concrete/steel culture traditionally associated with the construction sector.

This innovation must be guided by the specificities of these “custom-built” materials. Iron and its alloys guided Eiffel in his designs for a complete break with existing corbelling concepts, which brought ideas for constructions, which were unimaginable at the time, into reach. In addition to this, it allowed for an unrivalled lightness, which made steel an unquestionable metal to be used in large constructions, despite associated technology with higher costs in relation to classical Roman masonry. We owe it to ourselves to put composite materials in such a

Chapter written by Jean-François CARON.

perspective by identifying the characteristics (lightness, flexibility, etc.) and imagining custom-built structures which will make them as unquestionable tomorrow for use in construction as they are today for skis or tennis rackets. If the aforementioned steel is a good example of such innovative success, we must not, however, forget that it was first used in classical corbelling principles, by replacing rubble with compressed mortar (Iron Bridge on the River Severn in Coalbrookdale, England, 1774). Such a phase is still necessary to establish new materials (technical implementation tests, sustainability, etc.).

Composites do not derogate from this irrefutable fact. Today, composites are too often used as a simple replacement for steel in structures which have been optimized for many decades, and in which the most flexible composite, even if it has the advantage of being lighter, only has a small chance of being used. A breaking innovation must absolutely be created by putting composites into such a schema. Their performances have to be listed, even those which may be seen as a handicap in a traditional application. Contrary to steel or concrete, composites, just like reeds, bend but do not break.

For an easy transition, we should consider the example of wood, a “natural” composite material, a lignin matrix reinforced with cellulose fibers. This is proof that we can build in more flexible and different ways. It also allows us to question what composites can bring (either alone or combined) in terms of sustainable development and ecological impact, CO₂ emissions and life cycle analyses of constructions. Subject to considering the total lifespan of constructions, composites may turn out to be precious attributes for the environment. But prejudices concerning plastics and resins will be long lasting and, then, only truly innovative constructive systems will be able to convince those giving orders.

After a few general remarks and a succinct presentation of structural composites used in the construction sector, an attempt will be made to underline the specific characteristics which indicated *a priori* good candidates. Without claiming to be exhaustive, we will then number the existing significant and demonstrative applications which are written into an innovative schema through reproduction. The aspects linked to reinforcement and structure repair which appear in another chapter, will be set aside, as will the small or non-structural uses. Current standardizations and recommendations will be approached, as well as examples of innovative experimental applications in breaking, which may turn into evolutionary points for constructive systems controlled by the characteristics of a material.

Finally, a few elements linked to composites and to environmental constraints available in literature will also be raised and commented on.

13.2. Composites used in construction

13.2.1. General remarks

In this chapter, we define *composite materials* as a group of organic or mineral fibers bonded by an organic matrix. This connection between form and matter gives the group a set of new characteristics which cannot be guaranteed by isolated components, in terms of rigidity, varied physical properties (thermal, acoustic, etc.) fire resistance or durability. Groups not including organic materials such as cement matrices or mortars reinforced by organic fibers will be excluded, since, even though they represent a large volume of research and work today (plant fibers, for example), they do not traditionally belong to the field of structural composites (see [BAL 08], for example). Here, we are more interested in high performing mechanical groups, whose mechanical function presumes a strong cohesion which allows good transfers by matrix shearing and, therefore, important fiber tensions. Effectively, if the role of fibers is to ensure resistance and rigidity, it is only possible through close contact between the fiber and the matrix which transforms the bundle, a low resistance group of fibers working independently from each other, into a high performing solid rod. This fiber/matrix bond is also guaranteed by using a surface treatment from the fiber. This treatment involves materials with low porosity and specifically raised stiffness and resistance levels (in relation to the density), which excludes fibrous materials such as wools used for insulation, for example.

13.2.2. Fibers

We previously saw that many types of strengthening agents are currently available:

- mineral fibers;
- organic fibers;
- carbon fibers.

Mineral fibers are essentially *glass fibers* (let us forget asbestos fibers) produced by drawing melted glass across a platinum based alloy die heated by the Joule effect, amongst which a large range is intended for making composites.

Organic materials are essentially represented by *carbon and aramid fibers*.

Carbon fibers are made by two main processes: from residual bitumen or polyacrylonitrile (PAN). The best performers are made from heat oxidized PAN threads (300°C) then carbonized (1,500°C) under a nitrogen atmosphere. These are widely used in making high performance composites. *Aramid fibers* are obtained

from aromatic polyamides. As an anecdote, we can also cite polyethylene and natural fibers, new-comers which are being intensely researched (see [CHA 07] for example) because they open up very interesting perspectives but are still not used for structural applications. The difficulties to be overcome are, for example, to be able to guarantee a fiber's integrity from the moment it is picked until it is used. Or, even, a constantly high quality must be proposed to manufacturers, from one picking to the next. Indeed, by the yardstick of sustainable development and subject to responsible culture, these fibers could play an important role over the next few years. In this respect, hemp is very interesting [BAL 08]. For a long time, France has been an important provider of this plant which needs little water, little weeding or insecticides. Rigid and resistant, however, it is only used today for insulation by using the hemp fibers (fibers with weak mechanical characteristics because it deteriorates during the picking process), because, paradoxically, the science of picking, drying and threading has become somewhat lost with the appearance of synthetic fibers.

There are also *inorganic fibers* (boron) and *ceramic fibers* (silicium carbide) which are currently not used in construction applications.

The different fibers retained for this chapter are presented diagrammatically in Table 13.1.

Synthetically, the application type for these different fibers is closely linked to their properties. *Carbon* is light, rigid and resistant, but brittle in its rupture type (brutal rupture). Its sustainability and strength under fatigue or permanent loads is excellent. Its price is high, and relatively fluctuating, so much so that it is difficult to give a reliable figure (in 2008, around 50€ for a HR fiber). For some dynamic applications (shocks, impacts or explosions) *aramid* fibers are preferable, as they benefit from more ductile behavior under compression, due to their capacity to damage under this strain, to dissipate energy that carbon restores in an extremely brutal way. The price of these fibers is around the same as carbon. These two fibers are intended for structures under great strains and are considered to be costly. Today, we find them in tense systems such as cables or the intrados of beams. We will see that for cases of reinforcement or repair on constructions, carbon is widely chosen because of its stiffness and also its ease of implementation, although its high strength capacity is not really involved.

Glass fiber is still somewhat considered as being able to play an important role in terms of structure. This is due to its stiffness which is greatly different from that of steel; a stiffness which means that it is irreplaceable in a structure designed solely for steel. This is also due to the fact that its behavior under constant loading has not been studied in great detail, which has led to unforeseen and premature ruptures in some cable applications. Glass R responds slightly to these defects but it is more

expensive and is used today rather as a carbon replacement in aeronautic structures. Glass C was developed to solve the problem of glass having a bad natural resistance in basic environments for reinforcing cement matrices. Glass E is far from being the most used fiber, since it constitutes 95% of the composites which are made (large diffusion, essentially) and its value, without a doubt, is not fairly judged. Its capacity to deform elastically (1 to 2% for the limit strain), its intermediate rigidity between wood and aluminum in a GFRF composite (*Glass Fiber Reinforced Plastic*), its low density and price (approx. 2 to 4€/kg) compatible with habits in the construction domain, can make it a serious candidate for new structural applications. Some of these application will be discussed in this chapter.

Fiber nature	Base material	Density	Quality	Modulus E (Gpa)
Mineral	Glass	≈ 2.5	C $\Leftrightarrow$ good chemical resistance	70
			D $\Leftrightarrow$ good dielectric properties	50
			E $\Leftrightarrow$ good electric properties	70
			R and S $\Leftrightarrow$ high mechanical resistance	85
Organic	Aromatic polyamide ("aramid")	≈ 1.45	standard	65
			High modulus	130
			New generation	≥ 140
Carbon		≈ 1.7	HR $\Leftrightarrow$ high mechanical resistance	230
			HM $\Leftrightarrow$ high modulus	390
			VHM $\Leftrightarrow$ very high modulus	≥ 400

Table 13.1. Main fibers used in construction (according to [MOU 06])

13.2.3. *Different available fiber architecture*

According to the desired type of strengthening, different architecture are available. In construction, *1D shapes* are essentially used, meaning:

- *a thread* made of parallel elementary filaments, with or without twist/torsion, continuous (very long length) or cut (3 to 5 mm);
- *roving*, a set of continuous and parallel filaments, without twist;
- *a band*, made of continuous threads, in parallel side by side, defined by its width and mass in m^2 .

2D shapes are, however, available:

- fabrics, canvasses or taffetas, satins, serges, high modulus fabrics, one-directional or multi-dimensional (3D, 4D according to weaving directions);
- matts, fabric sheets of unwoven, continuous or discontinuous threads, randomly inserted into a plan.

13.2.4. *Matrices*

Two main composite families are encountered, according to whether the polymer constituting the matrix has a linear structure, meaning thermoplastic behavior, or therefore cross-linked structure, meaning thermosetting behavior.

For *thermoplastic matrices*, technology is currently in full evolution. Until very recently, we were essentially seeing polymers which were rather cheap which make products to be used in a setting with limited temperatures but which are easy to implement. Some varieties have large levels of resiliency and good thermal properties (polyether sulfate or polyether ketone, for example). Their use in civil engineering has only remained marginal.

Current research is directed toward high modulus copolymers, whose vitreous transition temperature for amorphous sequences is higher than working temperatures. It is, however, too early to consider them as materials which can be used in civil engineering. We will speak of polyamides or PEEKs.

Thermosetting matrices or *resin matrices* have mechanical and thermomechanical properties which are clearly higher than the aforementioned matrices. They are implemented in monomer fluid state, and their hardening time depends on the polymerization reaction at work. The main problem is that these matrices are difficult to recycle.

Those mainly encountered are:

- unsaturated polyesters (UPE) and their derivatives, such as vinylesters, which, when reinforced by glass fiber, allow us to obtain economical materials which can be used at room temperature;
- epoxide resins (EP) which have better mechanical, chemical and electric properties than the UPEs, but whose cost is relatively higher; they allow us to manufacture materials which can be used up to 150 or 200°C.

These two resin families are practically the only ones to be currently used in construction. It is suitable to add here also:

- phenolic resins which have low plasticity; the mechanical characteristics are not very good but the materials obtained from them can resist up to 400°C; however, their usage may be limited due to health reasons (components with carcinogenic risks);
- polyamide resins which allow us to obtain materials, which can be used at higher temperatures (400°C) but are particularly expensive;
- melamine resins with mechanical properties which are analogue compared to phenolic resins. Their electric properties are interesting. They are only lightly flammable and have a good resistance to abrasion. They can be colored and are used to make protective and decorative panels;
- silicone resins which are used for electric insulation; associated with glass fibers, they are used due to their great heat resistance.

13.2.5. Transformation processes and semi-products for construction

Here, it is not a question of laying out in great detail the multiple transformation processes which exist for composite materials [GAY 05], [REY 98]. Here, we will limit ourselves to techniques used or likely to be used in construction and mainly in civil engineering.

In fact, if molding processes which are not, or are not very, compatible (since the need for a mold is expensive) with the small construction series were excluded, it really only leave us with monolithic or sandwich plates made from pre-pregs and pultruded profiles which can get their share of the limelight.

Pre-pregs are fibrous strengthening agents (one-directional or fabrics) coated with viscous resin and ready to use, which must be stored at low temperatures and used within strictly limited times. Their use makes it possible to master the quality of plates and products obtained from these prefabricated layers. Combining these

skins and a core (light materials, foam, honeycombs, balsa wood, or others) makes up what is known as a “sandwich structured composite/material”, which is intended for flexure applications. The skin composites support the tension/compression strains, the core ensures the repeated transversal shearing. We find that there are many panel structures made by using this principle, as we will see further on.

Pultruded profiles are used widely. The opposite of extrusion, this involves pulling the unpolymerized fiber/resin material across a die which is responsible for polymerizing at defined temperatures and pressures by using the containment induced by exerted tension. This technique, specific to composite materials, has been made possible thanks to the resistance of the fibers on which the tension is exerted. This is without a doubt the only fabrication process continuously available for these materials, and it is because of this that it is extremely interesting as it is relatively economical. These materials present a relative lateral weakness and a rupture mode the same for a “natural” pultruded reed. Pull winding improves this aspect by adding fibers outside the axis at the pultruded profiles. The possible structural solutions are beam based, in the spirit of metal construction. Many applications carried out in this way, highlight the low stiffness and assembly difficulties inherent to these pultruded profiles, either in carbon or glass. Used as they are to replace a steel profile, they undoubtedly only stand a small chance of being selected, with the exception for use in cables, as we will also see further on.

13.3. Applications today

Highlighting truly structural applications, the following list can be proposed:

- repair and reinforcement of existing constructions by using composite materials; without any doubt, currently the most developed and most economically promising, this will be dealt with in another chapter (Chapter 23);
- pre-tension and cable stay system, this involves replacing or completing steel cables in tense systems;
- composite rods for reinforced concrete.
- making decks or beams by composites;
- creating sandwich panel based cover systems.

There are leading countries in these domains. If it can be effectively said that repair and reinforcement are mastered throughout the entire world (Europe, USA, Japan), Great Britain and the USA are investing in the development new all-composite structures. Lastly, in Japan, Germany, Switzerland, and France, applications tested in the prestrain and cable stays domain are found. For this, a non-

exhaustive inventory has been drawn up later in the chapter (section 13.3.6). If there are only a few references, it is because this kind of work does not often generate many referenced publications (however, go to the site of the NGCC, *Network Group for Composites in Construction*, and see [BAN 06], [HOL 01].

13.3.1. Pre-stressing and cable staying in composite materials

Cable stay domain is certainly very interesting for composite materials because the cables are mainly loaded in the direction of the fibers. Moreover, the carbon composite is a pure quasi-elastic material, equipped with a very high resistance to rupture. It has a quasi-inexistent creep and an exceptional fatigue and corrosion strength. Another attribute is that this material is five times lighter than steel with a density close to 1.6. Composite rods must nonetheless be protected by a coating which makes it possible to avoid degradation during manipulation, and to reduce resin ageing. The big problem of using composite cables is thus, the anchorage system. To maximum the anchorage efficiency, strain concentrations that these composite materials find hard to bear must be avoided, in light of their lack of ductility. In the discipline of cable stays, Japan is unquestionably an avant-garde country. Four companies fight for the market, eleven pedestrian bridges and nine road bridges have been built with composite cables in Japan, and only three elsewhere in the world (two in Canada and one in the USA). The Rainbow Bridge (Pier Walkways) built in 1991 in Tokyo is, with its 983.24 m of length, the longest existing footbridge made with composite cables to this day. Tokyo Rope is the leader, having made twelve constructions, one of which is in Germany, and two in Canada.



Figure 13.1. *Laroin Footbridge (Freyssinet Photo Library)*

In Europe, we find composite cable stays bridges in France (Laroin 2002, Figure 13.1), Denmark (Herning, 1999), Switzerland (Winterthur 1996), United-Kingdom (Aberfeldy 1993), Austria (Notsch Kärnten 1990) and Germany (five constructions from 1980 to 1991). It is also in Düsseldorf, Germany, that the first prestressed construction by polyester matrix rods, armored with glass fibers was created in 1980 by Bayer AG. In Canada, two constructions, and in the USA eleven constructions with composite cables were built between 1991 and 2001. The longest composite cable stays bridge for vehicles is 410 m long and can be found in Aurora (Colorado). Despite a period in the beginning of the 1980s where three composite cables stays bridges per year were built in Japan, and two in Europe, this promising tendency failed to last. Composite stays remains a sporadic application, selected case by case.

Research on safer anchorages, (design, fatigue and ageing tests) are being pursued, generally linking together manufacturers and research institutes. It is within this framework that in Laroin (1964), the composite cable stays pedestrian footbridge, of 110 m spanning over the Gave de Pau was achieved. It required approximately 15 Km of carbon rods with a diameter of 6 mm.

The future of these processes is perhaps in off-shore platform development. Indeed, the lengths and sections of the cables and liners are as such that the weight becomes a real handicap for the platform which literally sees itself being led to the bottom by its anchorage. Obviously, a carbon cable is an experimentally interesting alternative here, allowing us to push back the deep limitations of these exploitations. However, the cost and capacities to produce carbon mean that these projects are late in becoming a reality.

13.3.2. Bars for reinforced concrete

Some reinforced concrete bridges and footbridges are submitted to aggressive environments and steel bars protection are not always a long term guarantee. Bars made from glass or carbon composites are likely to bring long lasting solutions. The domains of application for composite bars are especially:

- concretes exposed to de-icing salts;
- constructions next to, or in, sea water;
- chemical industries;
- applications requiring a low electric conductivity or an electromagnetic neutrality.

These strengthening systems can, moreover, allow for a path of instrumentation and sensors in the framework of intelligent structures. On the other hand, the lower

Young's modulus of composite rods limits applications to small span elements. The resins used at the moment are thermosets and, consequentially, all shaping and embedded systems must be achieved before polymerization.

There are bridges with composite bars in the USA (29 road bridges, 1 pedestrian bridge), in Canada (10 road, 1 pedestrian), and in Japan (2 road, 1 pedestrian). The first construction for pedestrians appeared in Japan in 1991. The first road bridge was in Canada, in 1995. In Europe, to our knowledge, this technique is not applied.

13.3.3. *Composite beams for crossing*

Corrosion sensitivity of pedestrian footbridges with a light weight bearing structure is great. A simple and often economic method, when rehabilitation turns into a necessity, is to replace them with a new construction. The use of composite beams as a weight bearing structure is thus an interesting development, and is already frequently used. In the USA, this technique has even become quite normal. There are no less than 109 pedestrian constructions and 12 for vehicles. The average length of pedestrian bridges is around 13 m, and the longest measures at 38 m (Bar Harbor, Maine 1995), and the shortest at 3.7 m. Road bridges measure on average 16 m, the longest being 63 m (Campbell, New York 2003, the longest in the world at the current time), and the shortest at 5.5 m.

Some of the first constructions carrying such beams date back to 1982 and can be found in China (Miyun Bridge, Beijing). The Guanyinqiao Bridge (Chongqing 1988) is the longest bridge in the world at the present moment with a length of 157 m. In Europe, 16 bridges with composite beams have been built: in Bulgaria (Ginzi, 1982 Highway Bridge, bridge measuring 12 m with glass fiber reinforced polyester beams), in Denmark (Kolding 1997), in Switzerland (Pontresina 1997), in Spain (Lleda 2001), in Norway (Fredrikstad 2003), in the Netherlands (4 constructions between 1985 and 2003) and in the United Kingdom (7 constructions between 1975 and 2003). It is actually in England that the first pedestrian bridge built with composite beams can be found (Westminster Cathedral Footbridge, London 1975). At the present day, France does not yet hold such a construction.

13.3.4. *Composite bridge decks*

Composite bridge decks offer various advantages, linked to their lightness, ease of implementation and reduction in the structure's own weight. Here we are dealing with sandwich panels with a foam or alveolar core, or bound panels from prefabricated pultruded profiles and transported by panels.

These bridge decks are designed to be the bearing structure of small range constructions. The replacement of damaged steel/bitumen or steel/wood bridge decks is an important market for rural areas in the USA: 83 road constructions, and 13 for pedestrians between 1995 and 2003. In China, 6 constructions all of which for pedestrians, were built between 1988 and 1993. In Japan, there are 2 constructions. In Europe, 18 constructions were built between 1990 and 2003. The first construction built in the USA in 1978 with a composite deck was the only one of its kind for ten years, until 1988, the year when the first composite beam pedestrian footbridge appeared in China. But the real beginning for composite decks would not arrive until 1996 with the development of prefabricated bridge decks in the USA. However, composite bridge decks did not generate a market in Asia or Europe.

13.3.5. Sandwich roofs

The only uses for composites in buildings was limited to door and window joineries, guard-rail and electric cable paths for a long time. Some roof systems, however, were developed. In random order, we will cite Dubai Airport (1972), Benzahi Dome (Libya 1970), Mondial House (London 1975), where 25 years of inspections never revealed any notable deterioration. More recently, the Home Planet Zone in the London Millenium Dome was created, a 36 m diameter self-bearing roof made from sandwich pannels set out in quarters.

The year of 2004 saw the construction of a double curved complete composite sandwich roof, in Israel with two turrets in the center of Yitzhak Rabin in Tel Aviv. Another composite roof with a range of 25 m was created in Bahreïn as a glass fiber shell sandwich. The simple curve shape is, however, a lot less interesting as well as the level of completion and the more banal details, particularly because the shell is made of continuously straight edges.

However, in these examples, very often the sandwich composition solution could have been replaced by less expensive shells made from traditional materials (concrete or steel). It is the research linked to technological innovation which has guided the choice of material rather than a reflection on the adequacy between shape, function and material.

13.3.6. Some examples of constructions

Here are a few detailed constructions, chosen for their exemplarity.

1.3.6.1. *Aberfeldy Footbridge (Scotland, 1993)*

This footbridge which links together the two parts of the main golf course in Aberfeldy is the first construction entirely made of composite materials. This is a cable stayed footbridge with aramid cables. In this project, the research department worked in tight collaboration with the University of Dundee: civil engineering students put up the bridge. Thanks to an original method, made possible by the lightness of the elements, putting the pillars into place did not require a crane on site. The footbridge's composite ramp and the completion of the wear resistant deck should offer a lifespan of over 20 years before it needs to be restored. The minimum foundations and quick assembly ensured an economically competitive solution.

13.3.6.2. *Bonds Mill Lift Bridge (England, 1994)*

Bonds Mill Lift Bridge is entirely made of ACCS (Advanced Composites Construction System) composites using an epoxide resin for bonding, so as to form one single beam with six main cells filled with epoxide foam. The deck is made from "double-ply" plates. The bridge, completely made of composites and replacing a fixed construction, was really chosen for its economic competitiveness, its lightness, its great resistance to external influences and its low maintenance level. The power of motors has been remarkably reduced. One test, seven years after the bridge's installation, shows that the bridge deck is still in a good state.

13.3.6.3. *Bridge at No-Name Creek (Kansas, 1996)*

This road crossing was the first to be made entirely of composites on a public highway in the USA. It demonstrates the efficiency of decks as a bearing structure for small range constructions. The bridge was transported onto the site in three parts. The ramps and the wearing surface were put into place when the panels were being made in the factory. The bridge took one day to put up.

13.3.6.4. *Pontresina Bridge (Switzerland, 1997)*

The Pontresina Bridge is an all composite construction which is only used in winter. This means that it assembled and taken down every year. This is a construction made of glass fiber lattice beams in a polyester matrix made of bonded joints. The entire construction was achieved with the participation of the CCLab (Composite Construction Laboratory) of the EPFL (Ecole polytechnique fédérale de Lausanne/Lausanne Federal Polytechnic). One of the important points here is the demonstration of what structural bonding with composites can bring to the construction domain.

13.3.6.5. *Laroin Footbridge (France, 2000)*

The pedestrian footbridge at Laroin in the department of the Atlantic-Pyrenees is the first work of art built in France with composite cable stays. They are formed by 6 mm diameter rods. Research carried out by the contractor (Freyssinet) linked with the fiber provider (Soficar) and the Navier Research Unit (ENPC/LCPC) have led remarkably to the development of cable anchorage blocks, which were used on the construction site.

13.3.6.6. *Eye-catcher*

Eye-catcher is a small, five-storey building located in Bâle (Switzerland) and made entirely out of composites. Pultruded glass/resin fibers (Fiberline Composite) make up the bearing structure designed as a metal construction.

13.4. Perspectives and projects

The innovative construction made from composite materials above reproduces, we have seen, techniques using traditional materials (steel, concrete, wood, etc.). Innovation by reproduction is a normal process when a new material is introduced: replace traditional materials by a new material to explore the possibilities and the reliability of the new one. But, very quickly, the limits of these methods come to light: construction techniques are adapted to the material for which they were developed, thanks to lots of experience. This is why the traditional material is generally unbeatable, on the economic as well as the technical front.

New construction methods must be developed, methods which in turn will be adapted to a new material in particular, benefiting fully from its mechanical properties.

Research on building techniques for civil engineering constructions adapted to composite materials must surely be framed by four key requirements:

- optimal use of fiber mechanical properties;
- simplicity of connections between the different elements;
- structure shape optimization in relation to its loading;
- low building cost through using standard industrial components.

In the following, a few achievements or projects which are written into this framework are cited, in a non-exhaustive way. If most of these are developed in the technical network of French equipment, it is because this type of prospective research is often neither divulged, nor easily accessible.

13.4.1. Composite crossings and footbridges

13.4.1.1. Multimaterial beams and bonded connections

In a prospective spirit, after having lived through the entire steel or entire concrete period, it is, without a doubt, good to no longer restrict ourselves to an all composite period. Following a track which links together many materials, putting each in their most appropriate setting, is certainly a way of introducing composite materials in an innovative way. This is slightly comparable to what is done for repair and reinforcement, putting carbon on the tense intrados to increase the structural rigidity.



Figure 13.2. *Prototype of a road bridge deck, high performance concrete (HPC)/Wood/Epoxy-carbon (LCPC)*

One construction project, Gilman Drive (San Diego, USA) has proposed many innovations, in this sense. It involved building an ambitious road bridge, partly guyed in carbon, with 137 m of range and 18.3 m of length. The project consisted of developing an innovative beam linking concrete and carbon composite (CCSS, *Concrete Filled Carbon Shell System*) and fibers reinforced concrete decks connected to glass and carbon hybrid box beams by composite clamps (HTS). If this construction seems to be focused on the state of the project, the CCS concept has been successfully tests for the Kings Stormwater Channel Bridge (California).

Such material associations have also been achieved in the framework of a European contract, NR2C (*New Road Construction Concept* [NRC 07]). It was particularly concerned with imagining beam or sandwich bridge deck solutions integration different materials, such as HP (high performance), light, fibrous concretes, woods or honeycombs, and high performance composite materials with glass or carbon fibers. Two solutions, carbon/wood/HPC and glass/light concrete

have been explored by the LCPC/ENPC for the first solution (Figure 13.2) and by EPFL at Lausanne for the second solution [KEL 07]. A prototype section of a carbon/wood/concrete road bridge of 11 m range of 2.5 m of width was made and tested successfully in this framework at the LCPC. The main attribute of this project was certainly also the work carried out around wood/concrete or wood/composite assembly techniques.

Indeed, as it was previously stated in key requirements, knowing how to assemble is fundamental, and specific techniques will optimize composite use. Too often, and now still, recommended solutions rely on the more or less successful adaptation of metal construction classic techniques, bolting and riveting, which endanger the integrity of the heterogeneous fibrous material and lead to important oversizing. Bonding is incontestably the *taylor-made* assembly technique for this type of material [CET 06], [COG 06], [KEL 09].

13.4.1.2. *Self-stressed footbridges*

Composite materials are used for building skis, arches, etc. for their low density, their high resistance but also for the important deformations before rupture. However, most of civil engineering structures of average and large span are dimensioned by displacements (deflection) and rarely by their resistances. For a small footbridge with a 10 m span, the obtained deflection with a steel beam as a bearing element, will be half of that expected for the same beam made of carbon, whereas the resistance of the carbon beam will be four times bigger. This construction will therefore be refused so as to avoid sea-sickness of its passengers! The adopted solution is to use “more” composites to make it more rigid. But the result is designing oversized structures in terms of resistances, over weighed, and suddenly too costly to hope to go beyond experimentation. This is somewhat the case for the existing structures previously presented. This flexibility, researched for skis, can it become an advantage, the spring which triggers the turn?

13.4.1.2.1. The Bowstring footbridge, reinvented with composites

The arch shape is a very classical constructive system. But this type of construction, if a material permits such level of strains, could be obtained by elastically curving a straight element; and a cable could keep it bent.. Moreover, elastic energy stored in bending could prestress the cable. Figure 13.3 shows such a model of this concept of footbridge; the arches, cables and stays are made from pultruded composite materials, with high performance technologies and industrial manufacturing, therefore it is economic. The deflection obtained under loading is weak, the structure is light, not oversized, and we have benefited from the specific material’s capacity, here, flexibility.

Details of the concept, modeling and calculations can be found in [CAR 09].



Figure 13.3. *Composite bowstring, scale 1/10 (ENPC)*

13.4.1.2.2. Footbridge according to Da Vinci

Another concept using the deformability of the composites is studied. Here, a sandwich panel is prestressed by bending, by a central support which is a tense cable. This astuteness is already used in the Da Vinci catapult which consists of an arm made of bent wood, kept bent by a tense cable. The base shooting is not modified when the projectile is deposited because the cord acts like a rigid support. Indeed, its relaxation also slackens the wood arm which retightens the cord, and this works so long as the cord stays tense. Thus the apparent rigidity of the system becomes infinite. This principle is re-used here. The composite sandwich panel is prestressed by the central support, which is a cable, under tension (almost invisible at midspan in Figure 13.4). This tense cable thus acts as a support which cannot buckle so long as it stays tense. Technologically and architecturally speaking, this discrete cable, easy to anchor, potentially long, can actually bring a positive attribute to the concept of crossings. Calculations show that in this setting, composite materials are very well adapted. Their weak stiffness is not a disadvantage, in this case. Building a prototype from these glass fiber sandwich panels was achieved (infusion process) and the concept was validated [BAV 08]. A very closed concept is patented in [CIP 03]



Figure 13.4. *A footbridge prestressed by bending – infusion technology (Navier)*

13.4.2. Composite gridshells

13.4.2.1. Gridshells, an original construction process

The name gridshell often means a structure with the shape and rigidity of a double curved shell but which is made of a grid and not a continuous surface. These structures may cross over large span by using a small amount of material. They can be made out of any material: steel, aluminum, wood or even cardboard, etc. Generally, metal structures are made of rectilinear elements which define faces on the grid surface. The complexity of the obtained geometry requires the development of a large number of assembly parts, as complex as they are costly. To stage this disadvantage, an original construction process has been developed. Long continuous means are assembled on the ground and linked together, which gives the grid a total absence of rigidity in shearing and will allow for large deformations. The grid is then elastically deformed elastically by flexure until the desired shape is reached and the boundary conditions are fixed. It is then rigidified by using a third direction of bars or wind-bracing cables so as to suppress the degree of freedom in shearing and to give all its rigidity to the shell. In the world, only three gridshells have been made by using this method, the Mannheim Bundesgartenhaus by Frei Otto (1975) is one of them.

13.4.2.2. Composites, *taylor made for gridshells*

In existing gridshells, wood has been chosen due to its low density but not for its resistance (30 MPa at the best). Glass fiber reinforced polymers (GFRP) have much higher resistances all by remaining relatively flexible, which allows for much bigger elastic bends, and therefore economic shaping (Figure 13.5). As strains in bars are nearly exclusively axial strains, fibers are only required in the main direction of the bar. Using pultruded fibers is thus completely adapted, it also allows the manufacture of long length tubes and reduces the problem of junction. Moreover, creating connectors between the tubes, identical for all joints, is very simple. However, it must be underlined that long term behavior of pultruded profiles, particularly under flexure, is rather unknown, and that in gridshell applications, as for the footbridges described above, there is still work to do, particularly for glass-polyester pultruded fibers [ADE 03], [CAR 07].



Figure 13.5. *Assembly stage of a composite gridshell (ENPC)*

13.4.2.3. Prototypes

Many experimental gridshells have been built at the ENPC (Figure 13.6) with pultruded tubes made from glass fiber reinforced vinylester resin. Prediction of the

shapes is achieved by using nonlinear shape research tools [DOU 10]. The two structures from the ENPC cover around 150 m² each and was coated with a polyester textile and with the help of Ferrari SA, Abaca, Esmery-Caron Structures, and ENSG (Ecole Nationale des Sciences Géographiques).



Figure 13.6. GFRP gridshell/coated polyester (ENPC)

13.5. Recommendations, norms and standards

With the need to frame and develop the use of composites in construction, many professional organizations have taken part in writing norms and standards. For example, the *American Petroleum Institute* and other bodies have published on pipes. Equally so, the *American Concrete Institute* has published on repair and reinforcement. A guide by the French Association for Civil Engineering in 2007 [AFG 07] even exists. The Japanese and Canadians are also very active on this theme. The European Committee for Standardization (CEN) proposed an entire series of ISO norms, particularly concerning the mechanical or physicochemical procedures for composites. More specifically concerning the recommendations for building structures or civil engineering composites, initiatives also exist. Many

congresses, journal articles and works are sources of information for composite in construction [BAN 06], [HOL 01], [MYE 06].

13.6. Composites and the environment: reflections

Composites certainly have a role to play in controlling environmental impacts. Obviously, the few facts that we can find do not seem, *a priori*, to play too much in their favor, and their reputation is tenacious. “Plastics” derived from fossil products do not generate good press. It has been quickly forgotten that only around 4% of consumed oil is reserved for developing these materials, while 85% is definitively burned in different ways for heating and transport. It has also been quickly forgotten that if plastic bags are mislaid in nature, it is a problem which is before anything, linked to usage and not to the material, which is criticized for being “durable”, which is today, a target. It is also forgotten that some of these plastics, as well as lasting, are recyclable.

Obviously serious problems persist, some polymers which are used to make composites, are not easily recycled (thermosetting resins), and their development has a strong impact on the environment. Moreover, developing fibers is generally rich in energy consumption as are manufacturing processes.

It is however certain that in many cases, a total analysis, still called life cycle analysis (LCA) may demonstrate the interest of composite solutions:

- if it appears as unquestionable (aeronautics or sport and leisure);
- when a low mass, good corrosion resistance, integrated design (fewer underparts in an organ), function integration for example, make the composite solution less costly.

Reading grids and criteria exist for comparing the environmental performances of buildings, such as those which were listed in the “construction durable/sustainable construction” report [UTO 05], estimating impacts in terms of non-renewable, energetic and non-energetic, natural resource consumption, of CO₂, NO_x, SO_x emissions, of dusts, noises and, for building sites, exploitation and end-of-life. In these grids today, composite materials are not often planned. However, documents [GRE 04] exist which classify different technologies and composite materials according to impact. For example, carbon fiber has a very important impact in spite of the structural optimization that it authorizes. Glass fiber is preferable when possible. Pultrusion is analyzed as a technology which is sufficiently mastered to have a reasonable environmental cost in comparison to artisanal impregnation, “contact” techniques in open molds. It may also be noted the existence of an LCA assessment of glass-resin pultruded fibers, which are far from being negative: low

CO₂ emissions, non-toxicity, performances, reduced maintenance, lightness, etc. Some productions have therefore been preceded by ADEME [BAN 01] and recycling networks do exist.

13.7. Conclusion

The point made here on composites in construction does not claim to be exhaustive, as many aspects have not been approached. Repair and reinforcement will appear in another chapter (Chapter 23). The set of applications which have no real structural vocation have been deliberately forgotten, although representing from afar the biggest number of applications. This involves tubings, facade panels, bridge protection, guard-rails and other gratings (industrial sector). Here, a new material can offer yet, for an existing element, a real “plus” in terms of mechanical resistance, lightness, insulation, corrosion or fire resistance, electric insulation or function integration.

What has been presented here concerns building or engineering structures which, by their structural responsibility, create more difficult problems but also more enthusiasm for the engineer. Certain fibers, resins, development or design technologies seem particularly well adapted for technical, economic or environmental reasons in the world of constructions (pultrusion or binding, for example) and these materials newly arriving at maturity have certainly a particular role to play by their performance in improving environmental quality

If the volume of composite applications progresses little or not at all, it is maybe then that these materials and techniques should be integrated today in new and better adapted structural solutions, bringing a real added value, compensating for a more important cost. To conclude it must be pointed out that if we have avoided talking about civil engineering constructions such as wind turbines (or more generally all high technological structures being developed for a better control over energy) it is because they are closer (in terms of technology and market) to the aeronautic or naval domain, than construction and are thus one step ahead, etc.

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Chapter 14

Textile Materials: Architectural Applications

14.1. Introduction

Architectural constructions using textile membranes allow us to discover another logic of space and atmospheres. Their constructive performances allow for the design of a large range of buildings, going from simple temporary constructions with low dimensions to long lasting, complex, large-scale structures (Figure 14.1). Recent advances in terms of recyclability and energetic behavior accentuate their future thanks to their capacity to bring relevant solutions to the needs and concerns of sustainable development.



Figure 14.1. *School in Maspalomas; Denver airport*

Chapter written by Bernard MAURIN and Romain FERRARI.

A short flashback shows that, except for troglodyte constructions, tents constitute the oldest mode of habitation. The use of natural fibers has always allowed man to protect himself from bad weather (nomad, open or military tents) or to control wind energy (marine sailing, windmill blades or aircraft wings, airships). From animal origins (animal skins) and then to vegetal (cotton, flax, wool), the low mechanical performances of these fibers, however, have limited their application to temporary or low span constructions, with everything amplified by a design mode more based on an empirical know-how than a truly rational analysis.

In the second half of the 20th century, the emergence of rot-proof synthetic fibers with higher mechanical resistances thus led to a new interest in this type of construction. Their development has nonetheless remained very limited, essentially for technical reasons: absence of previous construction archetypes as sources for creativity, but also lack of technical supports (as those available for wood, concrete or steel buildings), design difficulties (once imperfectly solved by using models), lack of information from builders and apparent vulnerability of the material. Emblematic constructions by pioneers such as O. Frei in the 1970s, however, opened up the use of calculation tools and adapted manufacturing processes, thus leading to a real passion for these buildings [OTT 82]. This development has, in addition, been reinforced by the emergence of new concerns, such as economical material research or the reduction of environmental impacts, as well as new needs, such as flexible and evolutionary structures or large covered surfaces (collective or storage areas). Our planet will soon be home to ten billion people and, according to some, it is time we thought about “economic esthetics”.

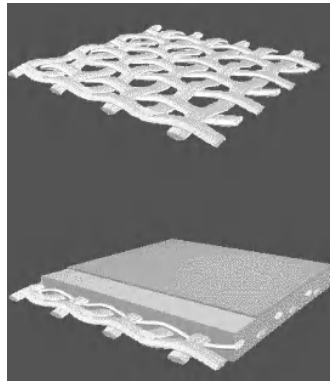
The evolution from transient and moving architecture to a long-lasting, contemporary architecture has, then, gradually been brought about. It may give adapted solutions when the limitations of the time schedule are great (prefabrication in factories, rapid assembly and dismounting), in critical geomechanical contexts (soil settlement or seismicity), when reusing the site in the short time is planned or when a modulation in light is desired (color and opacity of the fabric).

14.2. Architectural textile membranes

14.2.1. *Different fabric types*

There are two essential fabric families on the market. The first, generally produced in Europe, is a family of complexes made from weaving polyester (PES), then covered with a PVC coating and having a surface treatment, often in vinylidene polyfluoride (PDVF). Weaving plays the role of the “frame” that determines the mechanical characteristics of the fabric. Coating ensures UV protection of the yarn, its antifungal properties, fire resistance, membrane coloration and its assembly by

thermal welding (Figure 14.2). The final surface treatment gives anti-adherence properties to the fabric and makes it easier to clean; it also plays a role in its behavior with regard to solar radiation. Different types of membranes are made, corresponding to specific weights and different resistance levels.



Fluotop 1002T	
Yarn	High tenacity polyester 2 x 1 100 dtex
Coating	Plastisol
Weight	1 050 g/m ²
Tensile strength warp / weft	420 / 400 daN for 5 cm
Tear strength warp / weft	55 / 50 daN
Adhesion	12 daN for 5 cm
Flame retardancy	M2/B1
Surface treatment	Fluotop T2 100 % PVDF

Figure 14.2. PES/PVC fabric: yarn, coating and surfacing; fabric characteristics

The second group is that which contains membranes made of glass fiber yarn (E glass) and coated with Teflon (PTFE). Essentially produced in the USA, they present higher mechanical properties, however, with a higher factor price.

14.2.2. Conceptual design

The original idea for a textile architecture project is often born when an architect and an engineer meet each other. The role of the engineer is to ensure its feasibility as early as possible. The very specific world of shapes for this type of building, meaning curved shapes, may be seen as opposite but complementary to traditional architecture, essentially dealing with straight lines and orthogonality. This new vocabulary is seductive, but may quickly disturb when realization constraints condition its free expression. The work in synergy between the architect and the engineer is essential now, more so than ever.

The initial sketches are then formalized by the architect, then the engineering office takes over in order to determine the precise shape of the fabric through calculations, as well as the positioning of its fixing points. The engineer then dimensions the elements while taking care to respect regulation requirements for resistance and rigidity, particularly under climatic effects. The following stage consists of determining the plane, cutting shapes for the fabric that once assembled in the

factory, create the final membrane (Figure 14.3). This is then transported to the site, erected and put in tension during the installation process.

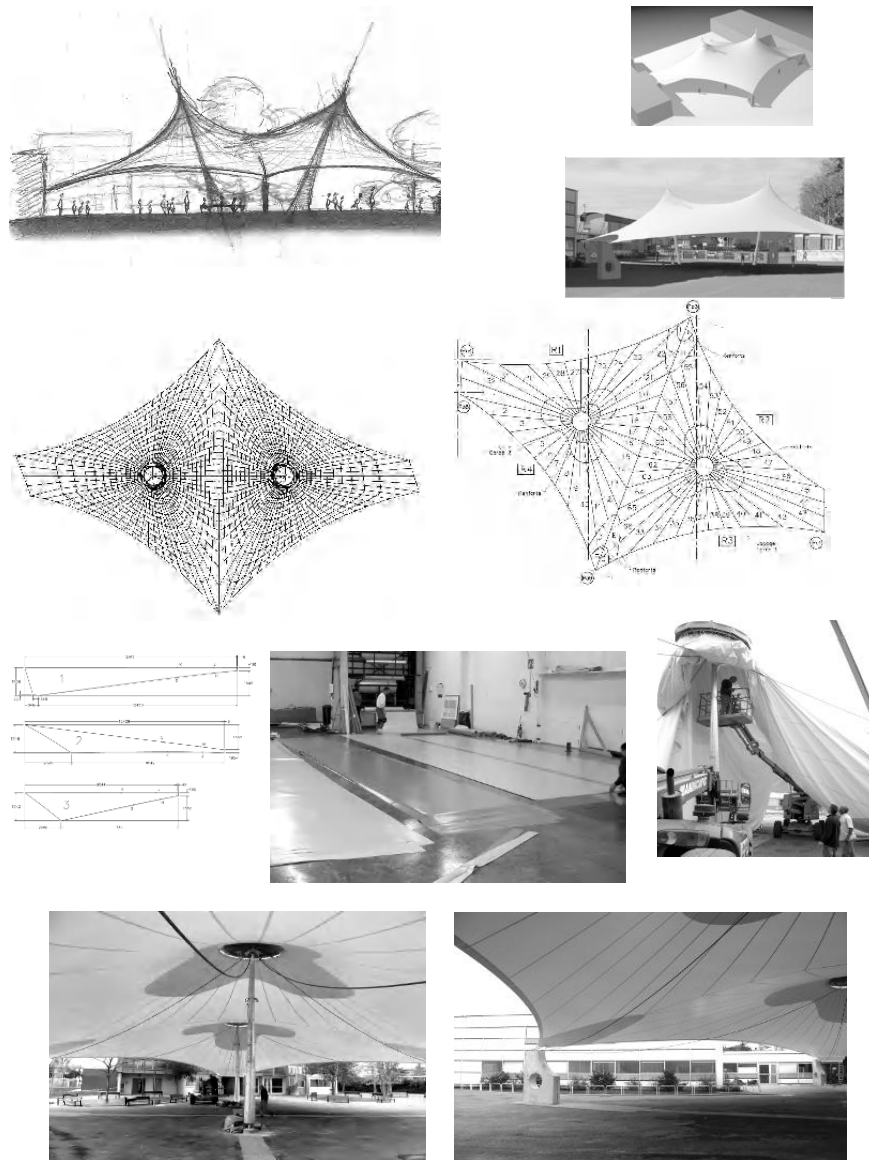


Figure 14.3. *Different design phase: initial sketches, rendering, geometry calculation, determining cutting shapes, assembly and installation, final membrane (credits: AbAcA eng.)*

14.3. Tensile membranes engineering

14.3.1. Two keywords: curvature and pretension

Knowing that a horizontal cable cannot oppose to a vertical force, it must be in a “V” shape so as to be able to resist (Figure 14.4). In addition, the less it is flat, the better its rigidity will be (T_2 tension being lower than T_1 , meaning a lower cable deformation). This V shape anticipates the necessary curvature that must be adopted by a membrane so as to resist to external actions.

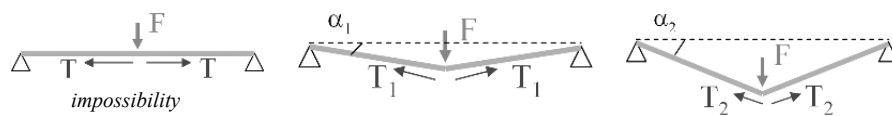


Figure 14.4. Cable: need for curvature

In addition, if we clamp two vertical cables by giving them an initial pretension, they will both contribute to the system's rigidity so long as the lower cable 2 does not slacken. If this occurs, the rigidity will then be divided by two, only due to the upper cable 1 (change from situation A to situation B, shown in Figure 14.5).

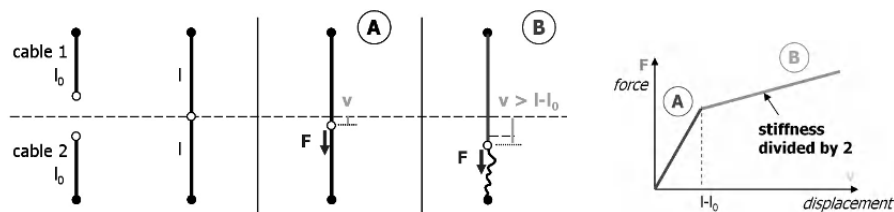


Figure 14.5. Rigidity of two pretensed cables

The association in the plane of two opposite V cables allows us to then combine the advantages of curvature and pretension (Figure 14.6). Pretension allows putting the V “curves” to be put into place and vice versa, the two working complementarily. The transition to the 3D case may then be carried out by rotating the lower V cable. The system obtained in this way is rigid in all directions. It allows us to anticipate the shape of a double curvature tensile surface. We notice that the two directions of curvature are found in opposition (“anticlastic” curved surface).

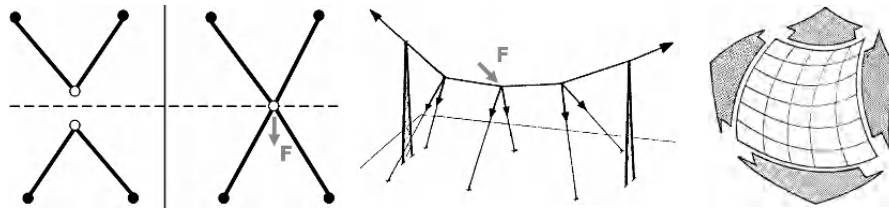


Figure 14.6. Tensile cable net: transition from the plane to the surface

14.3.2. Form-finding

The question of determining the shape realized by a tensile membrane between specified anchoring points has remained problematic for a long time [MOT 82]. The need for tension moreover implies a necessary control on its intensity in the membrane, in order to prevent some parts from not being in tension. An insufficient intensity may indeed results in insufficient fabric rigidity, thus weakening it under climatic effects.

The first approaches have essentially been based on the use of physical models. Minimal surfaces areas, allowing for the identification of a uniform tension membrane materialized by a soap film, was then a concept developed by pioneers such as O. Frei. Measuring the points, following a scale factor, therefore leads to defining the fabric's shape (Figure 14.7). Another approach consists of using fabric models (Lycra for example). Even if these methods are still used, essentially at the beginning of a project or for teaching means, they have been replaced in the engineering phase by numerical models because of their lack of precision and relative heaviness.



Figure 14.7. Physical model: soap film and achieved membrane (Tanzbrunnen, Cologne); fabric model

The first numerical approach was developed when designing the Munich Olympic stadium (1972) [LIN 71]. It is based on a tensile cable net whose shape and state of tension were determined by the so-called “force density” method (Figure 14.8). This technique gives a high level of precision while being user-friendly. It was then quickly extended to tensile membranes and lots of software was born.

Other numerical approaches were proposed afterwards, mainly using the “dynamic relaxation” method [BAR 75] and techniques based on the “finite element” method [HAB 82].

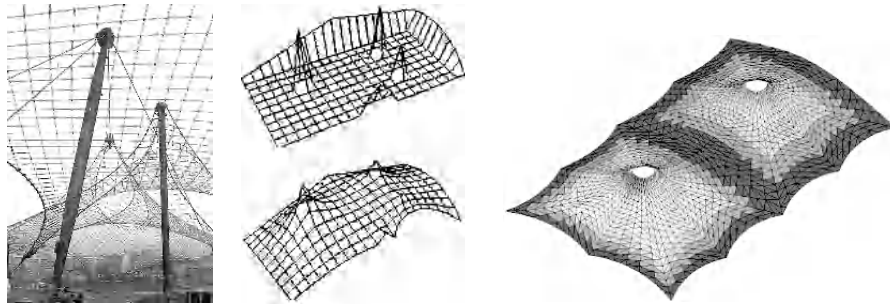


Figure 14.8. Numerical models: Munich stadium and force density methods; dynamic relaxation method (InTens® software)

This software also make it possible to carry out the form-finding and analysis of pneumatic membranes. These structures are kept in tension by an internal inflated pressure (a few millibars). In this case, the surface defines a typical shape known as a “synclastic” (Figure 14.9). Membranes of all sizes are therefore achievable, either by pressurizing the whole building, or by using “cushions” juxtaposed onto a bearing framework.



Figure 14.9. Pneumatic membranes: “Big Top” and “Allianz Arena” stadium (Munich)

14.3.3. Behavior under external loads

The study of behavior under climatic effects relies on two stages. The first consists of determining the stresses in the fabric due to snow and wind loading. This wind effect may be problematic because it comes from a fluid-structure coupling phenomenon. This means that overpressured or depression zones on the membrane must be identified. Except for cases of simple or well-known shapes, numerical

analysis or studies carried out using wind tunnel tests are necessary. The second stage aims to calculate the effects of these actions and to make sure that the integrity of the building and the safety of people are respected. It is therefore checked that the deformations do not exceed a defined limit and that the membrane's strength and structural components are not overcome. This allows us to choose the type of convenient fabric and to dimension all the components (cables, masts, anchoring devices).

Calculations are performed in a particular context of the complex behavior of fabrics (orthotropic, nonlinear elasticity) and of geometric order (large displacements, existence of initial pretension). They require specific procedures developed from the finite element method.

14.3.4. *Fabric patterning*

As a cloth can be manufactured starting from pieces of fabric cut out and then assembled together, the realization of a tensile membrane requires determining the shape of its plane cuttings. This operation is nevertheless complex because it must take numerous parameters into account. The first is related to the fabric's double curvature. This means that, after having partitioned it according to cutting lines (seams), it is necessary to "flatten" each of these parts (known as "strips") onto a plane. In addition, in order to take into account the membrane initial pretension, the obtained shapes must be reduced before their final assembly by thermal welding. This necessitates a perfect knowledge of the state of pretension (form-finding) as well as the material mechanical behavior (Figure 14.10).

If these operations are not correctly performed, once the membrane is installed, it may present folds or low-tension zones which, beyond questions of esthetics, may harm its integrity. Even if the existence of several software makes it possible to perform these stages, the engineer's know-how, combined with characterization tests of the fabric, still remain as an essential aspect, the only guarantee for the final result.

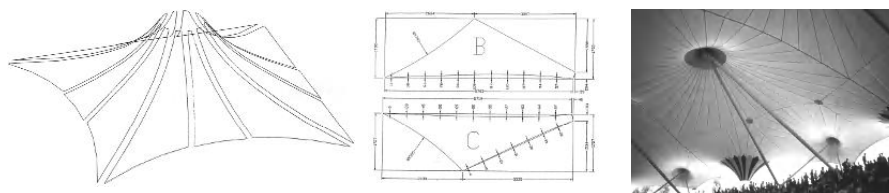


Figure 14.10. *Cutting the fabric: 3D and 2D strips; assembled membrane (Asterix Park, France)*

14.4. Eco-design in textile architecture

14.4.1. Fabric recycling

The development of the Vinyloop® process by the Solvay group, making it possible to separate PVC from other materials, followed by studies in collaboration with Ferrari, allowed in 2005 to finalize the Taxyloop® solution adapted to PES/PVC textile membranes (Figure 14.11). After gathering worn out fabrics at collection points, a succession of crushing, selective dissolution and then fiber separation processes, followed by a precipitation of PVC lets us recycle this material, offering an alternative to burying it in landfills or incineration.

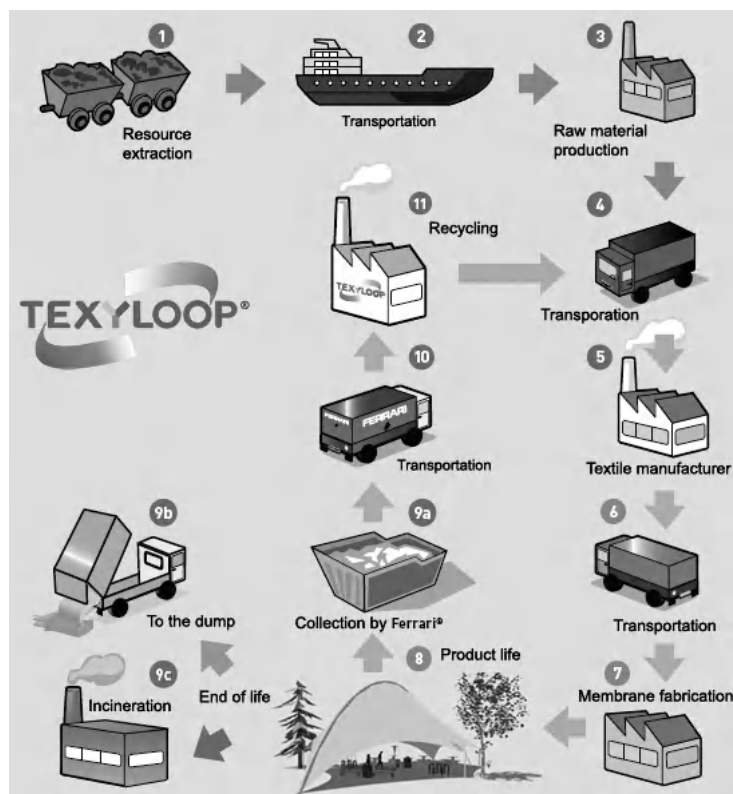


Figure 14.11. Recycling a PES/PVC membrane according to processes by Taxyloop®

Life cycle analysis (LCA) has been performed to quantify the benefits of such recycling. The results on several significant indicators are hence presented in Figure 14.12 for one type of fabric. They highlight an important benefit for the set of

parameters. From a general point of view, we observe that the most important points of impact (80% on average) relates to the extraction and production of raw materials. The creation of materials through recycling is thus decisive in this respect to significantly reduce environmental impacts.

The PES/PVC textile solution demonstrates all its relevance here, and the development on a world scale of collection points as well as recycling factories should contribute to making this solution a major player in the architectural landscape of tomorrow.

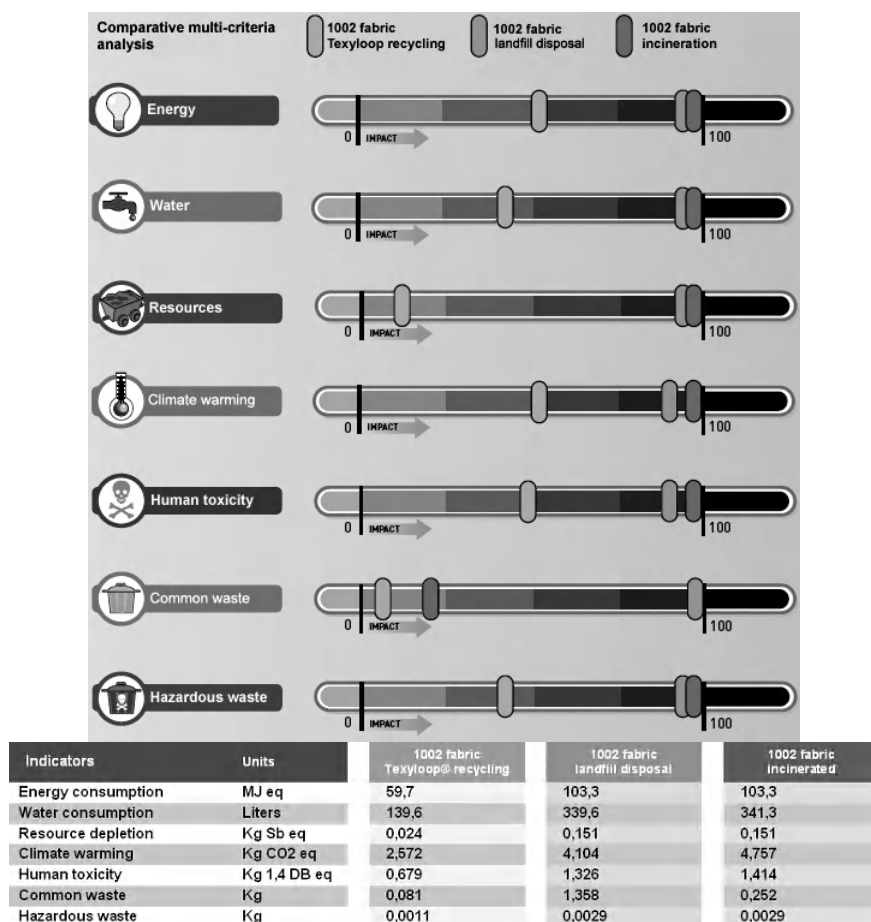


Figure 14.12. Comparative LCA (ISO 14040-14044) between recycling, land filling and incineration (stages 7 to 8 in Figure 14.11 are excluded since they must be performed case by case – for low impact however)

14.4.2. Thermal aspects

Many recent, or in progress, developments aim at improving energetic performances of fabric roofs. Their thermal behavior may therefore be improved by using opaque membranes and controlled emissivity (using pigments in surface treatment) or with double membrane solutions (with an interstice in between them). Thermal dimensioning tools are also emerging to quantify the advantages brought by these strategies.

As an example, TexTherm[®] software allows us to consider different situations according to the construction's localization (solar radiation) or its use (sport, theatre, storage, etc.) and to therefore determine the required power for the air treatment unit that must ensure a specified internal comfort.

TexTherm VE2 **PRECONSTRAINT**

OUTSIDE

Outside temperature (°C): 30
 Relative humidity (%): 60
 Solar radiation: PARIS
 Latitude (°): 49
 Altitude (m): 53

ENVELOPE

Single membrane: [dropdown]
 Double membrane: 1002 opaque lowE + 702 opaque lowE
 Roof membrane surface (m²): 1500
 Wall insulation: High (concrete wall WITH insulation and double glazed windows) U=1
 Wall surface (m²): 400

INSIDE

Inside temperature (°C): 20
 Relative humidity (%): 55
 Activity: Entertainment
 Number of people: 200

Preliminary calculation for AC units
 TexTherm VE2

Situation: Cooling
☐ solar gain ☐ human activity ☒ kW

Air conditioning unit (kW): 102
 kWh cost: 0,10
 Hour cost: 10,2

> Heat sources breakdown: (kW)

Fabric conduction	30
Fabric radiation	31
Human activity	60
Wall conduction	4

Help and recommendations | Membranes

FERRARI architecture

Figure 14.13. Pre-sizing calculation of the air treatment unit for a roof made of double membrane

A case study for a 1,500 m² roof located in Paris is presented (Figure 14.13). External and internal temperatures are 30°C and 20°C respectively; the relative humidity levels being 65% and 60%. Solar radiation is considered at its maximum (22nd June at midday) and 200 people take their places in this exhibition place. The power needed to ensure the specified internal conditions (air conditioning mode in this case) is roughly 200 kW for the case of a simple membrane roof. It is however

divided by two (by around 100 kW) if a double membrane with low emissivity is used. This difference lets us measure the quantity of energy saved.

14.5. Conclusion and perspectives

Textile materials present major capacities for developing architectural realizations. Beyond applications which allow us to design constructions of all sizes with material savings, the ability to adapt to different contexts with a low constructive impact on their close environment, they give a different approach for managing inside areas and for changing their atmosphere. The recent advances in terms of fabric recyclability and energetic control strengthen their position in the logic of sustainable development.

Other applications are also imaginable in relation to the emergence of new architectural tendencies, generally known as “non-standard” and whose formal language widely uses curved geometries (Figure 14.14). The realization of envelopes for these buildings often uses a primary bearing framework on which a secondary curved roofing is fixed.

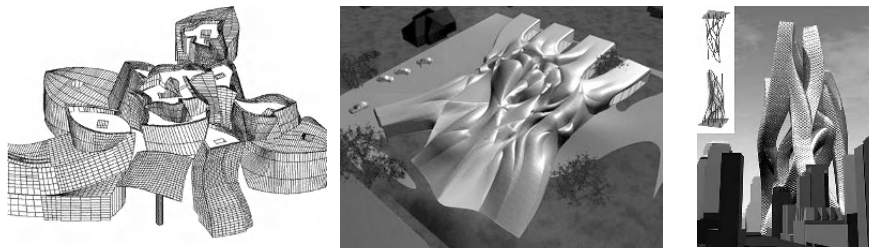


Figure 14.14. “Non-standard” architecture: shapes and curved envelopes

Several works are currently being led so as to allow the manufacturing of such envelopes by using panels attached to the framework. Some studies are at this time being developed regarding the design of selfstressed systems based on the principle of “tensegrity” [MOT 03] and made of two membranes under tension by an internal network of composite material profiles (Figure 14.15). Precast in factories, these lightweight panels may be deformed so as to give them a curved shape adapted to the bearing structure where they will be attached. The gap between the membranes enables the insertion of thermal or acoustic insulation elements and therefore an increase in the level of energetic performance.

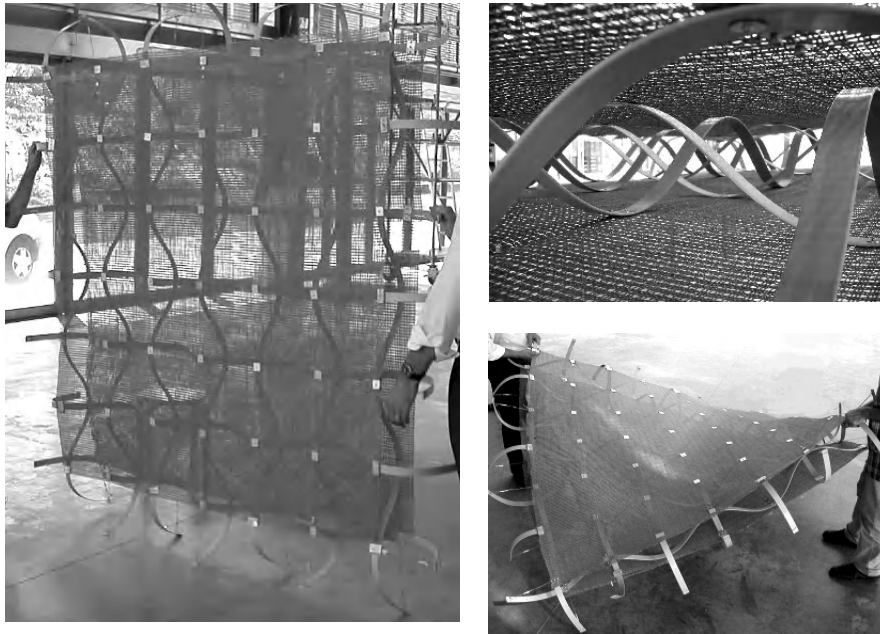


Figure 14.15. *Soft self-stressed tensegrity panel: two membranes put under tension by internal composite profiles*

14.6. Bibliography

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Chapter 15

Wood

For as far as our knowledge goes, wood has always been a material used by man, even up to two centuries ago, it was the universal material. It was used both as a source of energy and raw material for furnishings and housing. It was essential for making tools and even machines.

The 19th and 20th century witnessed the advent of steel and concrete which took the place of wood in many uses. The performance of these “new materials”, but also the rarefaction of wood subjected to multiple causes (deforestation to increase farming land surfaces, massive use of wood in the metal industry) made using this traditional material less systematic.

The great human losses from the two world wars, but also the attraction that new industrial channels could present for workers, triggered a rarefaction in the workforce in silviculture and in wood construction.

Many researchers and engineers from this era are more attracted by innovative perspectives and development linked to new materials. Wood has become neglected, skills and knowledge find it hard to evolve and adapt to new needs; the industry gradually declines.

Chapter written by Rémy MOUTERDE.

15.1. From the thinkable, to the possible

Today, building with wood is once again “thinkable”. The positive attributes, as much environmental as they are economical, contained in wood currently make its use very relevant today.

Wood is, above all, a natural resource, renewing itself regularly. We consider that under a temperate climate, a well maintained softwood forest provides trees reaching maturity at the end of twenty to thirty years, and can, then, be collected. The presence of forests on a territory makes it an interesting natural resource. 16 million hectares, meaning 30% of French land are currently forest areas and this surface is growing due to the desertification of the countryside. The annual biological increase resulting from a year of growth represents nearly 80 million m³ of wood, where only 50 million are collected. The stock is increasing and its recovery is essential, with a too large ageing degrading this natural capital.

Moreover, this resource is well spread all across France. Silviculture and companies dealing with first and second transformations of wood therefore allow the development of an essential local economy for a harmonious and logical country planning. It currently represents more than 500,000 jobs in France.

During its growth and across the mechanism of photosynthesis, wood fixes carbon gas present in the atmosphere as constitutive celluloses and hemicelluloses of its cells, and rejects oxygen. We estimate that a cubic meter of wood is capable of fixing a ton of CO₂. Fixing this carbon in a sustainable way thus prevents a part of carbon gas produced by human activity from modifying the gas layer in the atmosphere, responsible for the greenhouse effect. This benefit is only temporary and all natural decomposition of these end-of-life vegetal products or their destruction through combustion then releases the quantity of carbon which was fixed beforehand as a carbon gas. Managing forest heritage is therefore an important point for the future of our planet. Sampling lumber, and its non-degradation, associated with planting new trees, gives our forests the status of carbon wells. This expected effect is only an average term effect to the overproduction of greenhouse gasses. It must take place alongside a change in our behavior to slow down the inflationary effect of carbon gas production, for which are all responsible in some way or another.

Another important attribute in this environmental context is the low release of energy necessary for its exploitation and implementation, contrary to other materials usually used for construction. To be able to compare things objectively, Figure 15.1 below indicates energy consumption and carbon gas production for a similar problem necessary for the manufacture of a beam in three different materials: wood, concrete, and steel.

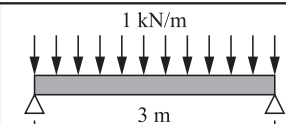
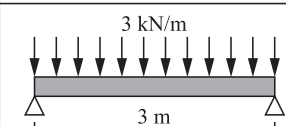
		Mass in kg	Energy in kJ	CO ₂ balance in kg
	Timber	30	30	-50
	Steel	30	1 800	20
	Concrete	300	1 800	110
	Timber	100	100	-160
	Steel	60	3 600	40
	Concrete	300	1 800	110

Figure 15.1. *Compared energy assessments*

However, the current use of wood only represents 10% of the value of materials used in buildings. Its regulation on a bigger scale would allow us to reach part of the objectives accepted in France at the time of the Rio and Kyoto agreements.

After the relative stagnation of techniques used in wood construction over many centuries, the last fifty years have shown a very large evolution in knowledge and technology. The industrialization of this sector, the appearance of derivative products, have made us rediscover all the potential of this natural material.

In France, since the last war, universities and higher education institutions have created specialized teaching on lean wood in research laboratories. With the CTBA (*Centre Technique du Bois et de l'Ameublement*/ The Wood and Furniture Technical Centre) and the CSTB (*Centre Scientifique et Technique du Bâtiment*/Building Science and Technology Center), they are behind the evolution of significant standardization for using this material, just by revealing its new uses and new possibilities. These different factors have promoted the creation of large international demonstrations (exhibitions, Olympic games, etc.) of buildings considered quite rightly as references.

15.2. Biological structure

Understanding wood, is first of all knowing the physicochemical and morphological organization which structures the different components. Their macroscopic organization then gives a new level of explanation. We will see, then, that this double reading allows us to explain the physical properties that we notice.

More than 30,000 wood plant species are listed. They are grouped into two main families:

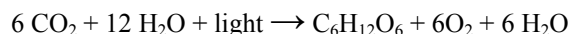
- softwood or gymnosperm, generally hardwood, but for a few exceptions (larch, etc.);
- hardwood or angiosperm, generally deciduous, but for a few exceptions (green oak, etc.).

15.2.1. Growth

Plants develop their organic matter and energy stores from mineral elements, water drawn from soil and atmospheric gases. They use solar energy to perform chemical reactions. This is mechanism of photosynthesis.

Photosynthesis occurs in the leaves, inside the chloroplasts containing chlorophyll. This green pigment takes in necessary light energy for a chemical reaction which combines mineral elements in order to produce organic matter. This process uses carbon dioxide taken from the atmosphere and water present in the sap to make glucose and dioxygen, which will be let into the atmosphere.

This process is represented by the following equation:



A cross-section of a tree trunk (Figure 15.2) demonstrates its internal structure.

Moving away from the exterior, we successively find:

A: the bark which protects the internal structure from external aggression;

B: *the liber* containing canals which transport the sap elaborated by the leaves (after photosynthesis and chlorophyll assimilation, water + mineral salts + glucose);

C: *the cambium*, layer generated by bi-cellular thickness, ensuring formation of spring and summer wood by cell division towards the interior;

D: *sapwood* containing canals transporting the raw sap (water + mineral salts) from the roots to the leaves;

E: heartwood or duramen, formed by dead cells, resisting mechanical strains.

Ligneous cells produced by the cambium only stay alive for the time it takes to finish forming their wall and die quickly afterwards. The transformation from sapwood into heartwood (duraminization) is a result of impregnating fibers into lignins and tannin and a partial filling of vacuums. Mineral elements are also fixed

in the duramen (potassium, calcium, magnesium, silica in some tropical woods). The visual and chemical differentiation between sapwood and duramen is more or less displayed according to the species (non-existent for some species, generally more noticeable for hardwoods than for softwood species).

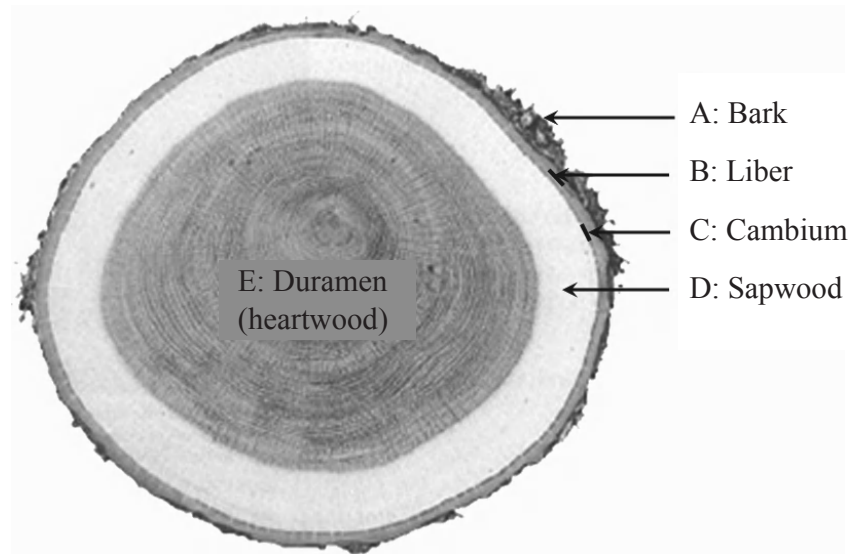


Figure 15.2. Cross-section of an oak trunk (source CNDB)

The peripheral area of a trunk is the biologically active part. Duramen only ensures a resistance function. It is made of dead cells which have stopped evolving.

The pith is the plant fabric in the middle of the trunk which is slightly soft. It is formed at the beginning of the tree's growth and does not change.

15.2.2. From the plank to the molecules

One of the characteristics of wood is related to its concentric (and vertical, of course!) growth. This growth leaves visible traces from year to year, called growth rings. Each annual ring is made of two distinct areas in temperate regions: the light-colored area is spring wood (earlywood) formed with the reappearance of vegetation, and the darker area, generally less extended than the previous one, corresponds to summer wood (latewood). Geographic and climatic conditions have a strong influence over the regularity of these rings (Figure 15.3).

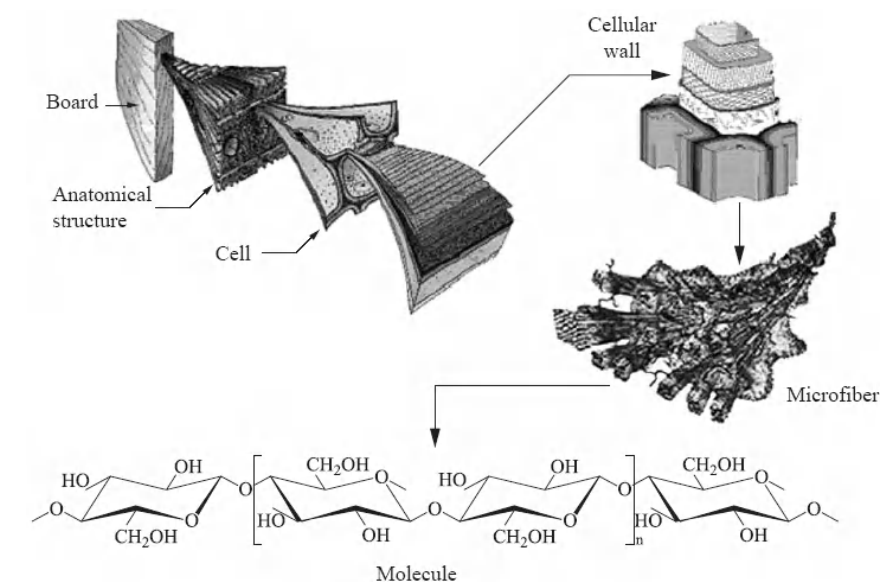


Figure 15.3. Organization of material, from the macro to microscopic (according to [HAR 98])

Wood from softwood fiber cells made at the beginning of the vegetation period (earlywood) is characterized by wide, thin walled fibers, the wood which is made at the end of the vegetation period (latewood) has narrow, thick walled fibers.

To ensure their resistance, the tracheids must have a thick wall, which relates to small ring widths and therefore to a biotope where their vegetation period is short with a late vegetation regrowth (north, altitude) limiting the formation of earlywood and giving a dense wood with tightened growth.

The fibrous cell wall of hardwood is generally thicker. Large rings, relating to a large production of latewood, are therefore more favorable for use in structure wood (biotope where the vegetation period is long, plain, temperate or hot climate).

The texture is defined as the ration expressed in percentages from the width of the final wood to the ring width. This measures the heterogeneity.

Differentiation from stem cells into specialized cells for particular roles, such as resistance, liquid and sugar conduction, reserve accumulation, may be very noticeable in hardwood or thin for softwood species. This results in different microscopic textures.

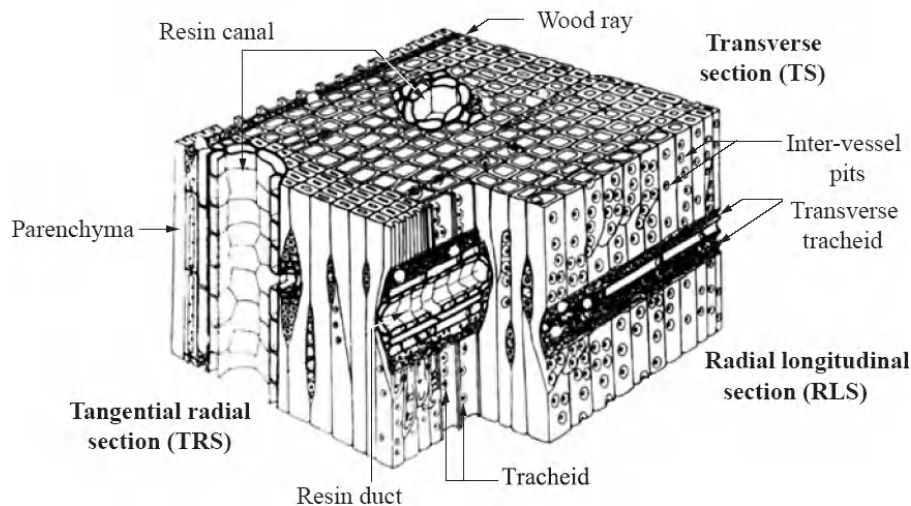


Figure 15.4. *Softwood cross-section (source CNDB)*

Softwood mainly contains two types of cells and canals: (Figure 15.4):

- tracheids which are fusiform cells laid out in an axial direction (90% of wood cells). These are fibrous vessels interconnected by existing pitting in the fibrous cell walls and allowing sap exchange between the cells;
- parenchyma cells forming wood rays. They are alive as long as they belong to the sapwood, but they are dead cells when they are part of the duramen. Wood rays are organized radially. They then form strengthening tissues which are perpendicular to the prominent axial direction in the material's make up.
- resin ducts, together with ray cells forming canals, allow the rejection of secreted substances. They are organized either in an axial, or a transversal way between the wood rays.

The make up of hardwood woods is more complex (Figure 15.5):

- longitudinal fibers called “wood fiber” (50 to 60% of the wood's mass) have a generally thicker wall than softwood families and they ensure the mechanical strength of the material;
- mainly longitudinal vessels (5 to 30% of wood according to the species) of variable diameters ensure the sap conduction;
- a transverse and longitudinal tissue, the parenchyma, stores the nutritive resources which are essential for the tree's development. The transverse tissue forms

wood rays organized in a radial way, as for softwood families, and they create the same type of strengthening effect.

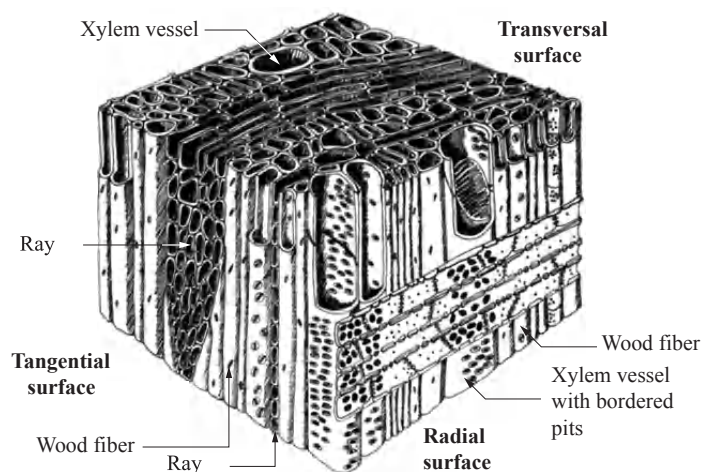


Figure 15.5. *Hardwood cross-section (source CNDB)*

15.2.3. Composition

The main chemical components of wood are cellulose (45%), hemicellulose (20%), and lignin (20%).

Cellulose and hemicellulose are sugar polymers (polysaccharides) resulting from a succession of biochemical reactions starting from the glucose synthesized by the leaves (Figure 15.6).

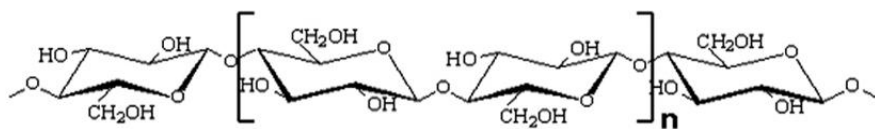


Figure 15.6. *Structure of cellulose polymerization*

Lignin is a liquid phenol. These three polymers represent at least 90% of the ligneous. Cellulose is a linear homopolymer composed of many D-Anhydroglucopyranose (AGU) units. They are interconnected by glycosidic bonds β and hydrogen bonds. The repetitive pattern is the dimer cellobiose. The ordering is

achieved in microfibrils (approximately 1,500 molecules). It constitutes the most resistant natural material of the plant kingdom: the breaking stress of a pure cellulose fiber, if it could exist in this form, would be in the order of 7,000 MPa. In ligneous matter, cellulose intervenes mainly in the make up of the cell walls but is not continuous (Figure 15.7).

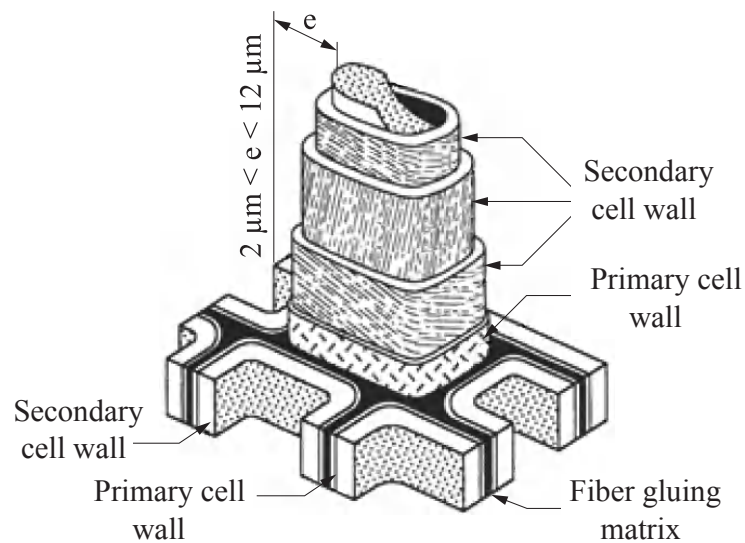


Figure 15.7. *Organization of the cell wall*

Fibrous cell walls, which constitute the ligneous matter bearing framework, are consisted of four successive layers of helicoid cellulose fibrillae turned in various directions in relation to the fiber's axis. This direction not only varies between layers (on average 70°, 20° then 80° on the three structuring layers) but also within each one of them (moreover at least 10° around the mean value). The thickness of the wall is variable and can go from 2 μm to 12 μm.

The matrix binding the fibrils is consisted of hemicellulose. The fibrous cells are transversely connected by organic acids (pectins) in the sapwood or by lignin in the duramen, and by hydrogen bonds. The wood rays organized in a radial way form a strengthening tissue which is perpendicular to the dominating axial direction in the material's organization. This micro and macroscopic organization shows clearly that wood is a natural composite material. Its organization can be compared completely with that of industrial "composites" materials using glass or carbon fibers, organized in successive layers, turned according to particular directions and included in organic polymer resin (Figure 15.8).

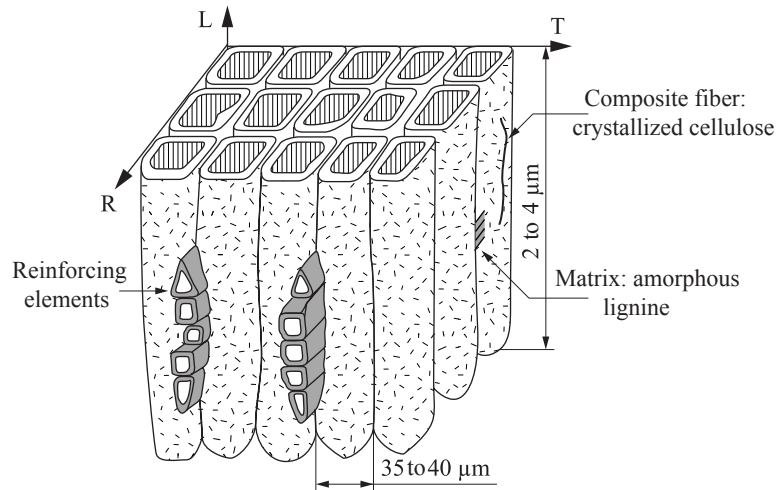


Figure 15.8. *Composite organization of wood (source CNDB)*

Characteristics related to the biological growth of materials appear either systematically or accidentally.

The knots are traces on the trunk of branches which exist, or which have existed. They can be adherent to wood and healthy (best situation) or not adherent, even rotten (worst situation). Either good or bad quality, the knots deviate or interrupt the wood's grain, which can lead to a considerable reduction in the wood's resistance to tension and flexure. Pruning the trees may have a strong influence on the size and consistency of the knots.

Particular climatic conditions (ice, dryness, etc.) may cause defects or growth problems resulting in slots, reduced adhesive strength of the annual ring (rolled edge, heart-check, frost cracks, internal sapwood, etc.). They involve local singularities which very often depreciate the material's properties.

Thus the natural character of wood, the diversity of the species and the random singularities of its growth (related to internal variability of its make up and its environment), the presence of cells (either living or dead), the different chemical components therefore make a heterogeneous material, with the physical and mechanical characteristics of being strongly anisotropic.

Understanding this organization makes it possible to explain certain characteristics of its physical properties.

15.2.4. Characteristics of physical behavior

15.2.4.1. Specific gravity

Specific gravity is a very important characteristic of wood, where many of its physical properties are correlated (retractability, thermal conductivity, mechanical properties, calorific value, etc.).

The cell walls are more or less thick, and the lumens¹ have a more or less large diameter, according to the species and the speed of their growth. Softwood trees with rapid growth rates have initial rings (spring wood), which are wider and make a lighter wood, compared to the same species with slow growth. However, hardwoods with rapid growth have final rings (summer wood) which are wider and make a denser wood compared to the same species with slow growth. The gravity of wood is, then, very varied according to the species (from 350 to 1,100 kg/m³) and inside the same species (with maximum variations of $\pm 15\%$).

Specific gravity is also influenced by the material's hygrometry, a variable water quantity, depending on wood's humidity rate being added to the dry matter. In general to define all the physicomachanical characteristics of a material, the reference humidity is selected at 12%.

15.2.4.2. Sensitivity to water

Wood is a hygroscopic material. It is likely, in a sponge-like way, to store or restore water according to the temperature and especially the relative humidity of ambient air.

On the one hand, the constitutive tubular structure of the fibers facilitates water storage in free form by capillarity phenomena. On the other hand, its main components (cellulose, hemicelluloses) are very absorbent. Their affinity for water is mainly due to the presence of many hydroxyl groups. They can be saturated with water, which is then retained in the cellular walls.

The measurement of a wood's humidity is defined as the ratio of the water mass which it contains compared to its anhydrous mass. It is expressed by the following formula:

$$\text{Humidity rate (\%)} = \frac{(\text{Humid mass} - \text{Anhydrous mass}) \times 100}{\text{Anhydrous mass}}$$

¹ Internal cavity of a fibrous vessel.

When being cut down, wood may contain more water than material; sometimes twice more in some poplars. The humidity is then higher than 100%.

During wood drying, the free water is initially evacuated by evaporation. This evaporation does not affect any of the material's physical behavior (volumetry, mechanical behavior). The saturation point corresponding to the total evacuation of free water corresponds to a water rate in the wood of 30% for all species.

When the free water has entirely disappeared (saturation point), only the bound water which impregnates the cells membranes is left. The departure of this bound water, under the natural or artificial action of ambient air, involves volumetric variations due to the variable thickness of the cell walls. These shrinkage or swelling phenomena result either in strain (deflection, warping, cupping), or by drying defects (cracks).

Shrinkage and swelling are directly proportional to the reduction or the increase in the humidity rate of the wood. These phenomena are strongly anisotropic and the amplitude of the observed dimensional variation depends on:

- the direction compared to the wood grain (axial, radial or tangential);
- the species;
- the number of points of humidity lost or regained between 0 and 30%.

Each species is characterized by three retractability coefficients which express the dimensional variations of a piece of wood for a humidity variation of 1%, according to each of the three directions.

The axial shrinkage is so weak that it is practically unnoticeable. It is in the tangential direction that this is most important; it is approximately 1.5 to 2 times higher than radial shrinkage. The macroscopic organization of the material and the presence of the radially directed wood rays explain these differences in behavior favoring the volumetric variations in the tangential direction.

Retractability is directly proportional to the cellulose content. These are the densest woods, consequently containing the most cellulose which presents the strongest shrinkage.

The species thus are distinguished as having:

- strong shrinkage levels: oak, beech, azobe, etc;
- average shrinkage: generally softwood trees;
- weak shrinkage: sipo, iroko, walnut tree, poplar, mahogany trees, etc.

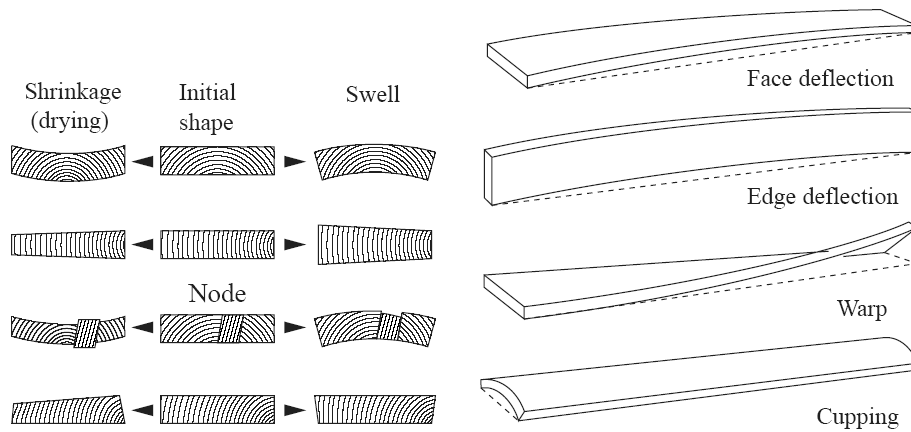


Figure 15.9. Hygroscopic deformations according to sawing position

During a badly controlled drying process, these retractability phenomena are responsible for the appearance of more or less deep slots affecting the round or squared wood. They also directly affect the sawing geometry, creating differential deformations according to the growth rings (cupping, warping, deflection, etc.) (Figure 15.9).

15.2.4.3. Dilation and thermal behavior

Wood hardly deforms under the effect of heat; this dilation is 10 times weaker in the axial direction.

As an indication, the mean values of wood dilation are:

- in the axial direction: $0.5 \cdot 10^{-5} \text{ m/m/K}$ or $0.5 \cdot 10^{-5} \text{ m.m}^{-1} \text{ K}^{-1}$;
- in the radial and tangential direction: $5 \cdot 10^{-5} \text{ m/m/K}$ or $5 \cdot 10^{-5} \text{ m.m}^{-1} \text{ K}^{-1}$.

Small deformation (strongly compensated by water departure) does not generate a modification of the geometry of the element wood.

The thermal conductivity of wood is low. The thermal conductivity coefficient of balsa wood is 0.054 W/m/K , and the one of oak 0.23 W/m/K .

It depends, of course, on specific gravity of the wood, but also on its humidity and temperature. This characteristic can be explained by the presence of air locked up in wood cells whose insulating capacity depends on its steam content.

This is a material which is 15 times more insulating than concrete, and 400 times more than steel.

Used as a structural material (post, framework), wood makes it possible to limit thermal bridges in a building. But it must often be used with an extra insulation (mineral wool, wood fibers, etc.) to limit the thickness of a wooden wall by respecting the RT 2005 norms.

15.2.4.4. Behavior to fire

Wood is a combustible organic material by nature. Its calorific value, which indicates the quantity of heat released when wood is completely burned, is proportional to its density. Its value is approximately 17 MJ/kg. Wood can never be fireproof because its maximum calorific value is higher than that of “fireproof” materials ($< 2.5\text{MJ/kg}$).

Norm NF IN 13501-1 defines the classification of materials used in buildings according to their fire performance. The EuroClasses (from A1 to F) take into account the velocity of fire development (in W/s) and the total energy released by the product (in MJ) at the same time, and are replaced during CE certification by the old classification referring to classification M (from M0 to M5). Two other additional classifications: s1, s2, s3 and d0, d1, d2 which make it possible to define the smoke and droplet production or ignited particles, respectively.

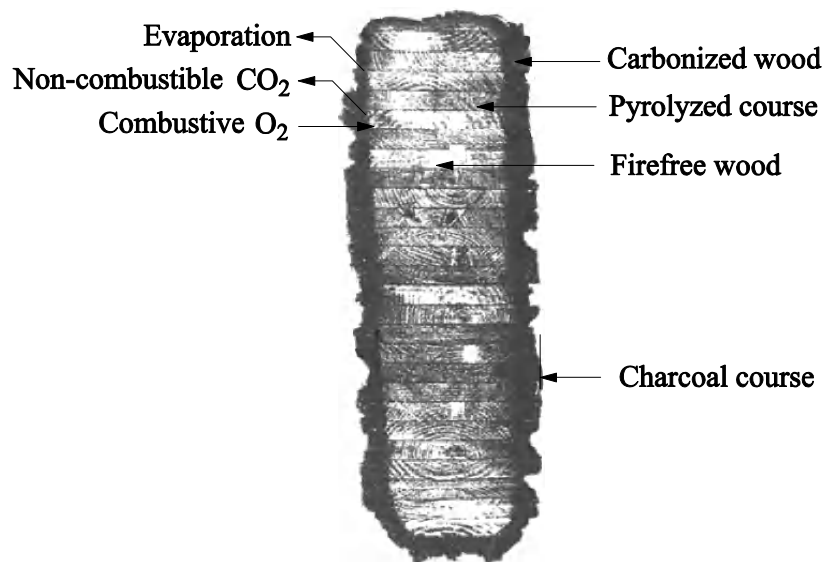


Figure 15.10. Cross-section of a piece of wood during a fire (source CNDB)

Wood products and its derivatives are generally located in class B, C or D. Solid wood (starting from a 22 mm thickness) and laminated wood (starting from a 40 mm thickness) are classified D-s2, d0.

The surface layer of a wooden element subjected to an intense source of heat gradually breaks down, igniting around 350°C. Its ignition is a function of the relationship between the surface, which is the heat source, and its volume. Moisture obviously plays a part in igniting wood. Its combustion speed is as slow as it is dense, and presents few defects, such as cracks (allowing the water to leave via the wood's core). All kinds of asperities are also favorable for combustion. From the point of ignition, a layer of charcoal is formed, under which a layer of wood known as "pyrolyzed" but not yet deconstructed can be found having a thickness varying between 5 and 10 mm. The progression of the carbonized layer towards the interior occurs when the pyrolyzed layer reaches a temperature of 500°C, after the evaporation of the water and the departure of flammable gases. When the carbonized layer reaches a sufficient thickness (10 to 15 mm), it begins insulating (charcoal is indeed eight times less conductive than wood) and stabilizes the combustion speed. This combustion can therefore be modeled and the EN 1995-2 define a conventional carbonization speed, taking into account the nature and the density of the species used. We consider, then, that, laminated softwood burns at a rate of 0.7 mm/mn.

In terms of *fire resistance*, wood, thanks to its slow combustion rate and the preservation of its mechanical characteristics, is regarded as a particularly reliable and predictable material.

15.2.4.5. *Durability*

Wood, a material rich in starch and cellulose, favors living organism development. It can be degraded by fungi or insects. These risks of attack are directly related to the moisture contained in wood and at ambient temperature.

Attacks on wood by lignivorous fungi only occur within a certain range of a wood's water content (between 22% and 30%). It can be benign and superficial, creating problems (moulds, blueing), or generate a more or less severe chemical decomposition of the cellulose (rot, hard rot) and of course, it can be blamed on the strength of the construction.

Xylophagous insects (the longhorn beetle, the hesperophanes and the lyctus, the small and large furniture beetle) lay eggs on the surface of wood or in the existing cracks. The resultant larvae, can develop in the wood for several years. The damage is related to the length of time they stay there, the frequency of the reproduction cycle, the size, the number and the voracity of the larvae. The small tunnels that they create decrease the mechanical strength of the construction.

The only insects consuming cellulose in adulthood are termites. They attack all species (except some tropical species) under particular biotopic conditions: temperature, moisture, darkness. They particularly like the wood already altered by fungus. The deterioration of the wood continues until the element is ruined and occurs without any external signs of attack. This always begins with elements which are closer to the ground, in general already deteriorated by mushrooms. The damage caused by termites in France for 250 years now are due to tropical species imported with the wood and which have been acclimatized.

15.2.4.6. Mechanical behavior

We previously saw that a wood's constitution changes it into a heterogeneous and anisotropic material. Its fibrous organization makes its mechanical behavior very different, according to the orientation of the mechanical strain rate compared to the direction of the fibers (direction of the grain).

Behavior is increasingly more satisfactory in the direction of the grain, than in transversal directions. The hollow tubes which are the fibrous wood cells also show different behavior under tension and compression. Under tension, behavior remains linear until brutal deconstruction by longitudinal uprooting of fibrous tissues. Following this is a rather brittle rupture of the tense elements. Under compression, behavior remains linear for strain extension which is shorter than when under tension because in this case, the ruining phenomenon initially occurs by the micro-buckling of the fibers, then by transversal uprooting. The combination of these two modes occurs in a more diffused way than for simple longitudinal uprooting under tension, which leads to a light stage of pseudoplasticity. Rupturing without overall instability of a compressed element is therefore rather ductile (Figure 15.11).

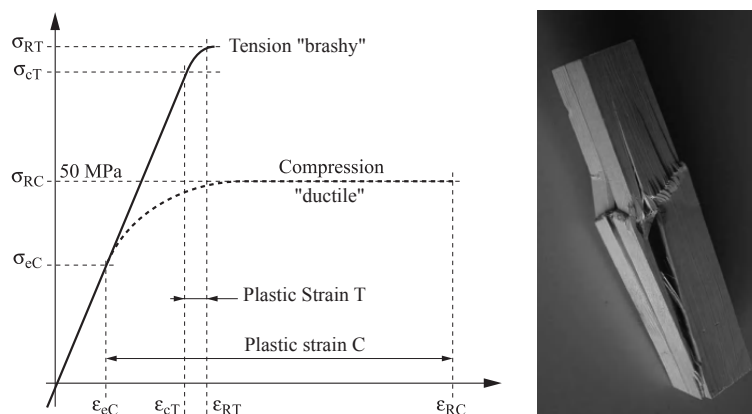


Figure 15.11. Strain–stress curves under tension and axial compression, and rupture under axial compression

In the transverse direction, either the crushing of the tubular structure, or the slipping and pulling of fibers, one compared to the other, give the material much poorer mechanical properties. The presence of wood rays organized radially creates a hooping effect between the fibers which reinforces the behavior in the radial direction. Still, the slipping resistance of the fibers is proportional to the material's density (Figure 15.12).

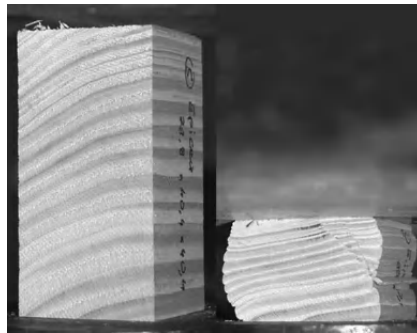


Figure 15.12. *Transverse compression test on a spruce sample*

The resistance and rupture mode under flexure are completely subjected to the relative ratio of resistances under tension and compression. According to the geometry of the section, or the value of the total normal constraint at the time of a strain superposition (compound flexure), the behavior of the element under flexion will be different. If resistance to tension is reached first, then the behavior will be brittle. If compression is reached, the flexure will be ductile. In this last case, when the pseudo-plastic stage under compression is reached, the neutral axis migrates towards the tense zone, in order to increase the height of the compressed wood, and to preserve the balance of internal strain.

All the mechanical characteristics of this material are strongly influenced by the density. For each species or family, it was necessary to create classes according to the strength, guaranteeing the mentioned characteristics for 95% of a population (Table 15.1).

The hygroscopic character of wood is considerably important with regard to mechanical behavior. An increase in 1% of the water content leads to a reduction in resistance. The relationship is almost linear for an humidity varying in the 8% and 20% range.

The impact of an increase in the water content is generally less favorable for the compression resistance than for tension resistance. The transverse bond between

fibers, which the compression resistance is dependent on, is indeed partly guaranteed by hydrogen bonds which disappear when the water content increases.

CLASS	C18	C22	C24	C27	C30	C35
Characteristic stress in MPa						
axial bending	18	22	24	27	30	35
axial tension	11	13	14	16	18	21
axial compression	18	20	21	22	23	25
longitudinal shear	2.0	2.4	2.5	2.8	3.0	3.4
transverse compression	4.8	5.1	5.3	5.6	5.7	6.0
transverse tension	0.3	0.3	0.4	0.4	0.4	0.4
Elastic modulus in MPa						
average length modulus E	9,000	10,000	11,000	12,000	12,000	13,000
longitudinal modulus 5%	6,000	6,700	7,400	8,000	8,000	8,400
average transverse modulus	300	330	370	400	400	430
Average shear modulus G	560	630	690	750	750	810
Density 5% in kg/m ³	320	340	350	370	380	400

Table 15.1. *Mechanical characteristics of softwood trees according to norm EN 338 [AFN 03]*

Wood also presents a viscoelastic character. The application of a long duration load leads to a reduction in the rupture load. This reduction tends to be stabilized after ten years. It is bigger when the wood's water content is high.

The strain characteristics are also affected by the creep phenomenon. It is essential to take this into account during dimensioning.

The presence of defects in wood makes it a material which is sensitive to scalar effects. The mechanical behavior of a test-piece depends on its dimension, and beyond this, on its strain volume. This is particularly true for behavior under tension (parallel and perpendicular in the direction of the grain) for which we have established a similarity to chain behavior. This similarity is usually used in brittle fracture mechanics. A succession of links is considered. Chain breakage is conditioned by the weakest link. In the wooden test-piece, the weakest link generally corresponds to an area containing a knot, a crack, a fungal deterioration or an important difference in the direction of the grain compared to the direction of the action.

15.3. Industrial approach of material

15.3.1. Improvement of natural material

The many singularities of this natural product and its great heterogeneity do not make it an industrial material for simple use. The wood sector as a whole has endeavored to make this construction material less random and closer to descriptions used for industrial materials like steel or aluminum. For this reason, classification rules, and a standardization in sawing were put in place. Labels and certifications proposing guaranteed hygrometry and complementary treatments appeared.

15.3.1.1. Aspect and mechanical classification

Two types of classification are currently used:

–*aspect classification* which takes into account the visual aspects of the material by taking into account the characteristics (depression, knots, slits, defects), on two or four sides of a piece of wood. It is mainly used to guarantee the wood quality used for facings;

–*structure classification* which guarantees the mechanical characteristics of a wood used in construction (see Table 15.1).

These two types of classification are associated with manual or mechanical sorting processes, thus by using certain mechanical performances, density or a videometry principle. These go hand in hand with a dimensional standardization of sawing.

15.3.1.2. Different breakdown modes

To limit the effects of wood shrinkage in wood during its drying (deformations, cracks), saws have gradually developed breakdown modes to guarantee quality.

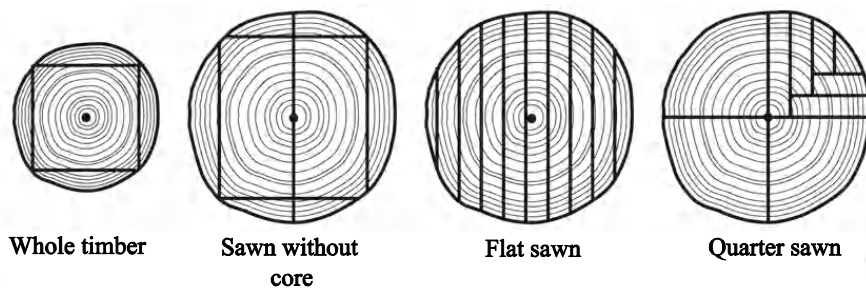


Figure 15.13. Different cutting modes of a trunk

For the framework wood, simple squaring preserving the pith inside the section was gradually abandoned for sawing in split core or without core. According to the initial diameter of the trunk, the extracted sections are either sufficient by themselves, or they are rejoined by gluing or bolting after drying. We also avoid a general shrinkage. The strain in each part is decreased by preliminary drying which brings back the material's hygrometry to a rate which is closer to its later use.

For the reconstituted parts, this deformation can also be avoided by that which is found to be directly contiguous. In this way, we also avoid the appearance of unwanted slits.

When using a solid round section, we can now create superficial surface load grooves. These concentrate the inevitable slits caused by shrinking and avoid their random formation at the part's final aspect.

For the carpentry and cabinetwork wood, specific cuts (quarters or false quarters) may be preferable to the traditional block cuts which are much cheaper. These particular cutting methods increase the number of plates with radial orientation. With radial shrinkage being weaker than tangential shrinkage, the strain on each plate is reduced.

15.3.1.3. *Drying*

The appearance of industrial ventilation driers and controlled hygrometry lets us replace natural drying, immobilizing important wood stock for several years. This makes it possible to dry large volumes of wood, with a level of hygrometry chosen which is often lower than what is permitted by natural drying, but without the appearance of slits or cracks. The drying time varies from three or four weeks to two days, according to the species and the thickness of the cut.

More and more we are trying to obtain sawing methods whose water content is the nearest possible to that which corresponds to its final intended use (5% for parquet floors, 12% for wood intended for gluing) in order to limit shrinkage phenomena. The industrially dried sections are often smaller so as to accelerate drying. The later gluing stage then makes it possible to reconstitute bulkier parts proposed for marketing.

15.3.1.4. *Conservative treatments*

15.3.1.4.1. Impregnation treatments

Several conservative treatments have been developed by industrialists for improving sustainability, fire resistance or the hydrophobia of the material. The treatments are either on the surface, by creating a film or a low-depth impregnation, or by deep treatments which require a partial vacuum using deep impregnation. This

is practiced, then, in autoclave processing. The penetration of the product is directly related to the density of the core wood which means that certain species cannot easily be impregnated (larch, oak).

The treatment products are classified in three types: oily products, organic materials dissolved in an petroleum solvent and salt solutions dissolved in water.

The ecotoxicity of oily products (creosote and anthracene oils) limit their use to certain external applications (telegraph poles, railroad crossing). The majority of the treatments use either oil solvents and hydrodispersable products applied by dipping or pulverization, or injected water-soluble salts containing chromium, copper, arsenic and boron.

The undeniable effectiveness of these products should not allow us to forget their strong toxicity for human beings, either in the application stage, or by slow diffusion over time, or at the time of recycling or destruction by incineration. Users try to limit its usage according to localization of the parts and incurred risks. For this reason, they choose naturally sustainable species, or eliminate the sapwood which is more sensitive to aggression from it beforehand. New treatments, either physical or chemical, try to propose alternatives to these toxic treatments.

15.3.1.4.2. Controlled thermal treatment

This physicochemical process is based on the pyrolysis of wood under an inert atmosphere at a maximum temperature of 240°. Hemicelluloses are then “cracked” and lignin starts to change, creating a more hydrophobic and more rigid pseudo lignin. The wood which is thus obtained, a brown color, presents some improved characteristics with regard to retractability and sensitivity to biological degradation agents, with the exception of termites. It is also less sensitive to punching but becomes both more rigid and brittle.

15.3.1.4.3. Wood hydrophobia

A wood’s reaction to hydrophobia by lipid esterification has been known for a long time. This reaction has often used a highly toxic agent.

Recent research tests try use new alternative agents such as ASAM (methyl alkenoate of succinic anhydride), a derivative of rapeseed oil obtained after a chemical reaction with acetic anhydride. The mixed anhydride obtained is thus a “green” chemical compound whose reaction to wood does not release any other toxic by-products, and proves entirely to be recyclable.

The impregnation of wood by mixed anhydride is performed in two stages: initially, within an autoclave, where the partial vacuum allows its penetration into the wood's core, then in a vat where wood is soaked in a heated anhydride bath at 140°C to promote the product's grafting on wood.

During treatment, ASAM transforms cellulose into cellulose ester, which cannot be consumed by the xylophagous insects because they do not have the correctly adapted digestive enzymes. During treatment, the oily ASAM solution fills the wood cells and gives it hydrophobic properties. The material is thus protected from moisture and external aggression, and does not require any more maintenance.

15.3.2. *Derivative products*

Natural wood is, as we have seen, limited in its applications. The origin of its production has high impact on the dimensions and shapes of the obtained products (log length, shape, width and thickness of the section). Its growth structure gives it a great anisotropy, favoring axial direction. The material's heterogeneity due to its characteristics and growth defects of trees restricts their performance. The industry of wood transformation therefore tries to reorganize natural material within a pre-defined framework to improve its behavior and its use.

The first products of this kind appeared in the middle of the 19th century (plywood) and has not stopped evolving since: evolution of industrial processes, discovery of new binders or glues by the chemical industry, requires new technical or decorative qualities or, now, the consideration of environmental and public health concerns.

The valorization of by-products from forest development (clearing wood) as well as first transformation waste (bark, sawdust, chips) is often one of the reasons for their appearance.

Manufacturing processes, the more or less advanced disorganization of natural material, from simple sawing to the defibration, the quantity and adhesive performances of the binder used are the reason behind the performances of these derived products which are true composite materials organized by industrialists.

All offered products:

- have a controlled hygrometry and guarantee;
- benefit from a purge of the most prejudicial characteristics;

– have, according to the application concerned, a linear organization with anisotropic or superficial characteristics, or with orthotropic or isotropic characteristics;

– see specific improved performances (damp-proof, fire resistance, acoustic properties, abrasive resistant, etc.) by using a specific binder, by adding extra products, or by a particular surface treatment (nature of the material or film used on the surface, but also a specific machining, etc.).

15.3.2.1. *Derivatives containing sawn timber*

15.3.2.1.1. Glued laminated timber (GLT)

Timber which is sawn and purged of defects is joined to form square blocks or continuous thin boards of the desired final length. The unit then is glued together, piled up with a possible bend to allow for curvilinear forms, then in pressed onto an embossing bench while the glue sets. The finished product can be very long, often more than 40 m, and contain important sections by multiplying the layers.

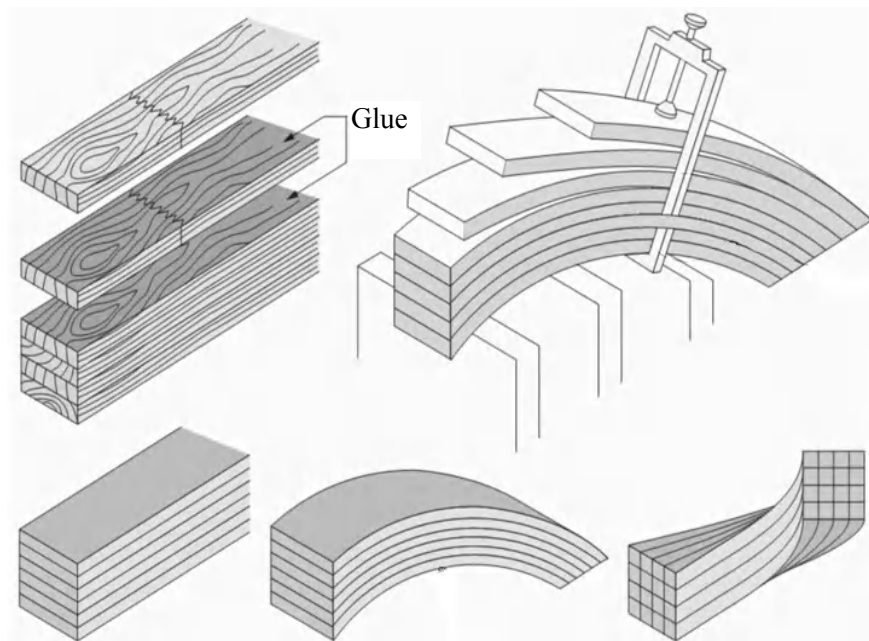


Figure 15.14. *Glued laminated timber manufacture*

We obtain a rectilinear or curvilinear element in one or more planes, according to the gluing bench. The obtained curve depends on the thickness of the plates. The bigger the desired curve, the thinner the plates should be (Figure 15.14).

15.3.2.1.2. Glued laminated timber panels

Sawn timber lathes which are purged of their defects and identical thickness are glued together on only one applications. We can join to them, on each facing, a thin ply, with the direction of the grain crossed with the direction of the core, to obtain blocks or multiply woods.

15.3.2.1.3. KLH cross-laminated timber (Kreuzlagenholz)

Lathes (8 mm thickness) or planks (22 mm thickness) of sawn timber are glued in crossed layers in odd numbers (3, 5 or 7 layer) in order to obtain solid panels. The orthotropic character of the obtained product and its rigidity means that it can be used directly as a structural element such as a slab or load bearing shell.

15.3.2.2. *Derivatives containing sliced or unrolled wood*

Thin sheets of wood of approximately 3 mm are obtained by cutting or unwinding of a sawn timber log. They are then reassembled by gluing to obtain products with different qualities.

15.3.2.2.1. Plywood PW

This is created by gluing of an odd number of sheets whose grain direction is crossed in relation to the preceding layer. The thicknesses go from 3 mm to 30 mm. The obtained product (2.50 m × 1.22 m or 3.10 m × 1.53 m) is orthotropic and according to the type of glue used, may have extra properties (external use, humid atmosphere, etc.). Gluing on a mould machined beforehand means that we can obtain products with simple or double curvature used for fitting and in the furniture industry (Figure 15.15).

15.3.2.2.2. Laminated wood or LVL (Laminated Veneer Lumber)

This has a similar procedure to plywood, containing sheets obtained by unwinding logs of 2 m in width, but gluing these sheets is achieved grain by grain using phenolic resin. The panels are joined by shifting the joins, to form beams or long panels (lengths up to 23 m, width up to 1.8 m, thicknesses from 20 to 80 mm). The mechanical properties of LVL are very interesting and it is often useful in the manufacturing of reconstituted beams or load bearing shells.

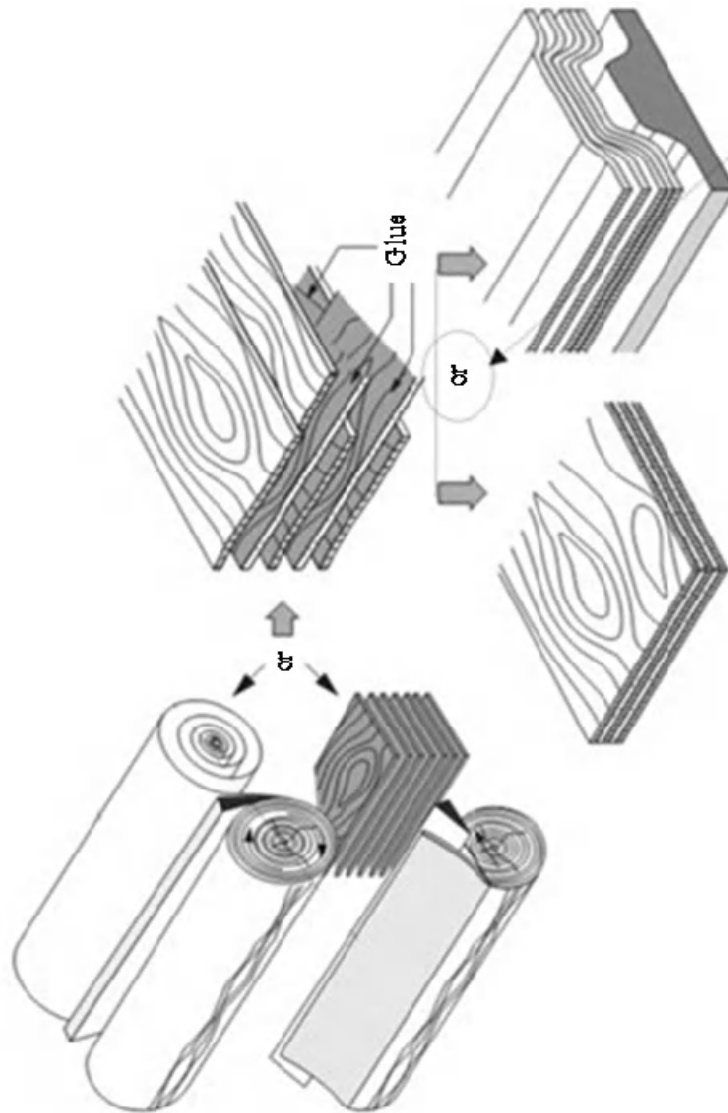


Figure 15.15. Plywood manufacture

15.3.2.3. *Derivatives containing chipped wood*

15.3.2.3.1. Particle panels

Wood used coming from industrial waste is either of sawdust or chips, more or less large in size. The binding agent used is generally a thermohardening resin, but sometimes hydraulic binders (lime, cement, plaster) and gives these panels very large fire and moisture resistance properties. The products obtained by these processes are generally isotropic, and have low mechanical resistance. These panels can be full or alveolar (Figure 15.16).

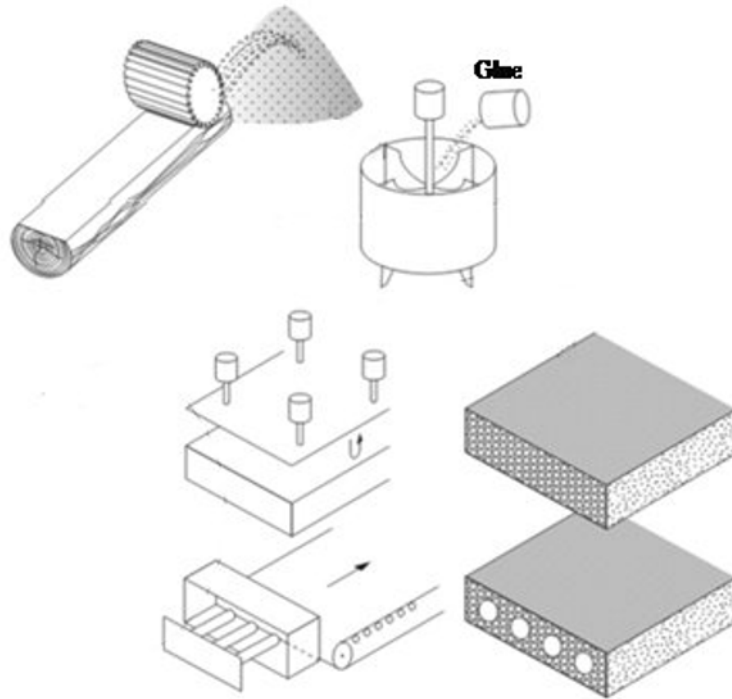


Figure 15.16. *Particle panels production*

The use of large dimension particles obtained from cutting softwood wood and their organization in the form of a three successive layered mattress (*OSB: Oriented strand board*) that enables to improve the mechanical performances of the panels. They display orthotropic behavior with mechanical qualities very similar to those in plywood. Their shear strength permits them to be used for winds-bracings or diaphragms.

15.3.2.3.2. Layered wood

Long thin layers, waste from unrolled wood for PSL (*parallel strand board*), or the large-sized chips (layers in length up to 300 mm) for LSL (*laminated strand board*), are glued together, then continually pressed into a die, to form either beams of important sections and long lengths (up to 20 m), or large dimension panels (20 m $\times$ 10 m).

The density of the product obtained (670 kg/m³) and its elasticity modulus which is greatly higher than for sawn timber (13,500 MPa) make this product particularly well adapted for strongly strained parts (large range).

15.3.2.3.3. Fiberboards

Waste produced from the first transformations of wood is primarily transformed into plates which are steam pressured then inserted into a defibrator which reduces them to wood fiber state. The lignin, which is softened during this operation, ensures partial or total joining. According to the density of fibers implemented in the panel, we obtain products with very different qualities. The tender fiberboards with weak density (250 to 300 kg/m³) are used for thermal and acoustic insulation of walls, floors and roofs.

Average density panels (750 kg/m³) are pressed and hot glued. We then obtain MDF (*Medium Density Fiberboard*). The fine and homogeneous structure of the panels obtained means they are used very frequently in fittings and the cabinet work.

High density panels (> 900 kg/m³) have a more restricted use. Using them in the core of some products for buildings or in cabinet work is primarily justified by their low costs.

Chipboard fiberboards agglomerated by phenolic resin display good behavior to atmospheric agents and do not need to be maintained. They are very good for outside use and partitioning rest rooms.

15.3.3. *Evolution of the glues*

By its macroscopic organization and multiple porosities that it contains, wood lends itself particularly well to the gluing. The mechanical adhesion due to the penetration of glue into a material adds to the glue's precise adhesion (attraction between molecules of the body to be glued, and the glue molecules). For a long time, we used glues of natural origins, particularly animal and vegetal base. The obtained gluing resistance was decreasing over time under the influence of heat, moisture and micro-organism attacks (algae, bacteria, mold).

Thanks to the use of chemicals, the appearance of many synthetic glues at the beginning of the 20th century, is the reason behind all wood panel industry and other derivative wood products.

The glues and resins used depend on the working moisture and temperature conditions of these products. Glues containing casein are the first to have been used for industrial use. Their behavior is poor in wet conditions and the development of mold due to the protids they contain require the use of antifungal products. Their use is now hardly reducing.

For structural uses, we generally use aminoplasts and phenoplasts as glues (phenol-formaldehyde, resine-formaldehyde, urea formaldehyde or melamine-urea-formaldehyde). These glues are currently the focus of much debate, due to the fact that some of the products contained within release harmful formaldehyde emissions.

Formaldehyde causes, even in low concentrations, irritations (itching, weeping), in the eyes, the respiratory tracts (nose, throat, lungs) and the skin (redness, itching, eczema). It may also have neurological consequences, resulting in increased fatigue, anxiety, migraines, nausea, drowsiness or vertigo. Exposure to formaldehyde may lead to sensitivity and the development of an allergy. When in contact with the skin, through cosmetics or textiles, it may cause contact allergies. This product is classified today in the first group of carcinogenic agents for humans.

Gluing processes have greatly evolved over the last twenty years. To avoid these health hazards, new glues (PURE cross-linked polyurethane, epoxy resins), with equivalent performances in dry atmospheres, have become known. Their behavior in moist environment currently seems to be insufficiently reliable, and PFR glues (phenol-resorcine-formol) are still preferred.

The almost systematic use of glue containing formaldehyde in the first industrial products requires their recycling or destruction to be performed with many precautions, so as to avoid too strong exposures to formaldehyde.

15.3.4. Developments in constructive technologies

The average resistance of wood associated with its weak density, makes it an excellent structural material. Its specific stress (σ/ρ) and its specific module (E/ρ) are widely higher than those for concrete. For a good quality species, this can be close to those for aluminum or steel (Table 15.2). In particular, it allows for a reduction in the foundations and allows a greater level of spatial freedom.

	$\sigma_{\max}$ (MPa)	Density	Specific strain σ/ρ	E Modulus(M Pa)	Specific modulus E/ρ
Steel	400	7.80	51.3	210,000	26,900
Aluminum	200	2.60	76.9	74,000	28,500
Concrete	40	2.5	16	30,000	12,000
C14 Spruce	14	0.45	31.1	7,000	15,600
C40 Spruce	40	0.45	88.9	14,000	31,100

Table 15.2. *Compared mechanical properties of some materials*

Improving natural material, by using derivative products, has been accompanied by a large evolution in the principles of designing timber construction, taking into account new possibilities offered by the appearance of new tools and machines, but also the technical and expressive possibilities of newly proposed materials.

15.3.4.1. Structural products. Inertia variation

Wood, by its natural constitution and its macroscopic organization, is provided for the construction of linear and rigid elements. These can be used directly in the constructive logics of stacking (log and beam construction) or frameworks (columns or post-beams). The material is then primarily strained under compression and flexure. A reflection on the organization of the matter in the section or its longitudinal profile is the root of great mechanical effectiveness. The shape of the section and/or the longitudinal profile are then adapted to the stress distribution induced by strains.

The current techniques for gluing associating different elements with different nature, have allowed industrialists in the wood trade to propose more effective

sections for the parts strained under flexure (Profile in the shape of an I or a box for beams) or under compression (profile in shape of a H, in a cross, or circular section for posts) (Figure 15.17).

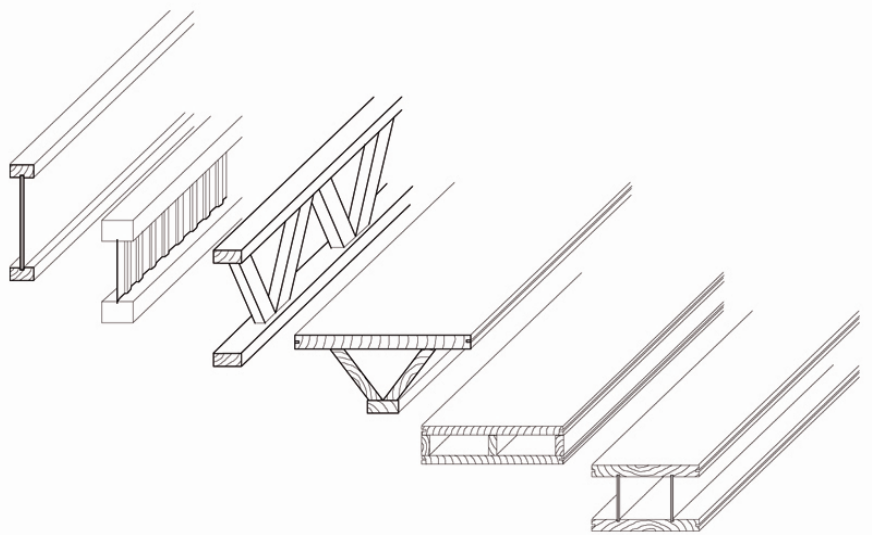


Figure 15.17. *Structural products manufactured in the wood industry*

Variations in inertia are easy to do thanks to the laminate technique or with cores of variable width similar to PRS (welded reconstituted sections of steel).

The profiles with variable inertia in certain beams with great ranges, or portico elements illustrate this procedure for mechanical effectiveness (Figure 15.18).

15.3.4.2. *Constructive logic*

As for other materials, structure design principles replacing normal strains by flexure (triangulation) or exploiting the funicular shapes of a given load are used. Therefore they make great savings in terms of material. The most spectacular evolution of these last years is, without question, the appearance of 3D structures (lattices, beam grids, flagstones, shells). This was made possible through the contribution of computers, facilitating the calculation of these highly hyperstatic structures, and also guaranteeing geometrical precision by digital machines, which is essential for the sizing and assembly of various elements.

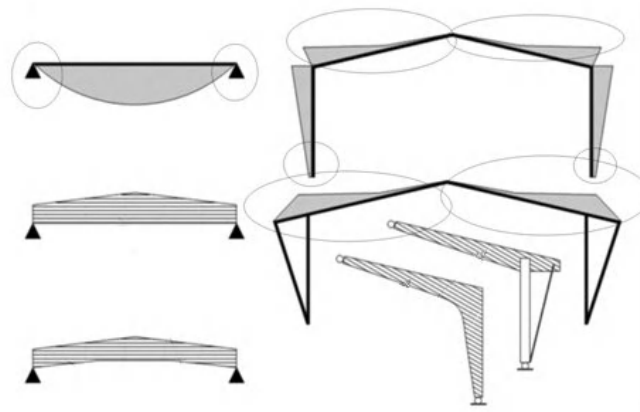


Figure 15.18. *Examples of elements with variable inertia adapted to the moment diagrams*

15.3.4.2.1. Thin shelled structures

Derivative products, with orthotropic characteristics, have also promoted, in the wood construction industry, the appearance of new constructive logic: the thin shell. Panels for construction can be used both as an envelope and for structuring. This constructive principle, using plate effects, means that these panels must be able to withstand shear forces.

According to the techniques and the semi-finished products used, the little useful matter providing the structural function leaves an important vacuum or only has low thickness. The released place can then be taken by an insulating material, allowing the construction to reach technical performances conforming with contemporary expectations.

15.3.4.2.2. Mixed structures

Lastly, it is also necessary to flag the recent evolutions using a mixture of materials in certain structures.

Steel is often greatly associated with wood. The strong tensile strength and ease of creating joints with wood means that its use as a tie beam can be very interesting. This is particularly the case for large range triangular trusses.

Concrete with null behavior under traction, is often associated with wood in collaborating floors where it is used as a compression table. The wood underneath takes away the tension strains.

15.3.4.3. *Joints*

The logic of material joining has greatly evolved. For a long time, joining was carried out per material, allowing the connection of a male part into a female part (Mortise and Tenon joints, notches, etc.). In the event of large strain rates, they present several disadvantages. Material's anisotropy gives them a poor mechanical performance, where the shears and transverse tension penalizing these performance. Tension strains are difficult to get back. Removing matter decreases the effective section and weakens the structures.

The appearance of industrial wire-drawing mills in the middle of the 19th century which gave way to the production of cheap metal accessories revolutionized the techniques of joining. Privileging the transmission of strains by shearing, these accessories primarily strain wood under transverse compression. A multitude of solutions use linear organs (points, bolts, pins, needles, fasteners, etc.), surface organs (brackets, connectors, cases, plates, etc.) or voluminal accessories (cramps, rings).

The pieces of wood used in joints are often duplicated (braces) in order to promote more effective double shears. Possible drillings and cavities imposed by the joining solution retained are greatly reduced. However, the behavior of wood in local bearing pressure and the possible group actions, often imposing a space between each organ, must rely on assembly surfaces which prove to be dimensioning for the whole structure. They then impose, that certain parts of the sections, are much larger than those needed for getting back the strains in a normal section of the element.

The completion of many of these joints which require a lot of drilling and machining with a high degree of accuracy, was only made possible by performances from machines with great dimensions (several tens of meters) and a large digital control. Indeed, the stakes must be reduced to the minimum to limit slippage in the joints at the time of loading. This has often proved to be impossible with traditional manual techniques.

Developments in gluing technologies are now the base of new advances.

The progress made in glue chemistry from now on authorizes assembly methods which being back high strains, allowing the completion of greatly strained civil engineer constructions, and placed under difficult hygrometrical conditions. The use of structural glues requires temperature and hygrometry conditions which are not adapted for use on a building site.

On the other hand, it is possible to set in the production area using epoxy resins, either metal inserts, or strengthening shafts. The inserts accept very important strains (up to 400 kN under tension) without increasing the useful section necessary to regain RDM (strength of material) strains. They allow for a fast and effective structural joining on the building site by using high-strength bolts. The strengthening shafts play an identical role as the metal reinforcements in reinforced concrete, and locally reinforce elements in highly strain zones. They may also lead to assembly between two elements.

15.4. Conclusion

The precise understanding of a material, on all the scales of its organization, has allowed professionals in the wood industry to continuously take advantage of it. Following the example of steel or concrete, wood has now become a genuine industrial material with standardized properties. Thanks to the development of many derivative products, which are increasingly more powerful, the quantity of wood used in a construction is now greatly reduced compared to the amount used in the last century.

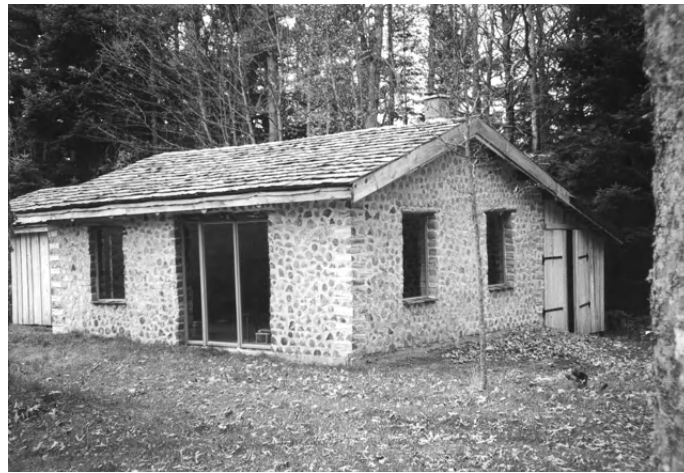


Figure 15.19. *Single house made of cordwood*

This undeniable progress was one of the causes for the revival of the wood industry and has allowed, through many exemplary achievements, to promote this material. This is also the reason behind a strong industrialization of the wood trade. As for other material industries, some factories spread about in the country are sufficient

to fulfill demands and concentrate work forces. In return, this involves a great increase in the need for transport to accommodate building companies, once again.

Wood demonstrates, as we have seen, many ecological assets which are not fully valorized by this industrial procedure. Other alternatives, still making their way in the industry, particularly cordwood, propose limiting the greenhouse effect, to fix a maximum of carbon while trying to use a lot of weakly transformed wood. These initiatives which develop a lower quality material, are perhaps the first steps towards a new evolution in the wood industry over the next decades.

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PART 5

Organic Binder-based Materials

Chapter 16

Bitumen, Road Construction and Sustainable Development

Moving, taking to the road; in our Western societies means following the black ribbon which grooves its way through our landscapes and allows us to move with a certain comfort which makes us the envy of developing countries. It has not always been this way. It may, then, be a good idea to return to the history of the introduction of bitumen in road engineering, in order to understand how this innovation could be a factor worth developing, and to think about current evolutions and how bitumen falls into the category of sustainable development.

16.1. A bit of history

16.1.1. *An ancient history*

As soon as man realized that he was in a position to create something, he was attracted by natural bitumen released from the ground. He then discovered and used its many properties. Archaeological research has updated the existence of an evolved technology, 5,000 years old, applied to building waterproofing and aquiferous constructions using bituminous materials. The people of Mesopotamia knew and used oil products such as they were collected on the ground's surface. These were viscous products, like naphtha oils or bitumens. The liquid bitumen spouted out of the ground, running on its surface and, after being recovered, was often mixed with minerals or with organic materials. The usual temperature was around 160°C, and

Chapter written by Bernard LOMBARDI.

these mortars could contain up to 25% bitumen. Lastly, bitumen was used in the making of many oral remedies, ointments, fumigations, etc.

Closer to us, the use of bitumen mixtures was limited to waterproofing the impermeability. A splendid construction, like the Popes' Palace in Avignon, includes several constructed pieces using natural bitumen. On the roofing, the stone slabs were joined with this bituminous material and the walls of the Palace's water tank, dug out of rock, were covered with bitumen softened by olive oil addition.

At the end of the 19th century, a growth of car traffic required an improvement in the quality of roadways and first of all, a reduction in dust emissions due to the traffic. At this time, groups were already organizing themselves against the pollution generated by car traffic. It was not a question of exhaust fumes but the large quantity of dust thrown up by tires on beaten earth.

Then, the first stabilization tests on grounds were performed using hydrocarbon binders applied at elevated temperature or at ambient temperature under emulsion form. In France, history will account for the first road laying, between 1889 and 1892, heavy oils coming from coal distillation were used. Spreading this "tar" had positive effects on the reduction of dust emissions and on the improvement of the bearing capacity of the road in rainy weather period, and encouraged technicians to widen the range of products in order to improve results. In 1902, the *Promenade des Anglais* in Nice was tarmacked and this process, then considered rustic, was improved and applied everywhere. Thus, the public was familiarized with this technique called "tarmacking". The use of this expression has been used for generations. Today still, the road user compares any road building site using bitumen to a building site using tar, although tar has not been used in France for many years.

At the same time, hydraulic structures were developed to allow the construction of roadways able to contain cement sand-gravel mixes, slag sand-gravel mixes, fly ash sand-gravel mix, reinforced or unreinforced concrete.

At this stage, it is appropriate to point out some definitions.

16.1.2. First definitions

Natural rock asphalt is a sedimentary rock impregnated with bitumen, with an average content of around 9%. The word natural rock asphalt is also used to indicate any layer or seepage of viscous hydrocarbons, which may contain largely variable quantities of mineral particles. This material, extracted from mines, and mixed with aggregates at more than 230°C, was used to prepare the straight run bitumen used

for producing the pavements and some roadways. In English this technique is mastic asphalt application. Nowadays, straight run bitumen is known as “synthetic” because the various available formulas no longer contain natural bitumen, the binder being bitumen coming from oil refining.

Bitumen is a natural mixture of solid or semi-solid hydrocarbons, brown or black in color, and odorless, which impregnates rocks known as “reservoir rocks”. This mixture is also in certain crude oils, known as bitumen crudes.

Tar is a generic term which applies to any liquid product, oily, viscous, brown or black in color with strong empyreumatic odor, obtained by dry distillation at more than 500°C, oxygen free atmosphere (destructive distillation), and many other organic matters, like coal, wood etc. *Road tar* was prepared from coal tar formed during coal pyrogenation in coke ovens.

Pitch is a more viscous form of tar. By convention, we distinguish tar and pitch compared to a viscosity limit measured by the softening point. All product obtained by pyrogenation (or pyrolysis) and having a softening point higher than 40°C, is a pitch.

16.1.3. Bitumen in contemporary times

The motor industry boom at the beginning of the 20th century, resulted in an exponential increase in the traffic, which forced the people responsible for “pathways” to consider the working qualities of modern roads: keeping good resistance in all weather conditions and particularly in rainy periods, being durable, comfortable, non-skidding, dust-free, easy to repair, easy and quick to build, while staying less expensive.

Hydrocarbon binders and bitumens in general answer these requirements.

16.1.4. Bitumen in road engineering

To use bitumen, it is necessary to reduce its viscosity in order to either correctly coat the aggregates which must be agglomerated during the bituminous mix preparation, or either be applied in a regular coat from 0.5 to 2 mm to put in place surface treatment. There are five main ways of doing this:

- to heat it at a temperature so that it is sufficiently liquefied to coat the aggregates; this is the hot-mix asphalt technique;
- to fluidify it by adding a solvent (fluidifying or fluxing);

- to disperse it into an emulsion in water before use;
- to make it foam by injecting an small amount of water just before use;
- to incorporate certain polymers which will cause a large drop in its viscosity beyond a certain temperature.

One then distinguishes the “hot techniques” from the “cold techniques” which are *a priori* more economic and more ecological but which are not able to replace the first in all their applications.

For the record, hot mix is prepared in a mixing plant which ensures a good dosage of granular cuts, aggregate dehydration and their heating to approximately 150°C before mixing them with hot bitumen. The hot mix is transferred onto the job site and is laid at this temperature. This technique consumes an important quantity of energy related to the need to evaporate all the water contained in the aggregates, and to increase the temperature of the aggregates to a value close to that of the bitumen.

In this process, calories can be saved if specific polymers intended to reduce viscosity are added to the bitumen. Thus, the mixing temperature can be reduced by approximately 30°C which decreases the combustion gas emissions.

Besides the technique of hot asphalt mixes, “cold” techniques also exist, which make it possible to reduce the amount of energy used by coating with cold and wet aggregates, using a fluidified or fluxed bitumen, or by means of a bitumen emulsion or finally, by starting the formation of a bitumen foam before coating. Under these conditions, the suppression of the operation of drying of the aggregates results in a major reduction of the fuel consumption.

In addition to the technique of hot or cold coating, another less laborious solution for the road maintenance exists: surface treatment. This technique consists to spray at least one binding coat (emulsion or fluxed binder) and to spread a layer of aggregates which are immediately rolled, so as to be in place before opening up to traffic. Such a production achieved with cold and wet aggregates requires minimum energy.

All these road construction techniques use two major components; aggregates and bitumen. In the context of sustainable development, it is necessary to take into account the life cycle analysis (LCA) of the used substances. This, then, leads us to point out the industrial operation necessary to develop bitumen.

16.2. Bitumen and bitumen binders today

16.2.1. Manufacturing bitumen

16.2.1.1. Direct distillation

Bitumen which constitutes the heaviest cut of certain crude oils, is drawn from the bottom of the “vacuum distillation tower” without any chemical transformation. The rheological properties of the bitumen depend on the nature of the original crude and the process. To satisfy technical needs, it very quickly became apparent that it was necessary to select specific crudes known as “bitumen crudes”, and to perform their distillation in a still tower designed for this operation.

This refining method consists of continuous heating the crudes mixture settled and de-salted beforehand in an oven. The “cocktail” of crude oils, brought to a temperature close to 370°C, is sent in a distillation tower whose internal pressure is comparable to atmospheric pressure. By sidestreams in this column, the refiner collects the light cuts like gases, gasoline, kerosene and gas-oil. The product recovered at the bottom of the tower is “atmospheric” crude oil or reduced crude oil.

The rest of the process is performed in a second tower, known as a “vacuum distillation tower,” or a tower with reduced pressure. The reduced crude oil is, after reheating it at approximately 400°C, sent to the vacuum tower where a pressure reduced to a few tens of hectopascals prevails.

Under these conditions, it is possible to directly manufacture all bitumen grades, from the 20/30 to the 160/220. It is important to note that at this stage, the bitumen produced in the bottom of the tower at an average outflow of several tens of tons per hour, must conform to specifications – particularly penetrability, a viscosity measurement which defines the grade of the product (see section 16.2.3.1).

16.2.1.2. Solvent desasphalting

In some cases where the separating power of the vacuum tower is not so efficient, whereas the lightly dense crude oil is not very rich in heavy cuts, it is then impossible to manufacture low penetrability bitumens. In this case, the physical separation of the crude oil components may continue without degradation, by benefiting from the differences in solubility of the lubricating and bituminous fractions in certain solvents. According to the solvent used, either butane or propane in liquid form, we obtain various bitumen grades while varying the feed nature and the desasphalting unit operating conditions, in particular the temperature, pressure and the relationship between the feed and the solvent. The bitumen obtained from this process, propane for example, is called PPA bitumen (*Propane-Precipitated-Asphalt*) and must be considered as bitumen from direct distillation.

16.2.1.3. *Air rectification*

For certain particular uses, it is necessary to slightly modify the thermal susceptibility of bitumens (variation of its viscosity with temperature). For this, we use an oxidation tower where the bituminous feed and the injected air circulate backwards. This operation is performed at a temperature ranging between 200 and 280°C according to different cases, and results in the dehydrogenation of certain hydrocarbon molecules which bind together, giving an increase in the softening point and a reduction in penetrability. The water produced by the reaction, as well as the light hydrocarbons, are evacuated with the gas current.

These “air rectified” bitumens, have a thermal susceptibility which is less than those of the same grade, prepared by direct distillation.

16.2.2. *Bitumen composition*

For a long time, researchers have tried to discover all its secrets, but we still have a long road ahead of us before reaching perfect knowledge of this product.

In section 16.2.1, it was noted that bitumen is the heaviest cut of certain crude oils, collected in bottom of the vacuum tower. At room temperature, it is generally black, quasi-solid and glossy. Bitumen is susceptible to temperature, but does not present a precise melting point because its viscosity is gradually decreasing when the temperature is increasing.

Bitumen reacts to mechanical strain as a viscoelastic material, and to temperature as a thermoplastic material.

Today, chemists admit that bitumen is a colloidal equilibrium, in which the asphaltene aggregates peptized by resins are dispersed in a continuous oily phase. This model is based, in particular, on work carried out by M. Corbett [COR 69] who defined generic families, SARA (saturated aromatic resin asphaltenes) while proceeding to multiple physical separations and to Ch. Gaestel [GAE 71] who introduced the concept of colloidal instability and the index I_C , defined as the relationship between the content of molecules tending to flocculate (asphaltenes and oils), and the content of molecules favoring peptization, following the formula:

$$I_C = \frac{[As] + [Hs]}{[Ha] + [Rs]}$$

where:

- [As] = asphaltene content;
- [Hs] = saturated oil content;
- [Ha] = aromatic and naphthenic-aromatic oil content;
- [Rs] = resin content.

This formula shows that when the asphaltene content grows and the content of peptized molecules decreases, the index of colloidal instability increases.

In the case of direct distillation bitumens for road application, the index of colloidal instability is weak, which corresponds to a lightly structured product which behaves like a sol (for solution), i.e. it presents the characteristics of a Newtonian fluid as soon as it is hot enough.

As an indication, this occurs as soon as the bitumen temperature reaches its softening point, increased by 80 to 100°C.

It is possible to modify bitumen by following different processes, but it is necessary to bear in mind that the colloidal equilibrium can become unstable after certain treatments and lead then, to an unusable final product.

16.2.3. Simple characterization of bitumen

In most countries, and in Europe in particular, bitumen is characterized by carrying out a certain number of standardized tests, amongst which the needle penetrations test and the softening point determination (ring-and-ball test), which allows us to know its consistency (for more, see [LOM 07]).

16.2.3.1. Penetration [NF EN 1426]

The needle penetration characteristic represents, expressed in tenths of millimeters, the penetration depth in a bitumen sample, after 5 seconds, by a standardized needle whose mass along with its carrier is 100 g. The penetrability value used most often is that measured at 25°C. It is used particularly for grading road bitumens. The lower the value obtained, the harder the bitumen.

In France, usual road bitumen belongs to one of the following grades: 20/30-35/50-50/70-70/100-160/220.

16.2.3.2. Softening point [NF EN 1427]

Bitumen has no precise melting point. Its consistency gradually decreases as the temperature increases. For this reason, determining the softening point must be performed under perfectly defined mechanical and thermal conditions.

The most widespread method consists of placing a steel ball of 3.5 g and 9.5 mm in diameter on a small bitumen disk of bitumen poured into a brass ring which is 19 mm in diameter. Together, placed in a container filled with water, is heated at a constant velocity of 5°C/min. The ring-and-ball test for obtaining the softening point (SP) is the temperature reached when the bitumen sample moved by the weight of the ball, presents a vertical deformation of 25 mm.

These two characteristics complement each other, as the diagram shows: “penetration = f(SP)” represented in Figure 16.1.

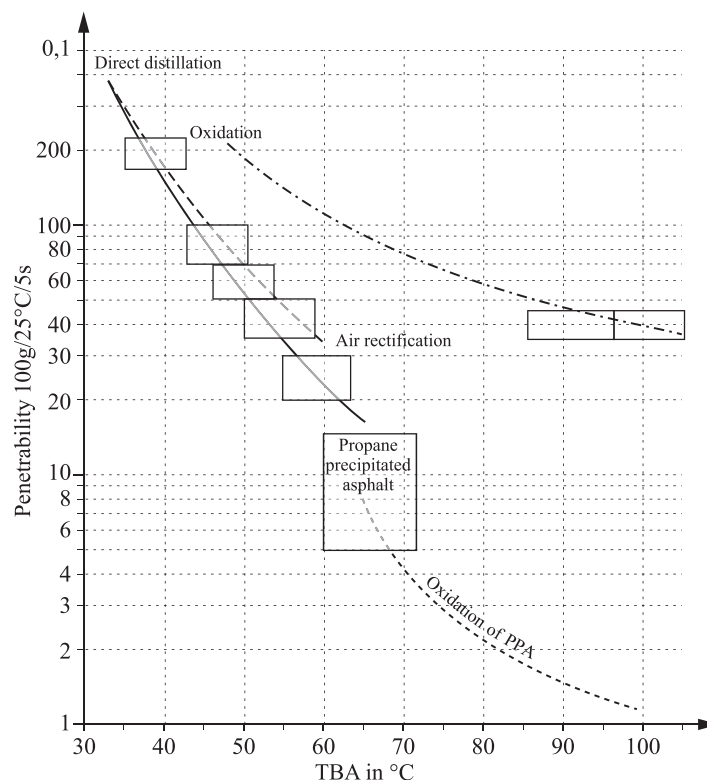


Figure 16.1. Diagram showing “penetration according to SP”

16.2.3.3. *Measuring the resistance to hardening under the influence of heat and the air. RTFOT method [NF EN 12607-1]*

This test subjects a thin film of bitumen or bitumen binder to the combined effects of heat and air in permanent renewal. It simulates the hardening subjected onto a bitumen binder during mixing in pugmill.

Practically, a binder sample, placed in a special bottle fixed on a sample carrying plate, positioned on a rotational axis crossing the back wall of the drying oven, is heated for 75 min, sees its surface being continuously renewed and receives a jet of hot air every 4 s. The influences of heat and air are evaluated from the mass variation and the evolution of the penetration and softening point. Other characteristics may also be taken into account [LOM 03].

It is advisable to remember that road bitumens are standardized products whose specifications appear in the norm NF EN 12591, in action as of January 1st 2010, a harmonized document conforming with the European Construction Products Directive (CPD) through its publication in JOUE (Official Journal of the European Communities), since December 2009. Its application will become mandatory as of January 1st 2011 thus imposing marking CE on all bitumens.

16.3. Bitumen, environment and health. REACH regulation

16.3.1. *Relating to the REACH regulation*

The REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemical substances) system intended to control chemical substances produced and imported in the EU, ready to evaluate the risks and to allow (or not), authorization for use or marketing.

This regulation is implemented in force by successive phases, and forces industrialists who produce or import chemical substances to carry out a complete examination of each substance marketed in Europe in order to create a file to be recorded at the ECHA (*European Chemical Agency*).

REACH imposes:

- the evaluation of all substances according to definite criteria;
- proving harmlessness to the manufacturer or importer.

These two points summarize the REACH revolution to be put into action.

How will industrialists face up to these new and very important limitations which will gradually be imposed for any substance manufactured or imported into the EU, in quantities higher than or equal to 1 ton per year and per manufacturer or importer?

Taking into account the innovation and complexity of the regulation, the sequential process was cut into several phases where the first phase, the pre-recording, is already completed. Three other stages to be carried out remain.

16.3.2. Bitumen and the REACH regulation

With regard to the oil industry, and more precisely the world of the bitumen and bitumen binders, constructions are very advanced, because the Member States on the one hand, and the European authorities on the other, have evaluated and had all the products in this industry evaluated for a very long time.

The task seems less difficult for CONCAWE (*Conservation of Clean Air and Water in Europe*), the European association in charge of HSE issues (Hygiene Safety and Environment), of files relative to petroleum products, and of the Eurobitume association, particularly active for files on bitumen and the bitumen binders. As for all substances, bitumen undergoes a valid recording process for all workers involved in the domain. This file details all the known uses and includes, also, all the additives necessary for such or such particular material, such as polymer modified bitumens, the fluidified and fluxed bitumens, or bituminous emulsions. Importantly, substances which come from a chemical reaction during the manufacture of a blending, are not taken in account by REACH.

The file on bitumen includes everything which refers directly to “bitumen” substances, but also, to all elements ensuring that the stated additives have been recorded under all the listed conditions of use. This record must be written by 30th November, 2010 at the latest. It is imperative that this expiry date be respected, because the absence of records will prohibit marketing. As mentioned beforehand, (section 16.3.1), bitumen suppliers gathered up all the data of corresponding to exposure of workers in civil engineering, in buildings and various industries, such as glues, primers, batteries or other industries, whether it is exposure by inhalation or through the skin, and those resulting from the impact on the environment for each use.

Eurobitume wanted to identify all the participants in the supply chain, from the refinery to the final customer, passing by manufacturers of binders, coatings, waterproofing membranes, paints or primers, civil engineering companies and applicators of waterproofing articles and materials. From this inventory, the imposed

procedures are in progress and involve, for example, classification, substance labeling, collation of case studies, the possible proposal for tests to be carried out, writing MDSS (Material Data Safety Sheets), or CSR (Chemical Safety Report) by using use and exposure scenarios. The final target is to reach a “substance/use” pair, qualified as safe.

Therefore, Eurobitume pointed out its current policies concerning identified hazards, namely the temperature level at which the bitumen binders can be handled. It is strongly advised to respect the recommendations concerning the storage, transport and handling temperatures of the bitumen binders. These recommendations guarantee, in the absence of studies proving other possible hazards, for uses without risk. The temperature of the road bitumens will not exceed 200°C, industrial bitumens will not exceed 230°C, and with regard to other binding agents, temperatures will stay approximately 30°C lower than the binder’s flashpoint temperature [EUR 08].

Establishing the huge list of uses for bitumen and bitumen binders, where 85% of tonnages are devoted to road construction and maintenance, 10% are used for manufacturing and the laying of roofing felts, and 5% find themselves in very specific applications, has made it possible to check, on a case-by-case basis, which products and processes respect people and the environment. Additionally, producers and importers ensure that works carried out in this way do not lead to any damage and confirm, if it were still necessary, that bitumen remains a neutral substance with respect to users and the environment, and always useful to protect surface and underground water against many sources of pollution.

16.3.3. Bitumen and hygiene, safety and the environment

As we have just seen, it is necessary to conduct studies and to accumulate results in order to show the harmlessness of a substance, or to give recommendations which will allow its use by reducing risks. To do so, we should use rigorous studies as a basis. For a long time, bitumen has been recognized as an inert material at room temperature, emitting only extremely small quantities of substances into the atmosphere. Two situations still asks a few investigations by means of the most recent analysis methods, namely the prolonged contact of bitumen with water intended for human consumption on the one hand, and the exposure of workers to bitumen smoke on the other hand.

From 2000 to 2004, tests consisting of putting pure bitumen into contact with pure water for 15 days, with a surface ratio between the bitumen and the water volume of 60 cm²/l, have highlighted that bitumen is not a source of pollution. The results of measurements for physicochemical parameters are all clearly on the right side of regulation thresholds, and are very often below detection thresholds. This

also applies to mineral and organic micropollutants, including Polycyclic Aromatic Hydrocarbons (PAH) which are all below detection thresholds.

With regard to bitumen smoke, many studies were performed and the available results have recently been the much discussed subject of the *Bitumen Industry Health Symposium*, held in Rome in September 2009.

Schematically, the International Agency for Research on Cancer (IARC) performed an epidemiological study concerning workers using bitumen. It used 35,000 European workers exposed to bitumen smoke for 20 to 25 years, and aimed to evaluate the impact of this smoke on causes for death of workers using bituminous materials. The study showed that workers exposed to bitumen smoke, although in better health than the population in general, presented a light increase in the number of lung cancers, compared to civil engineering workers, not exposed to bitumen smoke but they were not, however, able to draw up a link between fume and exposure to fume. The study was not able to identify the causes of this increase, which could be due to various merging factors, such as exposure to coal tar, or asbestos, nicotine addiction or lifestyle.

The conclusions of this first study recommended an extra “case study”, which was to identify the causes of the light increase in the number of cancers revealed in the epidemiologic study. This step consists of an in-depth analysis of the life of people with cancer, by questioning parents and colleagues in order to identify the professional or personal factors which may have contributed to the disease. It took five years to exam 1,253 files, and the results show no link between lung cancer and exposure to bitumen fume.

On the other hand, the results explain the comparatively higher death rate observed in the first study by smoking cigarettes, and the exposure to coal tar over time. In addition, the study highlighted the continued reduction in exposure to bitumen fume during the last few decades.

Lastly, tests carried out by the Fraunhofer Institute ITEM of Hanover in Germany, consisted of making laboratory rats inhale bitumen fume. Over 2 years, 6 hours per day, 5 days per week (equivalent to an employees working life), some groups of animals breathed fume in various concentrations, up to 1,000 times the real concentration on the job site. The comparison with a group of rats breathing fresh air showed, after statistical processing, that there was no significant increase in the number of tumors. This study, then, establishes that bitumen fume is not carcinogenic for rats.

Similarly, many measurements were taken in 2007 and 2008 by a work hygienist who prepared a report on the exposure scenario of road workers laying hot-mix

asphalt in very varied technical and climatic requirements [DEY 08]. The main determining effects acting on the emissions were statistically listed. Aerosols and volatile fractions which characterize bitumen fume represent two different chemical agents, and their “predictors” are also different. The conditions of application for bituminous materials have a large influence on the emissions of benzene soluble fractions, whereas external conditions have a remarkable influence on gas fraction emissions. In certain cases, the gas fraction resulting from residual bitumen compounds may represent 90% of organic emissions, whereas Polycyclic Aromatic Hydrocarbons only contribute to 0.4%.

It appears, then, that there are two different types of chemical risks, which would justify taking into account adapted preventive measures. In particular, recommendations concerning maximum handling temperatures according to the grade of the bitumen concerned, let us significantly reduce organic compounds emissions.

By statistically processing these measurements, it shows that French workers are under very favorable conditions, even by taking account of the currently lowest thresholds, proposed by ACGIH (American Conference of Industrial Hygienists) in the USA. The probability of exceeding this VME is 0.13%, which is classed as “green” by ALTREX.

In light of all these elements, the IARC should publish the new version of the bitumen monograph without delay, where it would be logical to read that bitumen remains no labeled with regard to carcinogenic risk, as for the other chemical risks. Without delay, during the 30th World Day for Safety and Health at Work in the civil engineering activity spent in Blois, on June 12th, 2009, Professor of Medicine and specialist in work-related cancers Françoise Conso stated that there was nothing left to research with regard to the carcinogenic potential of bitumen fume. The conclusion is clear; bitumen should not be labeled, and it is high time that money was spent in more worrying sectors.

16.4. Bitumen and sustainable development

Developed companies have become aware that they must protect their lifestyle while drawing a minimum of non-renewable natural resources and by reducing energy consumption.

How do bitumen and bitumen binders fit into this process?

First of all, let us note that bitumen producers reduce the consumption of their industrial tools year after year. Each time a ton of bitumen is produced, greenhouse gases in the atmosphere are reduced.

Bitumen is a component of a non-renewable resource, crude oil, but it is virtually the only petroleum product with a very long lifespan. Indeed, bitumen is a construction material, used in France at approximately 85%, to manufacture bitumen binders which can be entirely recycled several times. Bituminous materials, according to their formulation, are ready to be applied in variable thicknesses, from 1.5 cm to 20 cm, according to the requirements from small maintenance works to the construction of a new roadway for strong levels of traffic. The flexibility of these materials allows maintenance techniques which are perfectly adapted to the requirements of the job site in question. In the past roadway maintenance was performed very often by laying a new coat of asphalt mix, 6 to 8 cm in thickness, which allows us to find very good surface characteristics, to ensure perfect waterproofing of the road and to reinforce its bearing capacity. Laying successive asphalt mix coats which cannot be done infinitely, it is necessary to mill roadways from now on, and to re-use these aggregates in the construction, or for another project.

Bitumen and bitumen materials therefore fit in well with this sustainable development procedure, because the possibility of re-treating a roadway in situ by re-using 100% of its components has to be mentioned.

Bitumen, used by man for a very long time, is a major achievement in sustainable development, without even knowing it! It allows road construction, step by step, according to the evolution of traffic, leading to a long life network, all while minimizing resource consumption. Its remarkable coating qualities and ability to neutralize minerals are essential for using certain wastes in asphalt.

From these few lines, it can be demonstrated in a factual way that bitumen is a significant component for constructing and maintaining the road network, the main artery for road transport. Road transport, although somewhat criticized, has represented for a long time, a significant positive attribute for economics, society and the culture of citizens. It needs high quality infrastructures for obvious safety and life quality reasons, for users and residents alike.

16.5. Conclusion

Today, where many questions are being raised regarding the future of our civilization in relation to its consumption of non-renewable natural resources, experts agree on the fact that bitumen and bitumen binders fulfill the criteria for

sustainable development in all their uses. This material is developed from distilling fossil matter, without any particular chemical reaction, and users are trying to reduce their consumption, although its availability is estimated to last for another one hundred years under current technical economic conditions. Bitumen is an organic glue which can be recycled, presenting a significant hydrophobic character which, once in place, is not the source of any emission of polluting agent in the environment. Some consider it to be a carbon well, which can be completely recycled, several times.

Lastly, regarding the possible risks in relation to human health and environment, the most recent results from studies performed throughout the world, lead us to a comforting conclusion. Respecting good practices on job sites, creates healthy work conditions for employees, when it is achieved.

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16.7. More information

On bitumen and its road applications:

CORTE J.F., DI BENEDETTO H., *Matériaux routiers bitumineux 1: description et propriétés des constituants*, Hermès, Paris, 2004.

DI BENEDETTO H., CORTE J.F., *Matériaux routiers bitumineux 2: description et propriétés thermomécaniques des mélanges*, Hermès, Paris, 2004.

The magazine *Bitume.info* from the GPB (*Groupement Professionnel des Bitumes*), and their website, bring together lots of information regarding this material.

We also advise readers to consult publications from the Eurobitume association, of the Federation of European and International Public Service Unions for the road industry, in the section on bitumen road emulsions manufacturers, from the bitumen department.

Websites:

- GPB: www.bitume.info;
- EUROBITUME: www.eurobitume.org;
- USIRF: www.usirf.com;
- SFERB: www.usirf.com/L-USIRF/organisation/SFERB;
- Office des asphaltes www.asphaltes.org/apropos.html.

Chapter 17

Industrial Mortars and Repairing Concrete Products

17.1. Definitions

Industrial mortar is a mixture of sands, special hydraulic binders, additives (organic and/or mineral) industrially formulated and ready to mix. A mixture in which only the mixing liquid is added (water, most of the time).

Mortars currently being used include between ten and fifteen different components. The most developed products may contain up to twenty. Mortars can therefore be very different to each other, according to the nature and percentages of the components, the mixing, the implementation and the curing.

Mortars are present in all types of constructions, buildings or civil engineering works (bridges, dams, tunnels, etc.), in new works and in renovations in domains such as protection and decoration, insulation, tillage, fixing, assembly, reinforcement, repair and the structural adhesion.

On the market, we also find products in the form of pastes, requiring (or not) the addition of hydraulic binders and which are ready to be used.

According to the addition rate, we will either speak of additive hydraulic binders (AHB), or modified hydraulic binders (MHB).

AHB are formulated from a hydraulic binder and the addition of organic or mineral compounds in proportions lower than or equal to 5%.

MHB (or PCC, *precipitated calcium carbonate*) are formulated from hydraulic binder which is modified by adding organic or mineral elements in a proportion higher than 5%.

17.2. The contribution of organic compounds in formulating industrial mortars

Industrial mortars must offer specific characteristics according to their intended use. To obtain a particular performance level, industrialists have resorted to organic compounds in the formulation phase. The main routes for improving or modifying material properties may be grouped into several families according to implementation or expected performances.

17.2.1. Contributions for usage

17.2.1.1. Adhesion

This is a property of the material, when in plastic state, which allows it to stick to the support in any position. To improve the performances of industrial mortars, formulators have a large array of molecules which play an intrinsic part in the manufacturing process.

The first method exploits the product's wettability while allowing it to form a paste with weak superficial tension and high polarity by adding polysaccharide ether.

The second method uses a *tack* or a sticking effect on a surface. It is obtained by adding resin and/or cellulose ether (copolymers with a vitreous transition temperature lower than room temperature). The tack is characterized by the material's capacity to stay in place during its hardening phase.

17.2.1.2. Rheology

This involves the various forms of the product's behaviors in plastic phase. According to the application limitations or the product's use, the formulator will either look for fluidity, thixotropy (the opposite), or the possibility of mechanized implementation, a parameter which should be maintained.

17.2.1.3. *Fluidity*

This property is characterized by the ease of implementation with low limitations.

The industrialist will use plasticizers from the melamine family during formulation for a self-compacting effect, or super plasticizers from the last generation, such as polycarboxylates for obtaining self-levelers.

These molecules, adsorbed on particles by creating steric repulsion, reduce the friction between cement and sand. They allow the mixed mortar to flow at a low liquid rate.

17.2.1.4. *Thixotropy*

This is a mortar's capacity to stay in place without creeping under its own weight.

This characteristic is obtained by adding mineral (clays, etc.) or organic thickeners from the polysaccharide family (starch, xanthane, guar, etc.) during formation which will form a gel.

The paste obtained, has a reduced mobility from its interstitial water.

17.2.1.5. *Pumpability*

Mortars are a granular mixture comprising a certain volume of vacuums. These vacuums must be filled by the paste (binder, water and air) to give the product the necessary deformability.

Preserving pumpability means preserving the paste's cohesion and homogeneity. For this, various formulation solution are possible:

- adding air-entraining agents (these are mainly surface agents) whose role is to stabilize and control the size of the air bubbles trapped in the mixture;
- using cohesion agents (hydroxylated polymers in the form of colloids) which prevent the mortar from drying (separation of solids and liquids).

Using these organic compounds does not stop us from paying attention to the product's granulometric curve according to the type of pump used (screw, piston, etc.).

17.2.1.6. *Kinetic setting*

By kinetic setting, we mean the time available for the user to implement the product (perhaps more well known under the name of workable life), in addition to the time needed for the paste to reach solid state. This time is calculated starting from the contact between the liquid and mortar.

This time is sensitive to the carrier's temperature and hygrometry conditions, as well as climatic conditions. In cold and wet weather, setting is slowed down (several hours to several days) or even blocked *a contrario* by hot and dry weather. Setting can also be extremely fast (a few minutes).

To *accelerate setting*, the formulator uses:

- mineral solutions: chlorides, nitrates, etc;
- an organic mineral solution, consisting of special cements from the aluminum family which require the addition of organic compounds from carboxylate family (citrate, tartrate, etc.);
- an organic solution by the use of calcium formate.

The choice between the various solutions is conditioned by the desired kinetic setting, more or less quickly accelerating hydrate formation.

To *delay setting*, the formulator uses:

- organic solutions based on the complexation of the ions in the solution coming from cement;
- compounds such as sugar derivatives, such as gluconates, polysaccharides, some carboxylates.

The choice between the various solutions is conditioned by the desired kinetic setting, more or less quickly delay oversaturating the precursory ions of hydrate formation.

In industrial mortars, controlling kinetic setting is the fruit of a delay/accelerating equilibrium, and conditions the acquisition of mechanical performances. This second phase is also called hardening.

17.2.2. *Contributions for expected performances*

Industrial mortars have multiple uses. The user looks for different properties, such as controlling dimensional variation, adapted flexibility according to the carrier or the application, and early performance maintained over the long term.

17.2.2.1. *Control dimensional variations*

When mortars containing hydraulic binders (in plastic phase) have a volume higher than for hardened materials, the water is consumed by hydration reactions and evaporates in the capillaries of the cement matrix, which generates tension and cracks.

To attenuate this phenomenon, the formulator has various solutions at his disposition. He may decrease the tension in the capillaries by adding hydroxylated polymers.

He may compensate for shrinkage by a controlled expansion of the mortar in plastic phase. For this, there are two possible approaches:

- Expansion by gas bubble formation. These products contain ingredients which generate gas bubbles a little while after contact with the mixing water. Carbon or aluminum powders are generally used to produce the gas bubbles.
- Expansion by ettringite formation. Contrary to the preceding case, adding the aluminums causes a reaction between the cement and the calcium sulfate contained in the mortar during hardening. This expansion occurs when the anhydrides turn into ettringite. The expansion is sensitive to moisture conditions.

17.2.2.2. *Flexibility*

Industrial mortars are used to repair, protect, waterproof or decorate construction surfaces. The diversity of the carriers in terms of nature, cohesion and aspect require products with a rigidity which must be adapted.

In light of the cement matrix rigidity, using polymers is essential in order to obtain more flexible materials which can be adapted to the carrier or the application.

The incorporation rate of polymers allows us to classify industrial mortars into two categories:

- major cement matrix mortars which stay as rigid materials with, nevertheless, an increased deformability (mastic cements) supporting stresses, moving less than a millimeter;
- major organic matrix mortars (cement is only used to dry the product) offer high flexibility levels and can support movements of several millimeters (case of flexible impermeabilization mortars allowing strains of up to 5 mm).

The polymers used in these applications are different block copolymers (acrylic/styrene, vinylacetate/ethylene, etc.) whose vitreous transition temperature is lower than 20°C.

17.2.2.3. *Mechanical performances*

This is a matter of characterizing the performances of mortar in terms of adhesive strength, compression, and flexure/tension. The use of polymers as plasticizers, super plasticizers or polypropylene fibers improves the mechanical behavior of the industrial products. All these measurements are included in standardized tests.

17.2.2.4. *Adhesion*

A standardized test (EN 1542 recommended by the European norm EN 1504-3) allows us to characterize the adhesive performance between the hardened mortar and the carrier. The results are expressed in MPa at a given time. We can therefore evaluate the material cohesion in the case of structural repair, for example. Indeed, perfect adhesion between the mortar used for repair and the concrete carrier is a way of gauging a good transfer of the strains inflicted onto the construction.

17.2.2.5. *Compression*

It is a question, here, of measuring the bursting strength of the hardened product. The standardized test (EN 12190 recommended by the European norm) gives values of rupture under compression which are expressed in MPa in a given time (2 hours, 5 hours, 1 day, 7 days, 28 days, etc.). Following up these values means that we can gauge the speed of the rise in mortar strength. In particular, they allow us to validate the moment when the construction is put back into service, according to expected performances.

This is, for example, the case of drain covers (drain openings on roadways) which are put back into service within 2 hours, in both summer and winter. For such performances, the formulator will exploit the acceleration parameters and delay setting, as well as on the product's rheological properties to ease its implementation.

17.2.2.6. *Flexure/tension*

Associated with compression, these standardized measurements (according to the European standard EN 196-1) mean that we can characterize behavior of a hardened mortar under flexure or tension. The data is expressed in MPa at a given time (the same for compression).

In general, on a traditional hydraulic product (ready-mixed concrete, for example), the measured values are about a tenth of those for compression.

Using polymers and synthetic fibers in mortar formulation will allow for a noticeable improvement in this ratio. For example, a R4 grade hydraulic mortar with synthetic fibers used for repair will be characterized by 7 MPa under flexure and

35 MPa under compression over two days. For values of 12 MPa under flexure and 65 MPa under compression, the duration will be 28 days.

A mortar containing epoxy resin offers higher ratios, around 35 MPa under flexure for 100 MPa under compression over 28 days.

17.3. Repairing concretes

Since the end of WWII, concrete is mainly used in the construction industry, either for buildings or works of art. A material known for its excellent molding properties, it is part of our daily environment. But it is subject to the joint effects of ageing, mechanical and physical aggressions and climatic conditions. Due to this matter, repairing concretes has become a constant concern for today's society.

The normative environment is evolving.

17.3.1. Norm EN 1504

The European norm on products and systems for the protection and repair of concrete structures – EN 1504 – came into effect in France on 1st January, 2009. The reference will therefore be modified: the label NF will be completely revised and will have to conform to this new reference which is made of 10 chapters:

- EN 1504-1. Definitions;
- EN 1504-2. Surface protection systems;
- EN 1504-3. Structural and non-structural products and repair systems;
- EN 1504-4. Concrete injection products and systems;
- EN 1504-5. Bonding systems and products;
- EN 1504-6. Anchorage and sealing systems and products;
- EN 1504-7. Products and systems for preventing armor corrosion;
- EN 1504-8. Quality control and conformity evaluation;
- EN 1504-9. General usage principles of products and systems;
- EN 1504-10. Application of products and systems and product quality control;

which replace some French norms (Table 17.1).

Application domain	NF Norms	EN Norms
Sealing by hydraulic binders	P 18-821	EN 1504-6
Sealing by resins	P 18-822	EN 1504-6
Setting by hydraulic binders	P 18-821	No norm
Setting by resins	P 18-822	No norm
Repair using hydraulic binders	P 18-840	EN 1504-3
Repair using resins	P 18-840	EN 1504-3
Structural bonding using hydraulic binders	P 18-870	EN 1504-5
Structural bonding using resins	P 18-870	EN 1504-5
Injection using hydraulic binders	P 18-880	EN 1504-4
Injection using resins	P 18-880	EN 1504-4
Surface protection system	GA * P18-902	EN 1504-2
Products and systems for preventing armor corrosion	No norm	EN 1504-7

Table 17.1. *Correspondence between old and new norms (*application guide)*

We will note that the setting section in norms NF P 18-821 and NF P 18-822 is not taken up again by EN 1504 and that, in addition, norms NF P 95-101 to 107 “Works of art, repair and reinforcement of concrete and masonry constructions” are being revised.

17.3.2. Implementation of repair strategies

Repairing a concrete construction is not an alleviating operation. It requires, on behalf of the applicator, real skill. Indeed, it is specialist work because the stakes, in terms of performance and durability, are extremely high. To repair means “to return the work to its aspects and original performances”.

To obtain a long lasting and quality result, it is imperative to set up a repair strategy which must take into account the three following points:

- treating pathology;
- repairing concretes;
- protecting the work from future aggressions;

and is articulated in four phases:

- an analysis to know the nature of pathology and the state of the concrete;
- a study of the specifications to choose the retained technical solutions;
- the implementation of products and performance tests;
- protecting the construction durability.

17.3.2.1. *Analysis*

This phase is very important and must not be neglected. The main parameters which must be validated are:

- carbonation depth;
- presence of chloride and/or sulfate ions;
- reinforcement coating depth;
- mechanical performances of concrete (compression, tension/flexure).

In light of the results (carbonation, Cl^- or SO_4^{2-} ions and armor coating) the choice, for treating corrosion of steels representing more than 80% of the causes of concrete degradation, will either go:

- towards a solution of steel passivation by adsorption a passivating paint or a styrene /butadiene mortar repair mixture;
- towards a corrosion inhibition by the user by an impregnation inhibitor (amino/alcohol, glycerol/phosphate, etc.). The purpose of this last approach is to limit material purging (objective is to preserve the old material) while proposing a total corrosion treatment, and therefore avoiding the creation of induced anodes or galvanic effect outside the repaired areas.

Mechanical performance values means that we can choose among all the products used for repair the one which will be compatible with the carrier.

17.3.2.2. *Specifications*

Drawing up “product” specifications is important. It is necessary to take into account:

- stresses imposed by the carrier;
- implementation conditions (manual or mechanical);
- difficulties accessing the construction;

- qualification teams (ready to wet products preferable to multi-component products, source of potential error);
- predictable climatic conditions (hot in summer, cold in winter, etc.);
- environmental conditions (residential buildings, presence of flowing water and animals, etc.);
- desired completion;
- color of the hardened product compared to the carrier (good repair work is not visible);
- compatibility with future coating (paints, fillers, etc.).

17.3.2.3. *Implementation*

The quality of the preparation and implementation depends on the quality of the repair work. Therefore:

- any trace of rust on apparent steels must be eliminated and work must be purged of all non-cohesive elements;
- before applying the repair work products, it is necessary to refer to the technical data sheets provided by the manufacturers, and to respect instructions (mixing time, use temperature, etc.). For example, when using a hydraulic binder based mortar, the carrier must be wetted beforehand. However, using a product containing epoxy resin requires a perfectly dry carrier (risk of blistering).

17.3.2.4. *Protection*

After having carried out repairs, protecting the work should be considered so as to ensure better durability. There are several cases:

- either the concrete remains bare, in which case the using a surface water repellent (containing silane, fluorinated or not), allows for a notable delay in penetrating aggressive agents, by limiting the drainage duct.
- or, the concrete is covered with a flexible sealing filler. This filler, containing MHB, lets us obtain, in two brush strokes in less than 24 hours, a crack growth resistant film, of a few millimeters in thickness (up to 5.2 mm for certain reinforced products);
- either the concrete is covered with a layer of paint;
- or it is covered with a hard coat containing hydraulic binders.

17.3.3. Families repair products

Graded according to function, the various types of products used for repairing concrete are presented in Table 17.2. We must note then, that to take the complexity of the formulas into account, for reparation works, the use of products for a sole manufacturer who is capable of guaranteeing perfect compatibility between the various components of the implementation system must always be favored.

Function	Type of product
Treatment: - reinforcement corrosion	Corrosion inhibitor: - amino alcohol - glycerophosphate - etc. passivating paints
Repair: - structural or non-structural repair - structural or non-structural repair	Products containing cement (AHB or CC): - repair mortars - finishing fillers - grout Organic base products (MHB or PCC): - mastic cements - resin mortars - finishing pastes - grout
Protection	Bare concretes: - surface water repellents - surface hydro/oleofuges Sealed concretes: - membranes - flexible coating - impermeable bitumens Painted or lazured concretes: - paints - stains Coated concretes: - hydraulic base - single layer - organic base thick plastic coatings

Table 17.2. Various types of repair products

17.4. Conclusion

The contribution of organic compounds in the world of mortar formulation offers a whole range of possibilities to the formulator, making it possible to create products which are perfectly adapted to the expectations and limitations of the applicators. In addition, the prospects opened up by new compounds (carbon nanotubes in particular) or new technologies (dust free, for example) give us an insight into the products of tomorrow, i.e. powerful, easy-use products, respecting the user and the environment.

17.5. For more information

AFNOR (French standards organization)

GA P18 902, “Guide d’application. Produits et systèmes pour la protection et la réparation de structures en béton. Recommandations pour la sélection des systèmes de protection de surface des bétons destinés aux ouvrages de génie civil”, <http://www.afnor.org>, AFNOR Paris, 2004.

EN 1504, European standard, “Produits et systèmes pour la protection et la réparation des ouvrages en bétons”, <http://www.afnor.org>, AFNOR Paris, 2008.

NF 030, “Référentiel marque NF 030”, <http://www.afnor.org>, AFNOR Paris, January edition, 2009.

STRRES (French National Union business specialists for repair and enforcement structures)

“FABEM no. 1: reprise des bétons dégradés”, <http://www.strres.org>, *Guides du STRRES*, Paris, 2008.

“FABEM no. 2: traitement des fissures par calfeutrement, pontage et protection localisée”, <http://www.strres.org>, *Guides du STRRES*, Paris, 2008.

“FABEM no. 3: traitement des fissures par injection”, <http://www.strres.org>, *Guides du STRRES*, Paris, 2008.

“FABEM no. 4: protection des bétons”, <http://www.strres.org>, *Guides du STRRES*, Paris, 2008.

“Bétons et Mortiers”, <http://www.infociments.fr>, Cimbéton, Paris, 1995.

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Chapter 18

Waterborne Paints to Limit VOC Emissions: Interests and Limits

18.1. Introduction

In the last few years, our societies have become aware of the risks due to the impact of industrial activities on the evolution of ecological balance. The danger linked to volatile organic compounds (VOC) emissions is widely proven, in this context. Therefore, for a few years, regulation has imposed limitations on these emissions, in different industrial sectors. But, traditional liquid paints, in organic solvent phase, are the most important source of VOC emissions, after natural emissions and those from air and road transport, rejecting up to 800 g/L of these components for certain formulations during their drying process.

Regulations have imposed that these products must respect at least one of the two following criteria: be located below threshold limits, varying according to product and applications, on maximum VOC quantities rejected in relation to applied volumes [DE 04] or to reject less than 50 to 100 mg/m³ according to the annual tonnage emitted and the activity sector, and according to the air treated by fixed installation which allows for partial collection of emitted VOC [DE 99]. In practice, in spray booths with a system for treating waste, which respects the second criterion, it is therefore possible to continue to apply products with an important VOC content. On the other hand, for applications in outside construction sites, the first criterion is the only one to be attained, and considering the nature of the product applied, one, respects this criterion.

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Water-based paints, then, constitute a response to regulation limitations on VOC emissions. Nevertheless we still need a certain quantity of organic solvents to solubilize resins (meaning co-solvents which can be found in water-based paints in quantities up to 240 g/L, even though certain formulations may contain approximately 10 times less). There are multiple advantages: for the atmosphere, for staff and safety, but contrary to certain generally accepted ideas, the collection and treatment of cleaning products is still absolutely necessary. More generally, these products create formulation and specific implementation problems which greatly moderate their capacity to solve all the problems alone. The lack of knowledge about these specificities is perhaps the main source of their misuse, to the detriment of their performances, and paradoxically, since it is a matter involving the main reason for their development, to the detriment of the environment.

18.2. Definition of paint

Paint is a dispersion of one or several pulverulent matters (pigments and extenders) in macromolecular compounds called “resin”, “binder”, “matrix” or “vehicle” [BRO 02], [GRA 97], [LAO 99], [PET 99]. It is a formulated composite material, and therefore is complex. The most important part is the polymeric matrix which ensures cohesion of the dry film and gives the coating its main properties. It often gives its name to the paint.

The most traditional paints are applied in a liquid state. That involves dissolving the organic binder in a solvent. Often, at the time of the application, we add a thinner to adjust the liquid paint’s viscosity. Solvents and thinners are the main VOCs contained in paint. They are characterized by a strong capacity to vaporize. When dry, nearly all the VOCs will have evaporated.

For solid powders in paint formulation, we distinguish pigments and extenders.

Pigments are used due to some of their optical, protective or decorative properties. They are anti-corrosive pigments (inhibiting or sacrificial), laminar pigments (micaceous iron oxide, aluminum and glass flakes), pigments with darkening agents (opacity) and pigments with coloring capacities which are generally synthetic organic products.

Extenders or fillers (oxides mainly silicas, calcium carbonate mainly chalk, aluminum silicates like china clay and mica, magnesium silicates like talc, barium and calcium sulfates, glass fibers, etc.) are distinguished from pigments by weaker refraction indices. For a long time, they have had the reputation of only being able to adjust the pigment volume concentration (PVC) at low costs. In fact, they present, like pigments, specific properties for each one. As an example, we may cite

coloring, rheological or mechanical properties (abrasive resistance, raised hardness or compaction aptitude, etc.).

Lastly, additives are used in small quantities to modify certain paint properties (reaction catalysts, rheological agents, agents protecting against light, biocides, etc.). For example, siccatives or driers are used in alkyd paints in order to accelerate the drying process. We may also cite anti-foam, anti-settling or anti-skin agents. Wetting and dispersing agents are also essential in formulation. Plasticizers allow for an adjustment in the coating's flexibility. In the case of water-based paints, we note some specificities for the additives used. In particular, incorporating tension agents allows for a reduction in the raised superficial tension, due to the low wettability of water. Moreover, binders which can dissolve in water may reinforce foam formation tendencies, and, in this case, it is necessary to add a particular anti-foam agent. In addition, to facilitate the formation of emulsion paint films, we should use coalescence agents.

18.3. Main features and properties of waterborne paints

18.3.1. *History of the development of waterborne paints*

These paint products have been in development since the 1970s. Initially, this development was limited by various problems during their development: low stability, sensitivity to water, tanks corrosion, difficulties in formulation, etc. But these difficulties have since been overcome, and paints in aqueous phase have seen a slow but regular development under the pressure of regulation in relation to the VOC waste materials in the atmosphere.

Thus, at the end of the last century, these paints accounted for 20 to 25% of the sale volume in the European Union, as well as in the USA; this volume is currently around 30%. If we go into detail, in 1999, they represented approximately 27% of tonnages sold in the industrial paint sector, and 60% the same year in paints used for decorative purposes, against 37% in this sector, in 1975 [CHA 05].

These products have therefore seen significant development.

18.3.2. *Various types of paint in aqueous phase*

Various types of paint exist in aqueous phase:

- real solutions or water-soluble paints;

- dispersions (latex);
- emulsions.

Real solutions are homogeneous mixtures in which the organic binder is completely solubilized (water-soluble binder). They create an obvious problem in the sense that, after drying, these binders preserve their solubility in water. On the contrary, dispersions are heterogeneous mixtures. If the dispersed phase is a liquid, and the dispersing phase being water, we are talking about “emulsions”. For these, we use binders which can be dissolved in water, characterized by reactional groups which are neutralized for avoiding precipitation. Neutralization products act as co-solvents and control the paint’s viscosity. They are used as “temporary plasticizers” and evaporate after application, to form a film which is not soluble in water, which preserves sensitivity to moisture, however. Drying can be purely physical or chemical in the case of two component (2-pack) products.

18.3.3. Film formation process

In the case of dispersions, the polymer is not soluble; it is generally dispersed in water. Here, we are referring to “latex”. These latexes consist of polymers with higher molar masses dispersed in water which allow interesting properties to be obtained in many applications.

After application and water elimination, the polymer particles become closer together and amalgamate to form a continuous matrix. This is called coalescence. The primary force which allows for this coalescence phenomenon is the reduction in surface energy. When the particles amalgamate, the polymer/air surface interface decreases, which results in minimizing the surface energy. However, so that the macromolecules interpenetrate, they must be free to diffuse in close-by particles. The movements of these macromolecules then require sufficient mobility, therefore a glass transition temperature lower than the drying temperature.

18.3.4. Various product families

There are multiple types of binders used in aqueous phase: alkyds, polyesters, epoxy and epoxy esters, phenols, etc. The most important group is acrylics dispersions.

Some formulations can be applied at room temperature, and others require drying in a furnace.

Table 18.1 recapitulates these various families and their main advantages and disadvantages [JOS 00].

Drying types	Families	Main advantages and disadvantages
At room temperature	Alkyd	- Drying at low temperature - Bad chemical resistance
	Acrylic dispersion	- Risk of flash rusting - Thermoplastic properties - Resistance to UV - Fast drying
	Epoxy	- High Cost - Easily recoverable - Two component product - Excellent adhesion properties
	Polyurethane	- High cost - Application in several layers - Resistance to UV
In a furnace	Alkyd, acrylic, polyester	- Energy cost related to drying at high temperatures (120 to 200 °C) - Excellent performances

Table 18.1. *Main families of paints in aqueous phase [JOS 00]*

18.4. Advantages and disadvantages for using water as a solvent

18.4.1. Advantages

The main advantage of these paints is decreasing VOC emissions. Moreover, reducing the quantity of organic solvents used in formulation has other beneficial consequences [CEF 05], [CHA 05].

Initially, these are non-flammable products, which limits risk of fire and explosion. In practice, there are many consequences for this non-inflammability: limiting the perimeter of the risk area during simultaneous welding operations, reducing the user's insurance premiums, production, transport and safer application of paint, etc. However, if these paints are involved in a fire, they will feed it.

Moreover, these products are odorless and less poisonous, which improves the application conditions: the toxicological and allergenic risks are lower; the operator's well-being is higher, etc. (see section 18.4.3).

In addition, cleaning the containers and equipment is simplified by using water instead of organic cleaning thinners used with conventional products. All the advantages presented previously therefore also apply cleaning the application materials, which consumes great quantities of thinners.

Lastly, they can be applied onto wet surfaces, within certain limitations.

18.4.2. Disadvantages

On the other hand, these products present a certain number of disadvantages which limit the scope of application [CEF 05].

18.4.2.1. Transport and storage

The first disadvantage relates to the need for higher storage temperatures to avoid freezing temperatures (temperatures higher than 5°C). Not respecting this requirement leads to irreversible degradation.

The risk of corrosion for traditional metal containers has introduced the use of protective varnishes or plastic packaging, and therefore, an increase in conditioning costs.

Moreover, the risks of microbiological degradation during storage are real, and the validity of the usage period is then reduced.

18.4.2.2. Surface preparation

It should be remembered that the quality of the surface preparation directly affects the adhesion, and this adhesion is the main parameter which conditioning the performance and durability of any coating. However, using paints in aqueous phase requires greater requirements for surface preparation than for solvent products. We can give these requirements in terms of surface cleanliness and roughness.

Thus, concerning wax and fat, the standards indicate that, whatever the applied product, the "surface shall be free from visible oil, grease and dirt" before blast-cleaning, hand and power tool cleaning or flame cleaning [ISO 98, ISO 07]. For products in aqueous phase, the tolerance for residual oil or grease contamination is reduced due to the product's incapacity to dissolve the possible residual traces of

these greasy substances after imperfect degreasing and, consequently, to wet the surface correctly to allow for optimal adhesion.

Independently of this intolerance to residual contamination from greasy substances, the major problem for water is its very weak capacity to wet surfaces, compared to organic solvents (72 dynes/cm for water, and between 30 and 35 dynes/cm for organic solvents). On rough surfaces, this results in a greater difficulty for penetrating in the roughness with a reduction, on the one hand, in mechanical anchoring and, on the other, polymeric material surfaces in contact with the substrate, thus the number of interfacial binds which ensure adhesion.

18.4.2.3. *Material and application conditions*

These products impose particular strains on the material and the application conditions, as well as on the skill of the operators:

- the use of stainless steel materials because of corrosion, and Teflon joints (swelling of traditional joints);
- all traces of the solvent product must be totally eliminated when a product in aqueous phase is used with the same material after a product in solvent phase;
- delicate application by conventional spraying;
- the “hardness” of the water used for dilution must be controlled;
- it must not be applied too thickly so as to avoid sag;
- dry thicknesses are generally lower;
- a sufficient relative humidity is needed during the application (higher than 60%). But if it is applied to metallic surfaces, the substrate must remain simultaneously non-condensing, which involves not exceeding a relative humidity of 80%;
- the potlife is shorter and is perhaps exceeded without apparent viscosity modification.

18.4.2.4. *Drying*

In the same way, the drying conditions are more demanding here than for a paint in organic solvent phase.

Indeed, the evaporation of VOCs is controlled more strongly by the temperature and the relative humidity of ambient air. This involves controlled ventilation during the drying process, particularly in closed spaces. In all cases, drying is much longer: up to 200 days, rather than 21 days for products in solvent phase. Consequently, the covering time between coats is also longer, which increases the total application time for multi-coats systems. 5 times more energy is needed to evaporate water, compared to an organic solvent.

In addition, a characteristic of anti-corrosive primers in aqueous phase is the risk of developing flash rusting. To limit this risk, we recommend fast drying for the primer, less than 4 hours. This problem considerably limits the direct use of paints in aqueous phase on metallic substrates. However, these products are used as an intermediate or top coat in anti-corrosive systems, the primer being a product in classic solvent phase, powder paint or high solid paint (see section 18.5). We are, then, referring to a “hybrid system”, which constitutes a possible response to the regulation limitations, so as to limit VOC emissions during the drying process, by considering the paint system in its entirety.

18.4.2.5. *Cost*

In fact, the cost of implementing these products is higher, when we take into account a lower shelf-life, difficulties of formulation and application, the cost of resins and additives, the higher number of coats (applied dry thicknesses are lower), the cost of drying and longer times between coats, a lower durability, etc.

18.4.3. *Health and safety hazards*

Hazards related to pigments, fillers, binders and additives are the same, whatever the type of paint. On the other hand, hazards related to solvents, higher for solvent phase paints, are low for water-based paints. There are still hazards, because glycol ethers (susceptible to cutaneous effects, on blood cells and reproduction) are often used as co-solvents in waterborne paints. On the other hand, there are no hazards related to isocyanates. In the same way, using aliphatic amines in very small quantities in water-soluble paint limits hazards related to these products [CHA 05].

18.4.4. *Conclusion*

Despite their disadvantages, paints in aqueous phase develop permanently improving performances. Regulation pressures effectively stimulate research and development amongst suppliers.

With regard to controlling these performances, the emergence of new products and the imposed disappearance of tested products create a major problem with the loss of experiment feedbacks, which have been capitalized for many years, and the need for a quick evaluation of the new products' performance. This situation involves defining and validating new adapted performance tests. Still, research and development required us to bring innovative responses [IRI 01], [IRI 07], [JOR 06], [PER 00], [PER 01].

18.5. Advantages and disadvantages of using water-based paints in relation to alternative solutions

Water-based paints present a certain number of disadvantages which prevent them from completely replacing paints in solvent phase. But these limitations must be considered taking into account other alternative solutions, such as powder coating, radiation curing paints, or high solid paints, which also display specific disadvantages.

18.5.1. Powder coatings

Powder coatings are a very interesting alternative solution, because they do not contain any solvents. We distinguish thermoplastic powder coatings (fluorinated polyamides and polymers) and thermosetting powder coatings (polyester, epoxides, polyurethanes and acrylic resins). The principle of their application consists of depositing powder particles onto the substrate and melting them, either by pre-heating the metal, or by time in the furnace, to form a continuous film by coalescence. For thermosetting powder coatings, a complementary heat treatment may be necessary to complete cross-linkage. Various implementation methods are possible: electrostatic powder printing for thermosetting powders, fluidized bed for thermoplastic powders.

But, powder coatings consume a great quantity of energy during implementation. In addition, the equipment used (electrostatic spray gun or fluidized bed) is not easily transportable, which means, generally, that the application is to be performed in specialized workshops. Moreover, their use is limited to metallic substrates. Indeed, their application is complicated on thermally sensitive substrates (risk of substrate degradation), which are electrically non-conductive (inadaptability of electrostatic processes) or which present insufficient thermal inertia (maintenance of the substrate's temperature above the powder's melting point). However, specific studies motivated by regulation limits on VOC emissions, particularly for the application of composite materials used in aeronautics, explore the use of this type of paint for other types of substrate.

18.5.2. Radiation curing paints

In the same way, radiation curing paints are free from VOCs which are likely to evaporate when drying. But they contain many monomers and volatile toxic additives, which limit their interest from an environmental point of view, and are essentially only applicable in workshops. Effectively, we use solvents, called

“reactive diluents”, to regulate viscosity. They react during cross-linkage, aid in film formation and thus influence some of the properties [BRO 02].

In this case, the organic binder is not dissolved in a solvent to eliminate it, but the monomer, or the prepolymer, is directly polymerized, so as to obtain the end product in one stage, i.e. the polymer. The polymerization reaction is started by radical means. The formulation contains photo-initiators (2 to 6%) and/or photo sensitive reactions, producing radicals under the influence of radiation, which start the polymerization reaction.

An important characteristic of these products is their fast drying time, which creates problems for an anti-corrosive application, due to the stresses generated in the film (risks of cracking) and at the paint/metal interface (loss of adhesion). Their anti-corrosive use is reduced to epoxidic systems (relatively low shrinkage and good adhesion) on plane surfaces (geometry limiting strains) [BRO 02].

18.5.3. High solids paints

High solids paints are still paints in solvent phase, but which contain a limited quantity of VOC (approximately 10% in volume). Therefore, these are high viscosity products which lead to particular application and thus material difficulties (flexible pumps and guns with warming systems) as well as specific skills. Shorter drying times have their advantages, particularly the reduction of stand-by periods due to maintenance. But, there are also disadvantages related to the very short pot lives.

18.6. Conclusion: the need for an eco-assessment

Even if paints in aqueous phase present an unquestionable alternative for reducing VOC emissions, above all we must not forget that they still contain a certain quantity of organic solvents. These solvents are necessary to regulate various properties, for example, related to application conditions, drying or gelling resistance. Moreover, these products remain as complex formulations including chemical species which must be handled with care due to health and safety hazards.

Also, we should not lose sight of the fact that these alternative products do not regulate the problems related to waste and rinsing effluents. They may even generate perverse effects. Indeed, the cost of treating waste water is still important. The false perception of producing clean waste, associated with the cost high of its treatment, may lead to drains rejecting rinsing “water”, this behavior being less spontaneous with traditional products. In addition, the best effectiveness of organic solvents for

cleaning materials may lead certain companies to use them even after applying paints in aqueous phase. These behaviors, which are also part of an industrial reality, could result in reducing the expected benefits of using these products.

Generally speaking, the completed eco-assessment related to using paints in aqueous phase still needs to be drawn up. The interest in their use, on the basis of their complete life cycle analysis, has not yet been formally manifested.

Nevertheless, these products are of obvious interests in terms of reducing VOC emissions and health and safety hazards. We do not doubt that life cycle assessments will show their environmental interest in relation to paints in organic solvent phase. This process of evaluating impacts and risks is also necessary to rationalize concerns (either justified or not), linked to the use of paint products with which we are in permanent contact, and which would be difficult to go without. Moreover, is the main advantage of these new products only that they let us ask good questions, and above all, give us back well supported answers?

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PART 6

Organic Compounds Built-in into Cement Matrices

Chapter 19

Rheological Admixtures

In this chapter, we consider organic admixtures action on the rheology of freshly-mixed concrete (for other admixture grades, see [MOU 06]). These organic molecules, in negligible quantities in the mixture, have already revolutionized concrete construction technologies twice, by allowing the mix design of high-performance concrete (HPC), or self-compacting concrete (SCC). We will focus on the family dominating the market, i.e. rheological admixtures which can change the behavior of fresh concrete. Firstly, we consider the role played by rheological admixtures in the history of concretes and their formulation. Then, we will return in detail to rheological behavior of concretes on a microscopic and macroscopic scale, for a better understanding of the effect that adding rheological admixtures may have on the mixture.

19.1. History of rheological admixtures

If we consider a hydraulic concrete (i.e. created with a binder able to react with water and to form stable compounds), the material's specifications may involve many targets, such as early-age deformation limit values or the capacity to resist certain types of chemical aggressions. However, whatever the specifications, two characteristics will appear systematically: its mechanical strength when hardened and its behavior when fresh (or its behavior in "liquid" state, or even its rheology). Mechanical strength lets the created element fulfill its function once the concrete has hardened, and the behavior when fresh quite simply lets the element be created and therefore, exist.

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Unfortunately, these two characteristics of the material reject each other without the use of rheological admixtures. Indeed, theory and practice show that mechanical strength in the hardened state is higher when the quantity of water used in the mixture is low (the low limit being the quantity of water just necessary for the chemical reaction of cement to take place). In addition, the material is more fluid when in fresh state, as the excess water quantity relative to the water quantity necessary for the cement hydration reaction is large. It seems, then, impossible to combine fluidity and strength.

Rheological admixtures make it possible to modify this limitation in the cement system. By increasing their dosage, it is then possible to decrease the water quantity to increase mechanical strength at constant rheology. HPC is a result of this practice. It is also possible, by varying their dosage, to improve the fresh mixture's fluidity, and thus with constant mechanical strength. According to their use, rheological admixtures will thus be called fluidifiers or water reducers.

The first rheological admixtures known as "plasticizers" were marketed in 1935. From this time, they were used in a few civil engineering building sites, but were only really developed in Europe after 1945. They were derived from the paper pulp industry (lignosulphonates). Later, these by-products from the paper industry were replaced by synthetic products. Poly-naphthalene-sulfonates (PNS) and poly-melamine-sulfonates (PMS) were therefore originally considered to be top-of-the-range products, for uses limited to important or specific productions. Then, they were established into the whole construction domain and the "superplasticizer" classification was created especially for them.

More recently, another contribution from the detergent industry: the search for new complexing agents of Ca^{++} ions to soften washing water led to the synthesis and development of poly-carboxylate polyethylenes (PCP) which could then be used for problems regarding the rheology of fresh concrete. They are the base of current products and aided in the development of SCCs.

Lastly, we can imagine that organic rheological admixtures for concrete will play a major role in the next revolution of hydraulic concretes. Indeed, the development of concretes with lower environmental impacts is currently a major societal objective. There is a reduction in the quantity of traditional cement when designing these environment-friendly concretes (EFC). Some developments may be cited here, such as the development of new binding agents, the more systematic use of composed cements, the use of other waste from industrial activity as a substitution for cement, and the choice of high substitution rates of cement by one or more mineral additions. However, substituting a part of cement by powders with a strong specific surface complicates the rheology of the final mixture by creating mixes with rapid flocculation (which corresponds to a loss in fluidity of the freshly-mixed concrete).

So as to use EFCs serenely with strong levels of cement substitution, it then seems necessary to develop new admixtures which allow us to control this flocculation.

19.2. Macroscopic behavior and microscopic interactions in a cementitious suspension

From a macroscopic point of view, there is an infinity of rheological behavior associated with the infinite number of existing or potential industrial cementitious materials. However, among these behaviors, we can identify large families.

Let us consider an example: the apparent viscosity (i.e. the ratio between shear stress and shear rate) of cementitious materials (from cement grout, for example, intended for injecting pre-strained sheaths to concrete with very high mechanical strength intended for making the most daring bridges). According to their composition, as well as the range of shear rates which they are subjected to, these materials will express, in steady state, either Newtonian behavior (i.e. constant apparent viscosity), or shear-thinning behavior (i.e. decreasing apparent viscosity with the shear velocity), or shear-thickening behavior (i.e. apparent viscosity growing with the velocity of shears). Moreover, it is often necessary, particularly for the least fluid materials, to apply a stress higher than yield stress, so that flow will take place. The behavior of shear thinning ordinary concretes can, then, be described by using a Bingham type model [TAT 83], whereas the behavior of shear thickening self-compacting concretes is better described by a Herschel Bulkley type model [DEL 98]. In the same way, cement grouts may be characterized starting from a Newtonian viscosity value [ROU 05], whereas cement pastes display shear thinning or shear thickening behaviors according to the range of shear rates studied [TOU 06].

These various behaviors stem from the scale of interaction between the mixture's different components. Cementitious materials can be considered as being a suspension of different sized particles (from nm to cm) in a continuous liquid phase. During the flow or during the resting phases, the interaction between particles generates the different macroscopic behaviors as observed. The interaction of the particles (and the fluid particles) could *a priori* be the following:

- colloidal interaction;
- Brownian movement;
- hydrodynamic effects;
- more or less direct contact between particles (friction, lubrication, collision).

According to particle size, their concentration in the mixture and the external forces (i.e. amplitude of the stress or strain rate applied to the material), one or more of these interactions may dominate [FLA 04a].

19.2.1. *Components and composition of cement suspensions*

Here, we consider the case of “pure” cement suspensions (cement grouts and pastes). The different types of interaction mentioned above and which all coexist on the scale of the cement paste will be described. For each one of these interactions, the systems in which they condition rheological behavior, and the way in which they can be influenced by the presence of organic admixtures will be detailed.

Water is the only liquid component in the mixture and if, as a first estimation, the effect of admixtures on the water’s viscosity is neglected [TOU 06], its Newtonian viscosity may be considered as being equal to that of pure water at 25 °C ($\mu_0 = 1 \text{ Pa.s}$). The cement particles, whose density ρ is approximately $3,000 \text{ kg/m}^3$, are in suspension in this liquid. Their size varies between 1 and $100 \text{ }\mu\text{m}$. To our knowledge, there is no method which allows us to simply integrate this aspect into the simple and general rheo-physics of cementitious materials. With the objective here only being to understand the way in which organic admixtures may influence microscopic interactions, and therefore macroscopic behavior when fresh, the cement grains will be described by using a characteristic dimension, taken as being equal to the average dimension for cement grains, namely $10 \text{ }\mu\text{m}$.

We will also consider that the mass ratio of water to cement E/C , in modern cementitious materials which interest us here, is understood to be between 0.25 and 0.50. This range covers the grouts and cement pastes containing a rheology admixture for the lowest values of the E/C ratio. Thereafter, we will describe the quantity of a species present in the mixture by its volume fraction ψ (i.e. the relationship between the volume of the species present in the sample and the total volume of the sample). Contrary to the mass fraction used traditionally in cementitious materials formulation, ψ lets us directly describe a suspension’s degree of obstruction, a fundamental parameter of rheological behavior. The solid volume fraction of such suspensions is then:

$$\phi = (1 + \rho_p E/C)^{-1}$$

and varies between 35 and 55%.

19.2.2. Distant inter-particle interactions

Just after the mixing phase, one of the dominant interactions is due to Van der Waals forces. For distances lower than 30 nm between particles, these forces may be written under the following form:

$$F_{vdW} \cong A_{(h)} \frac{\bar{a}}{12h^2}$$

with:

$$\bar{a} = 2a_k a_l / (a_k + a_l)$$

the harmonic average of the radius of the interacting particles, h is the inter-particle distance and $A_{(h)}$ is the Hamacker constant [FLA 04-02].

In addition, an electrostatic interaction force may appear between particles, due to opposite surface charges. This repulsion can be written as [FLA 02]:

$$F_{ES} \cong -2\pi\epsilon\epsilon_0\bar{a}\psi^2 \frac{\kappa e^{-\kappa h}}{(1 + e^{-\kappa h})}$$

where ϵ is the water's dielectric constant, ϵ_0 the vacuum's permittivity, and κ^{-1} the Debye length [FLA 02]. To avoid particle agglomeration in cement suspension, the repellent electrostatic force should be sufficient enough to counter the gravitational Van der Waals forces. However, due to the system's strong electrolyte concentration, the electrostatic forces are generally insufficient to prevent against agglomeration or flocculation. It is, then, necessary to use rheological admixtures.

The first generation of rheological admixtures aimed to increase the intensity of the repellent, electrostatic forces by using polyanionic organic polymers [FLA 01, RAM 98] which induce a negative electrostatic potential on the particles on which they adsorbed (see Figure 19.1). Therefore, many studies have focused on this subject, even if in 1979 Banfill [BAN 79] proposed the hypothesis that the steric effect due to these polymers could not be ignored in cement particle dispersion. Sixteen years later, Gartner *et al.* [GAR 94] showed that steric effects effectively dominated the electrostatic effects in the most effective molecules. It is, however, only recently that the idea of a steric action of last generation rheological admixtures became an accepted and controlled explanation for cement particle dispersion [SAK 95, YOS 97].

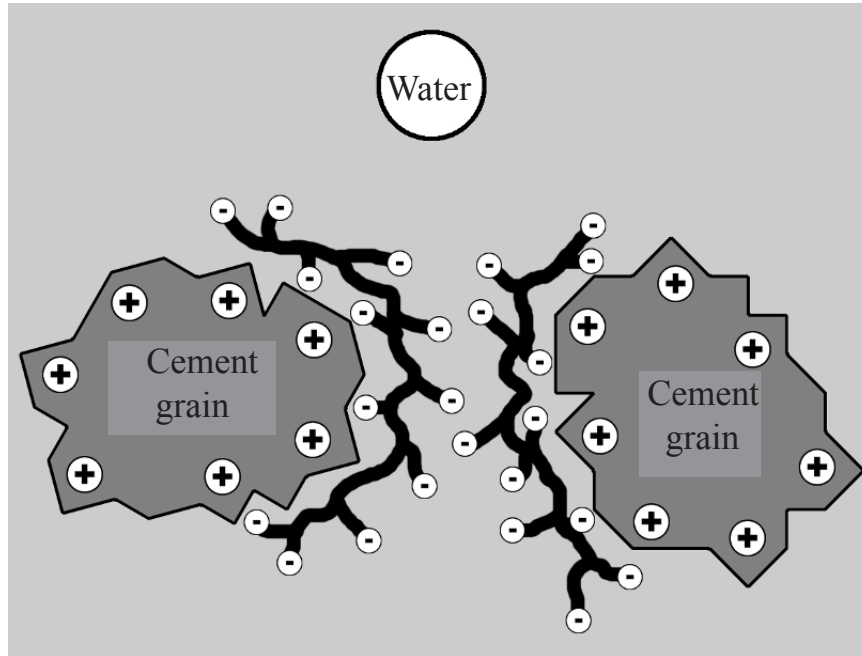


Figure 19.1. Dispersion by electrostatic effects, of first generation rheological admixtures

There are many expressions used to describe the interactions generated by these steric effects. They are all derived from an energy which is necessary for the interpenetration of organic polymer layers (see Figure 19.2). They describe the essential extra force needed to bring two cement particles closer together, at a distance lower than the adsorbed polymer layer. These expressions depend on the geometrical configuration adopted by the polymer on the cement particles' surface. For mushroom type configurations (i.e. where the polymer chain density is its strongest at a few nanometers from the particle's surface, and not on the surface itself), the following expression can be used:

$$F_{Ste} = \bar{a} \frac{3\pi k_B T}{5s^2} \left[\left(\frac{2L}{h} \right)^{5/3} - 1 \right]$$

where s is the distance between the two neighboring mushrooms, and L the chain length extended to the solvent's core.

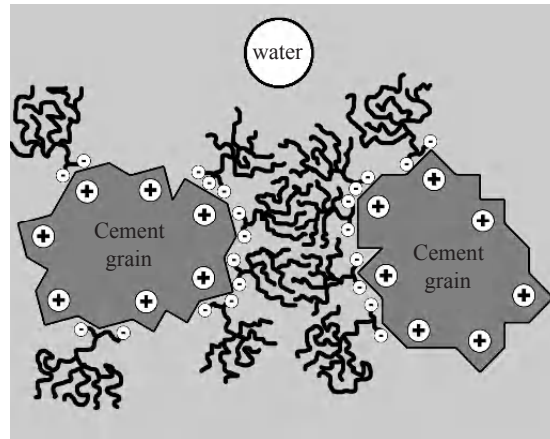


Figure 19.2. Dispersion by steric effect of second generation rheological admixtures

It is, then, possible to consider the integrality of these interactions and to propose the following scheme: coupling these different interactions generates a force between two neighboring particles, which depends on the distance separating them. At any given moment, a particle is surrounded by other particles with which it interacts. It is, then, possible to consider the total potential energy (Φ_0) of this particle as a function of the relative position of neighboring particles. For each particle, there is an instantaneous position connected to a minimum potential energy (i.e. each particle can be seen as being located in a potential well, resulting from the interaction forces generated by neighboring particles [COU 99]) which, as a first estimate, is located at a more or less equal distance between particles. In this framework, it is useful to introduce the characteristic average distance b between the centers of two neighboring particles. From these geometrical considerations, we obtain:

$$b = d(\Psi/\Psi_m)^{-1/3}$$

where Ψ_m is the volume fraction for maximum stacking. Ψ_m only depends on the shape and the granular distribution of the cement particles, as well as their spatial configuration. For identical spheres, it must be remembered that Ψ_m varies between 0.62 for cubic configurations and 0.74 for a cubic configuration with centered faces.

For cement pastes, the Van der Waals interaction forces mentioned above, when no rheology admixture is added to the system, dominate the other types of distant interactions and may generate an agglomeration or aggregation of the particles (i.e.

when the cement particles are agglomerated, the potential interaction energy is minimal). In this case, the cement particles form flocs, in which a quantity of water is trapped. These flocs take up an apparent (or effective) volume, higher than the cement particles alone. This aggregation phenomenon is prevented, as we have seen by the presence of rheological admixtures, either by electrostatic, or steric effects. The configuration of minimal potential energy then passes from aggregated to dispersed configuration. For aggregated structures, the meaning of b as the average distance between the centers of the particles loses its value, but the general framework proposed below stays valid.

If the potential interaction energy (colloidal) Φ_0 between the cement particles at a distance the same as the average distance between particles is insignificant, then the suspension behavior is Newtonian. This situation evidently takes place for important E/C ratios [STR 95] (weak solid volume fraction). In this case, the average distance between particles is large (cement grout for example), and the potential interaction energy is weak. This situation may also be seen for higher E/C ratios, if the potential interaction energy amplitude is greatly reduced by massive use of rheological admixtures (see [FLA 02], [PAP 04], [TAT 83] for more details). Conversely, if Φ_0 is not insignificant, the particles cannot easily move, in comparison to the others. In this case, the cement suspension will present *a priori* a yield stress τ_0 , since a macroscopic flow will only be possible if the energy needed to extract each particle from its potential well is applied to the system. The network of distant interactions between particles must therefore be broken in order to establish a homogeneous flow, where each particle will be extracted from its position of equilibrium.

Recent approaches such as the YODEL model [FLA 06] let us take the polydispersity of the cement particles into account. The yield stress of the suspension which depends on Ψ^2 can be written as:

$$\tau_0 = m_1 \frac{\Psi (\Psi - \Psi_{perc})^2}{\Psi_m (\Psi_m - \Psi)}$$

where Ψ_{perc} is a solid volume fraction of percolation, under which the cement particles are too far apart to interact, and the suspension does not have a yield stress. m_1 is a parameter which brings together everything which does not depend on the solid volume fraction, but on the interaction strain on the particles which can be changed by the dosage and nature of the rheology admixture used in the mixture. This model has proved its capacity to predict ceramic suspension thresholds containing submicronic particles on a wide range of volume fractions.

19.2.3. Contact type interactions

Being able to decrease the quantity of water in the mixture, while preserving sufficient fluidity through using rheological admixtures, had as an industrial consequence an increase in the solid quantity of matter in the mixture in order to increase the mechanical strengths at the hardened state (or to preserve them at reduced content cement). In addition to the remote interactions that we have just described, the cement particles are now sufficiently close to develop interactions of the direct contact type.

The prevalence of the contacts in the behavior of a suspension can only take place if there exists a considerable number of contacts within the suspension. This can be associated with the existence of a continuous network of contacts able to transmit an effort (process of percolation) for a solid volume fraction higher than a critical percolation value Ψ_c . There currently does not exist a theoretical approach making it possible to predict the value of the solid volume fraction for which this network of percolation appears but experimental and numerical results indicate that, for uniform spheres ($\Psi_m = 0,64$), Ψ_c lies between 0.50 and 0.60 [ONO 90]. In the case of polydisperse suspensions, Ψ_c is probably higher since the average distance between particles is proportional to $(\Psi/\Psi_m)^{-1/3}$ and thus increases when Ψ_m increase.

The smallest separation distance between the particles ε which can be reached depends on their nature. It may be equal to the roughness of the non-admixed cement particles, or to the thickness of the admixture coat adsorbed in admixed cement particles. Measurements by Sakai and Diamond [SAK 95] suggest that the thickness of this coat is around 10 nm.

It is important to note that with the high solid volume fractions which allow us to obtain modern rheological admixtures, the particles are so close to each other that they must push their neighboring particles to be able to move. This obstruction effect may lead to dilation in the network of granular contacts during the flow, and has a macroscopic consequence known as “dilatancy”.

Mansoutre *et al.* [MAN 99] therefore measured the normal force exerted on the upper plate in a parallel plate rheometer for non-admixed pastes ($\Psi_m = 0.45$), and observed the dilatancy phenomenon. They were able to distinguish three regimes:

- $\Psi < 0.38$. No normal force;
- $0.38 < \Psi < 0.41$. Normal force growing with Ψ ;

- $\Psi > 0.41$. Normal force associated with strong fluctuations.

The reduced volume solid fraction where a network of contacts and therefore a normal force seem to appear in the system is around $0.38/0.45 \cong 0.84$, which corresponds to the critical value obtained for mono-dispersed spheres. The important fluctuations seem to be due to a particularly evident obstruction effect, which may generate the temporary formation of granular arches within the suspension.

19.2.4. Hydrodynamic effects

Inclusion movements, such as cement grains, grains of sand or gravels in a fluid imply fluid flow. Firstly, let us consider the displacement of an inclusion in a fluid with Newtonian viscosity μ_0 at rest point. This inclusion is subjected to a drag force due to fluid flow, which is written in a laminar system:

$$F_{Stokes} \approx -\mu_0 d^2 \dot{\gamma}$$

If the suspension, and therefore the fluid, are flowing, similar forces appear which induce a dissipation of energy in the suspension which is higher than the dissipation of energy in the fluid alone. This dissipation increases with the mixture's shear rate. For non-colloidal particles, the behavior of the mixture remains Newtonian. Generally, its viscosity increases with the volume fraction in inclusions Ψ . For values of Ψ lower than a few percent, (E/C higher than 6 for cement suspensions), Einstein's analytical relation can be applied:

$$\mu = \mu_0 (1 + 2.5\Psi)$$

In practice, for values of Ψ ranging between 0.35 and 0.55, there is no analytical solution. Several empirical expressions were, however, proposed. These all predict that the mixture's viscosity diverges when $\Psi \rightarrow \Psi_m$. The most widely known relation is the Krieger-Dougherty relation [KRI 59]:

$$\mu = \mu_0 \left(1 - \frac{\Psi}{\Psi_m} \right)^{-2.5\Psi_m}$$

The Einstein evaluation, then, takes into account the fact that adding inclusions to a suspension (i.e. which already contains particles) generates a dissipation of energy which is higher than that for when they are added to the fluid alone.

As we have already described, non-dispersed cement particles may form flocs which trap water. In this case, the effective volume fraction of these flocs is higher than the real volume fraction of cement grains. Therefore, Mansoutre *et al.* [MAN 99] applied the Einstein relation to apparent viscosity measurements μ of cement pastes to a shear velocity of 100 s^{-1} in a rheometer with parallel plates. They could identify a value of Ψ_m equal to 0.45, where the viscosity of their cement pastes seemed to diverge. This low value of Ψ_m (compared to 0.62 for mono-dispersed sphere stacking) confirms the state of aggregation of the tested materials which were prepared without super-plasticizers.

Struble and Sun [STR 95] carried out similar experiments on strongly admixed cement pastes. They obtained values of Ψ_m ranging between 0.64 and 0.80, according to the type of cement tested and the shear rate for which the apparent viscosity was measured. The fact that the viscosity diverges for a Ψ value higher than the value of Ψ_m obtained for identical spheres in a face-centered cubic configuration (0.4) seems to be due to the polydispersity of the cement particles. Hu and De Larrard [HUC 96] proposed a semi-empirical relation allowing for a simple prediction of the maximum compactness of powders and granular materials used in civil engineering, according to the diameters of the smallest and coarsest grain of a granular skeleton:

$$\Psi_m = 1 - 0.45(d_{\min}/d_{\max})^{0.19}$$

With the ratio between $d_{\min}$ and $d_{\max}$ being around 100 in standard cement, Ψ_m could, then, effectively be around 0.80, as obtained by [STR 95] or other authors such as [HOD 07].

It may also be interesting to note that the cement particles, not being completely spherical, may adopt a preferential direction during flow. When aligned, in steady state on the stream line, they can then reach higher Ψ_m values.

For partially flocculated systems, Ψ_m values where the viscosity diverges may also be relatively high if the suspension shears are particularly intense. Indeed, the energy from strong shears may break the flocs and therefore bring the value of Ψ where the viscosity diverges towards the real solid volume fraction of the dispersed cement powder.

It seems, then, that the best way of reconciling these various experimental observations is to approach the relation between the formulation and hydrodynamic effects, not only by using value of Ψ , but by using the value of Ψ/Ψ_m at the same

time remembering that Ψ_m , the solid volume fraction where the viscosity diverges depends on the dispersion state of the cement grains (i.e. the shear velocity and the dosage of the rheology admixture). For strongly admixed and quickly sheared mixtures, Ψ_m tends towards the solid volume fraction for maximum packing (or maximum compactness) of the cement powder (around 0.80).

For technical, economic or environmental reasons, a considerable fraction of the cement powder is sometimes replaced by various alternative powders. Some of these substitution powders may reduce the apparent viscosity of the obtained paste for a given total, solid volume fraction. The simplest explanation is, in this case, that these smaller powders increase the mixture's solid, volume fraction of maximum packing value and thus, the solid volume fraction value where the viscosity diverges. This explanation, which is based on the concept of optimum granular compacticity, is confirmed by the fact that there is an optimum dosage of substitution powder where the apparent viscosity is minimal [FER 01], [FEL 06].

This granular explanation is, however, not sufficient since some of these powders, of equivalent sizes to the others, cause an increase in the apparent viscosity and/or mixture's threshold [FEL 06], [FER 01], [NEH 98]. It should be noted that these particles, often of a size about one μm , have strong colloidal properties where the effects are sometimes higher than those for the colloidal properties of cement grains, and may adsorb some of the rheology admixture. In this key domain for the future of environment-friendly concretes, a lot of research still needs to be carried out.

19.3. Conclusion

In this chapter, we have considered organic (or built-in) admixtures for concretes. These organic molecules, present in tiny quantities in the mixture, have already revolutionized concrete technologies twice, by making way for the development of high-performances concretes (HPC), as well as self-compacting concretes (SCC).

We have focused our attention on the family of admixtures which are dominating the market: rheological admixtures (i.e. those capable of modifying the behavior of fresh concrete). Firstly, we considered the role that rheological admixtures could play in the history of concretes and their formulation. Secondly, we studied the effect that the addition of rheological admixtures can have on the mixture in the rheological behavior of concretes on a microscopic and macroscopic scale.

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Chapter 20

Contributions of Organic Admixtures in Construction Processes

20.1. Introduction

The organic use of materials in cementing materials is not a new practice: M.Vénuat [VEN 84] reported on the use of egg whites and pork blood for Roman concretes, due to the plasticizing or air-entraining effects. However, the increasing incorporation of superplasticizers since the 1980s is a technological jump in the field of formulation and modern concrete performances, calling into question standard practices (currently, these questions are not entirely shared by the world of the BTP). Such questioning opens up new possibilities in the field of construction processes.

20.2. The situation without the contribution of organic chemistry

Without a significant contribution from organic chemistry, concrete properties were essentially controlled by its cement dosage. Indeed, the work of formulation concentrated on optimizing the granular skeleton (in order to minimize the necessary paste volume), and the water content was decided on obtaining sufficient workability. Consequently, the water/cement ratio was correlated by the cement dosage. Therefore, the mechanical resistance and durability performances equally depended on this. The range of hardened concrete performances was rather reduced. As for fresh concrete, it was impossible to obtain a very fluid consistency without

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compromising the material's homogeneity (resistance to segregation) and its performances when hard. We will point out here that a cement only needs approximately 25% water (mass ratio) to be hydrated, whereas concretes without additives usually include a water/cement ratio higher than 0.50. This surplus water (free water) is a source of porosity, permeability and delayed deformation for the material. We therefore comprehend the highly restrictive character of this formulation via cement dosage approach, and all the potential progress attributed by organic chemistry which will be described in the following sections. Let us note, however, that this approach is still going strong for some prescribers in the domain, since it is still common to impose a minimum cement dosage as a guarantee of quality, even on building projects, only to impose this criterion (contrary to the norms which no longer mention cement dosages, only as one of the parameters to be taken into account).

20.3. Contribution of superplasticizers

Alongside set-retarder, accelerating or air-entraining admixtures, plasticizers constitute the first generation of products able to lead to light decoupling of the cement dosage and water/cement ratio, but they only do this marginally, with a water reduction at constant workability around 10 l/m³. Superplasticizers allow us to consider a very significant reduction in free water, usually in the order of 20 to 40 l/m³. In these proportions, the aforementioned decoupling is very significant, and allows us to dissociate a good number of concrete properties: workability, mechanical resistance, durability, shrinkage/creep, etc. It should also be noted that the rise of superplasticizers is related to the appearance of a new generation at the end of the 1990s, with a clearly improved working time (from 30 minutes to 90, and even 120 minutes), which is an essential factor for new constructive processes within the framework of concrete manufactured away from building sites and cast in situ. In particular, the development of self-compacting concretes (SCC) was only made possible thanks to this advance.

20.4. Example of pre-stressed grouting

As an introduction to the presentation of modern concretes, we wish to illustrate, by using the example of grout for prestressing tendons, the impact of organic chemistry on cementing materials. The technique of pre-stressed concrete by "post-tension" methods consists of inserting sheaths, which can be threaded and pre-stressed cables can be put under tension into the concrete or structure. These cables must then be protected from corrosion and, to achieve this, current practice injects a fluid cement grout with a low E/C ratio, to coat them and perfectly fill the free space between these cables and the sheath's envelope. The space to be injected is reduced,

and the injection can be done over several tens of meters, with uneven dips which are sometimes significant. Superplasticizers have allowed us to obtain fluid grouts which facilitate the injection process and guarantee good filling. However, the grout's homogeneity after injection was seen to be bad in certain cases, due to a large sensitivity to bleeding, which is promoted by the sheath's slopes ("boycott" effect) and water filtration through strands.

Some formulations used were not robust enough and gave irregular results, particularly influenced by the implementation temperature (heat generally increases risks of bleeding). This led to cable ruptures due to corrosion, and a questioning on pre-stressed concrete works at the end of the 1990s, until a more developed and approved grout appeared in France (with superplasticizers, cohesion agents and a cement with controlled fineness). This example illustrates both the power and the limitations of organic chemistry, which always requires a careful selection of other components and their proportions, and cannot compensate for formulation defects alone. We can summarize this by the following formula: an admixture cannot correct bad cementing materials. Initial defects can even be exacerbated by the superplasticizer. In the path towards materials with strong superplasticizer doses, the cohesion agents may prove to be a useful complement for obtaining cementing materials with improved and controlled performances.

20.5. High performance concretes (HPC)

High performance concretes were developed in France at the end of the 1980s, through prestigious constructions, such as the Ile de Ré bridge, the Normandy bridge, or the large Arche de La Défense in Paris.

Their formulation is based on an important water reduction thanks to the use of highly dosed superplasticizers, while preserving fluid consistency [BHP 00]. In addition, this property is generally necessary for a satisfactory workability, given the significant increase in viscosity related to the low water/binder ratio (generally between 0.30 and 0.40). The use of ultrafines such as silica fumes, may help with obtaining HPC, with characteristic compressive strength ranging between 50 and 80 MPa. Even if it is common to understand the performance of HPCs by their level of resistance under compression, it is well known that lowering the water/binder ratio can improve other properties, durability in particular. This is why HPCs are systematically used today for large civil engineering constructions, or in marine environments (*offshore oil platforms*, port extensions, concrete barges, viaducts, etc.); they can resist chloride penetration, which allows lifespans longer than 100 years without the need for maintenance (Figure 20.1).

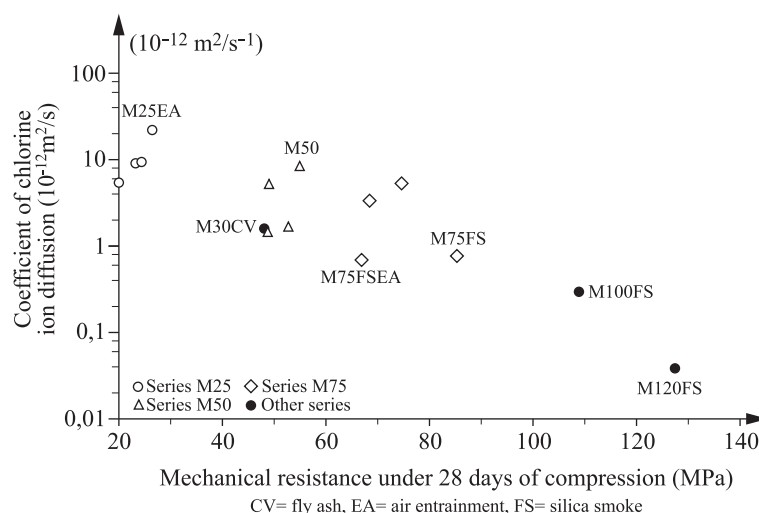


Figure 20.1. Amplitude of the decrease in the chloride diffusion coefficient according to the compressive strength (according to [BHP 00])

HPCs also allow us to design large range structures, with greater slenderness or to reduce obstruction of the structures.

Sometimes they are used for buildings under large strains, such as very high towers (La Défense towers in Paris or the CMA tower in Marseilles, for example). They are widely used in prefabrication fields, where their good, short-term resistance is exploited. Thus, the prefabrication of tunnel segments is performed in a factory with light steam curing (approximately 40°C) making it possible to reach 15 MPa after 6 hours (and therefore to unmold the segments in this time). For concrete which is cast in situ without thermal treatment other than to the effect of the concrete's exothermic hydration, we can reach 20 MPa in an age of 13 hours, equivalent to 20°C (example of the segments on the Normandy bridge). This means that we can accelerate the production rate while ensuring the safety of the building site when demoulding or setting the tension on pre-stressing strands.

20.6. Self-compacting concretes

Self-compacting concretes (SCC) constitute the last evolution to date of concretes used for buildings and civil engineering constructions [AFG 08]. Their large fluidity level when fresh gives them multiple advantages in terms of simplicity of implementation and socio-economic impacts, with a significant reduction in the labor difficulties for workers in charge of concreting, and a suppression of the noise

generation by vibrating apparatus used to compact concretes with ordinary fluidity levels (SCCs do not need vibration). In terms of the quality of concrete used (resistance, durability, esthetics), their potential is also higher than for traditional concretes which is highly dependent on the know-how of the workers. SCCs were developed in Japan at the end of the 1980s so as to resolve problems of implementation quality.

A self-compacting concrete is a very fluid concrete which can be implemented without vibration (compaction is achieved by the only gravitating effect) and give a compact and homogeneous material after hardening. Indeed, traditional concretes undergo a certain air entrapment during the transportation, and implementation, and generally requires an energy contribution (in the form of internal or external vibrations) letting the air trapped in the material escape. Traditional concretes with fluid consistency can, in certain cases, be implemented without vibration (this is the case for pile concretes or diaphragm walls) but regulations then take into account a lesser quality when in the hardened state. What distinguishes SCCs from fluid concretes, is their capacity to flow into formworks while preserving their homogeneity and compactness. SCCs are systematically formulated with superplasticizers (and possibly cohesion agents) to obtain very large fluidity levels while preserving, *via* a sufficiently low water/fines ratio, a good resistance to segregation and satisfactory properties in the hardened state.

SCCs can be used for practically all applications in buildings as well as in civil engineering. Only slightly shifted upper surfaces, traditionally created without formworks, need particular concreting devices (formwork or concrete maintenance system) which may result in a preference for using vibrated concrete.

SCCs display largely limited implementation stresses compared to ordinary vibrated concretes. We will point out here that for vibrated concretes, implementation must be performed by coats of not more than 50 cm (in proportion to body height of the vibrating needles), with a drop height lower than 1.5 m, and while avoiding moving the concrete by vibration effects at a distance of more than 2 m. For SCCs, drop heights up to 5 m (concrete is much more resistant to segregation) and horizontal displacements in the formwork from 5 to 10 m are accepted (according to segregation resistance SCC and the reinforcement density). This allows for a much faster implementation which, however, is limited by the climbing speed in the formwork (for questions of evacuating air bubbles). Of course, these formworks must resist the hydrostatic pressure exerted by the concrete, which is very fluid during the casting process.

On the other hand, SCCs cannot tolerate negligence with regard to waterproofing the formwork: where we would obtain a honeycomb with ordinary vibrated concrete, the risk of negative results is much greater with SCCs since we are likely

to empty the formwork. This typically relates to opening defects which are larger than 3 mm. For small waterproofing defects, on the contrary, SCCs are more tolerant as their cohesion avoids localized segregations (washed sand, dark aureoles, etc.) which harm the facing's color homogeneity.

For vertical applications, implementation can be performed at the top of the formwork (bucket or pump) as for ordinary vibrated concretes, or from the bottom (injection by pumping). This last possibility makes it possible to automate implementation and to limit the number of workers in charge of concreting (Figure 20.2).



Figure 20.2. *Vertical application. Concreting from the bottom*

For horizontal applications, the advantage of SCCs lies in their ease of levelling and screeding. Traditional screeding and floating processes are taken away and replaced by a bar surface treatment (less laborious since it is performed in upright position) known as “debubblizing”.

Many diversified constructions have been achieved in France by using SCCs from the end of the 1990s [CIM 03]. At the present time, SCC is widely used for prefabrication and its use is progressing for in situ casting (horizontal in small buildings, architectural concrete, congested or very densely reinforced works, etc.). It has been used, in particular, on certain large building sites abroad, for major civil engineering works. This shows that it is a high potential material which is quite controllable today (and well controlled by specialized companies for manufacturing and implementation).

SCCs have a significant positive impact on construction processes, allowing us to obtain concrete constructions of better esthetic quality (for example, courtrooms

in Pontoise made from white SCC, Figure 20.3) and structural constructions, with productivity gains and a revalorization of the profession's image. However, their development is slow for in situ concrete casting, mainly because of problems concerning robustness where we find some limitations to do with the contribution of organic molecules.



Figure 20.3. *White SCC court house in Pontoise*

20.7. Ultra-high performance fiber reinforced concrete (UHPFC)

UHPFCs are cement matrix materials with a characteristic compressive strength conventionally between 150 and 250 MPa [AFG 02]. These materials contain fibers (metal or synthetic) so as to obtain ductile behavior under tension and to avoid explosive ruptures under strong compression. The water/binder ratios of UHPFC formulations are very low (lower than 0.20) thanks to using strong superplasticizers and cement doses.

When fresh, UHPFC is very viscous but can be also very fluid, or even self-compacting. When hardened, it develops a strong initial shrinkage which largely limits the possibilities for in situ casting: most of the time, UHPFC elements are prefabricated. A very fine granulometry (absence of coarse aggregates and use of fine sands) and their mechanical performance under tensions allow us to construct very thin pieces (around 1 cm).

These materials have not yet found their place in the construction industry, but have enormous potential, particularly regarding durability, since they are extremely

compact (capillary porosity reduced to the maximum, only hydrate porosity is left) and therefore resistance to aggressive agent penetration.

It also should be noted that, contrary to the HPC, current UHPFC formulations are not adapted to local resources in components, but use “premixes” which guarantee robustness but increase the cost of the material.

20.8. Currently used concretes

Progress made in the field of the HPC, SCC and UHPFC, as well as associated problems, allows for a parallel evolution of concretes usually used in construction. We, then, note a regular increase in the consistency of concretes (today the majority of concretes used on building sites are fluid concretes, and practically all the formulations include a plasticizer or a superplasticizer) as well as extending the used range of resistance under compression (usually 25 to 40 MPa of characteristic compressive strength measured on a cylinder). This evolution of concretes, allowed thanks to the development of “special” concretes, is also a necessary vector for the reliability of new materials developed in laboratories. Tools for measuring the properties of fresh concretes are also in question (shear threshold, viscosity, water content, etc.) and the manufacturing material (precise water dosage in the mixer).

20.9. Perspectives

At the current time, superplasticizers are still products with controlled activity on the concrete shear thresholds, but their impact on viscosity and cohesion is not evaluated or controlled very well at the moment. From this point of view, we think that these products can be improved. In addition, modern concretes cannot often be characterized just by shear threshold and viscosity parameters, because of their thixotropic character. This thixotropy is, then, a key component for obtaining materials which are both fluid and resistant to segregation after implementation during their flow in the formwork. The effect of current superplasticizers is a weakened thixotropy, which sometimes obliges us to add a cohesive agent. In this field, we can also imagine new admixtures which allow us to control concrete thixotropy, which would make it possible, for example, to predict pressure on the formwork when concreting great heights with SCC.

Lastly, some new functions could be developed so as to modify the properties of cementing materials, for example, from the point of view of exothermy or resistance under tension.

In all these cases, admixtures will have to adapt to the variability of the components in cementing materials, and give formulations with a robustness which is compatible with available methods of fabrication.

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Chapter 21

Organic Fibers in Cementitious Materials

21.1. Introduction

Cement-based materials: mortars and concretes, have numerous properties such as a high rigidity, a low thermal and electric conductivity, and above all, an excellent compressive strength. Depending on the needs of the application and according to the formulation, this may range from a few tens to a hundred megapascals, even approximately 200 megapascals for ultra-high performance concretes (UHPC).

Two major disadvantages can, however, sometimes limit the use of these materials, namely their brittleness and their poor tensile strength (a few megapascals only). The development of fiber reinforced materials enables mitigating these disadvantages and developing, among others, thinner and stronger products that are also less sensitive to cracking. Indeed, when the load applied to the concrete approaches the rupture load, cracks are quickly propagated. The development of cracking includes three stages:

- micro-cracking,
- localization,
- and propagation leading to rupture (Figure 21.1).

Using fibers incorporated in the material then makes it possible to stop this process, or at least to limit it and to slow down its effects.

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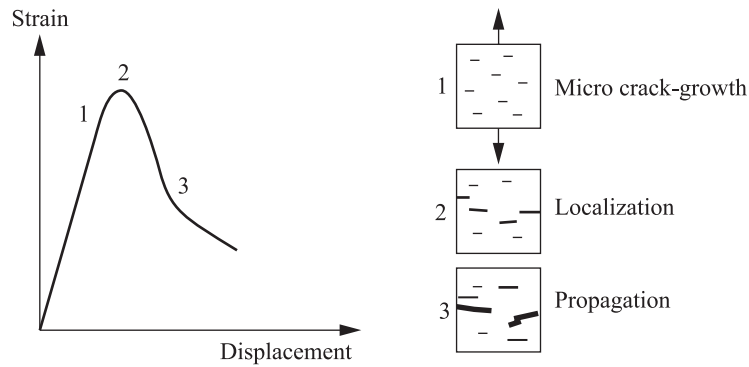


Figure 21.1. Schematic representation of crack growth in a concrete block subjected to direct tension according to [ROS 87] quoted by [MES 06]

Fibers have been used for a long time now, for reinforcing varied materials such as soil, brick or even plaster. Their association with cement-based materials is a much more recent process. Among the most used fibers, one may note steel, glass, asbestos and polypropylene fibers [FIB 07].

In addition to considerations related to cracking and ductility, other properties have appeared to be particularly interesting, such as an improvement in fire resistance for various types of concretes with added polypropylene microfibers [BIL 04], [FER 06], [FER 08], [KOD 03], [LIU 08]. Further, we can also note a renewed interest in natural organic fibers, which can often offer an interesting alternative in terms of management of local resources with a more favorable environmental and health impact [AGO 05], [COU 05], [LUG 06].

In this chapter, we will only focus on *organic* fibers (primarily made of carbon and hydrogen), for which it is important to consider the elastic modulus and density, in order to optimize their effectiveness in the composite.

However, to better locate the use of organic fibers in civil engineering, the comparison between their characteristics and those for other types of fibers will be approached in this introductory section.

21.1.1. Characteristics of main fibers

Various fibers may be classified according to their shape or their nature: metallic, mineral or organic, synthetic or natural. The physical and mechanical characteristics of some of the most commonly used fibers are given in Table 21.1 as an illustrative example.

Nature	Diameter or section $E \times L$ (μm)	Density	Elongation to fracture (%)	Elastic modulus (GPa)	Tensile strength (Gpa)
Steel	5-500	7.8	3-4	200	1-3
Glass	5-15	2.6	2-3.5	80	2-3
Polypropylene	10-1 000	0.9	10-20	3-10	0.3-0.6
Asbestos	0.02-20	2.5-3.4	2.3	200	3
Carbon	7.5	1.7-2	0.5-1	300-400	2-3
Cellulose	14-45	1.5	8-12	20-40	0.15-0.5
Amorphous cast iron	$e = 25$ $l = 1,000$	7.2	2	140	2

Table 21.1. *Physical and mechanical properties of a few fibers, according to different authors [BEA 82], [KHE 00]*

When the fiber's elastic modulus is high compared to that for the matrix, the fibers take back some of the load, which leads to an increase in the material's tensile strength. An increase in the fiber's length/diameter ratio usually leads to an increase in flexural resistance and the composite's tenacity. However, this ratio remains limited (around 200 to 300) so as to allow a good dispersion of fibers during mixing (the formation of fiber balls is thus avoided) and to preserve sufficient level of workability. The fibers are selected according to their properties, their availability and their cost.

21.1.2. Fiber reinforced cement material, application in civil engineering

The use of fibers is accompanied by a more or less important modification of the "matrix" formulation, i.e. mortar or concrete (granular skeleton, paste volume, etc) according to the nature of fiber, its shape, its dimensions and its dosage. Admixtures are usually used in order to compensate for a possible loss of fluidity of the fresh concrete. According to the case, the final products can be either pumped, cast or sprayed. The many innovations related to the formulation or the implementation techniques themselves, have allowed us to widen the range of applications of reinforced fiber products in civil engineering (Table 21.2).

Several types of fibers can be simultaneously used for particular applications, in order to seek out a combination of their properties, or even a synergy. We are then referring to “cocktails” of fibers or hybrid mixtures (example: steel and polypropylene fibers [SIV 07]).

Nature	Applications
Steel	Roofing elements of cellular concrete, carriageway surfacing, bridge decks, refractory products, concrete pipes, runways, pressure tanks, structures resistant to explosions, tunnel supports, segments, boats hulls, pavements, foundation pilings, etc.
Glass	Prefabricated panels, walls, sewers, thin shell concrete roofs, coatings for concrete blocks.
Polypropylene /Nylon	Foundation pilings, pre-stressed piles, facing panels, floating elements for unloading docks, roads repair materials, ballast coats for underwater pipes, supportings (polypropylene macro-fibers), underground coating (polypropylene macro-fibers).
Asbestos*	Walls, pipes, panels, thermal insulation materials, and fire protection, sewers, flat or curved roof plates, wall coating.
Carbon	Curved elements for floor constructions, simple or double curve membrane structures, boat hulls, scaffolding boards.

Table 21.2. *Fiber reinforced concrete applications in civil engineering according to [BEA 82] *: use prohibited in France since 1997 for health reasons*

21.2. The use of organic fibers in cementitious materials

21.2.1. *The contribution of organic fibers*

The major advantages of using organic fibers in civil engineering were already mentioned in the introduction. These are principally the limitation of cracking and the improvement of ductility in products developed for high value added applications. Certain very particular properties can be improved, such as for example resistance to fire in the case of polypropylene fibers.

Specific interests involve the use of natural organic fibers in particular, such as wood, hemp or even bamboo. Composites are lighter and generally have good thermal and acoustic properties which make them interesting for building detached housing. It is then a question of considering the environment and, in particular, taking the resources available in each country into account.

21.2.2. The most used organic fibers in cementitious materials

21.2.2.1. Synthetic organic fibers

The most often used synthetic organic fibers are polypropylene fibers, sometimes made up of a mixture of polypropylene and polyethylene. We will also note here the use of aramid fibers Kevlar™), polyester, polyvinyl alcohol [SCH 04] or even polyamide fibers (nylon) [KUR 00, SON 05] with a tensile strength approximately twice higher than those for polypropylene fibers [KHO 08a]. Using these organic fibers in cementitious materials is not as widespread as using metal fibers. Probably less widely studied, concretes reinforced with synthetic fibers are not studied in terms of dimensioning methods either. Indeed, the elastic modulus of most of these fibers remains relatively low, compared to that of concrete, despite attempts to increase this modulus by modifying the manufacturing process of these fibers. The potential interest of these fibers with respect to the composite is, then, limited. However, there may be many contributions to the properties of the final material, and they may be quantitatively significant: improving shock resistance, increase in strain capacity, reduction in crack growth, etc. [ZHE 95]. Table 21.3 gives the main properties for the majority of organic synthetic fibers. Their durability in moist or alkaline environments is generally very satisfactory, except for polyesters which are generally sensitive to alkalines.

Fiber type	Density	Tensile Strength (MPa)	Elastic modulus (GPa)	Ultimate elongation (%)
Acrylic resin	1.17	207-1,000	14.6-19.6	7.5-50
Asbestos/high modulus	1.44	3620	62/117	4.4/2.5
Nylon	1.16	965	5.17	20
Polyester	1.34-1.39	896-1,100	17.5	
Polyethylene	0.96	200-300	5	3

Table 21.3. Properties of main synthetic organic fibers [ZHE 95]
the properties of polypropylene appear in Table 21.1

21.2.2.2. *Natural organic fibers*

Natural organic fibers from wood, hemp or even bamboo, sisal and coconut, are fibers coming from materials available in great quantities in certain countries, mainly countries in full economic development. These fibers generally present sufficient properties to develop everyday construction products, particularly for detached housing [JUA 07], [SAV 00]. Moreover, they offer interesting environmental prospects, as an alternative to synthetic fibers, such as polypropylene fibers, subjected to economic competition [FAO 04]. These renewable natural fibers can be associated with cementing materials and be interesting in terms of saving resources. They may also consider the valorization of natural products or by-products, and develop new technological solutions, which present certain interests with regard to environmental or health concerns. For this reason, we will refer to the replacement of asbestos fibers used for making thin, plate type elements by wood or bamboo fibers [COU 05], [COU 95], [KHE 00]. Using natural organic fibers is also mentioned, to improve certain properties such as the composite's resistance to freeze-thaw cycles [NAI 05] and to cracking under plastic shrinkage [FIL 99].

One of the major difficulties related to the use of organic natural fibers remains, of course, the variability of the fiber properties. Indeed, they may come from several species whose production itself is at the mercy of the seasons. In addition, their production can differ locally as well as storage conditions and transformation processes. This variability in the fiber properties may, then, create large repercussions on the quality of the final products. Lastly, some natural fibers, such as sisal and coconut fibers are particularly sensitive in alkaline environments. They may also deteriorate due to mineralization [FIL 00]. However, a pre-treatment of fibres associated with a low-alkaline matrix allows improving the durability of the cement composite [FIL 03].

21.2.3. *Organic fiber/cement material composite*

21.2.3.1. *The fiber/matrix interface*

The fiber/matrix interface may be regarded as a phase in itself. Indeed, its microstructure may be different from that of the cement matrix. This interface is also called the interfacial transition zone, or even the interfacial halo. Its morphology depends on the nature of fiber, its affinity with the cement matrix, its geometry, the presence of a possible surface treatment, the formulation of the cementitious material as well as the material's fabrication process. The size and section of the fibers considerably influence the microstructure of the fiber/matrix interface, as well as the physico-chemical compatibility of the matrix and the fiber. For macro-fibers, the interface's microstructure may be considered as being similar to that of the

aggregates' interfacial transition zone. Degradation of the fiber/matrix association may occur by rupturing the fiber, or by detaching itself and being washed away.

21.2.3.2. *Physico-chemical compatibility*

According to the nature of fiber and its production method, there may be some physico-chemical incompatibilities with the cement matrix. For natural fibers, these incompatibilities generally result in setting and hardening disturbances (essentially delays) or in durability defects.

The choice of fibers to be incorporated into a cementitious material depends on a certain number of criteria, including resistance to the high alkalinity of cement. This is the case for polypropylene fibers which are completely inert.

However, some fibers are subjected to a chemical, even physical, degradation in the cementing environment. This is the case for polyester fibers, certain types of polyacrylonitrile fibers and the majority of plant fibers. Cellulose fibers, owing to the fact that they contain wood extracts (lignin, hemicellulose, starch, tannins, certain phenols and other sugars) lead to delayed setting of cement-based materials [MAH 05]. Fibers which contain significant amounts of lignin and hemicellulose are also more sensitive to the alkaline attack and chemical degradation. One way of remedying this problem consists of chemically pre-treating the fibers, in order to minimize the hygroscopic effect and reinforce the interfacial bond. Adding pozzolanic materials, such as silica fumes, also constitutes a way of decreasing the matrix alkalinity, and therefore the degree of degradation in the wood fibers.

21.3. A return to the use of some organic fibers

21.3.1. *Polypropylene fibers*

21.3.1.1. *Fibers available on the market*

There are currently several types of polypropylene fibers on the market. These fibers are characterized by their dimensions and presentation (Figure 21.2). Improving some of their characteristics means that it is possible to consider new applications. This is the case for fibers with high characteristics, that now allow us, with a degree of caution, to consider their use for structural applications. This is made possible in particular thanks to a higher elastic modulus.

Usually, we can distinguish two large families of polypropylene fibers: macro-fibers and micro-fibers. Micro-fibers can be fibrillated, such as monofilament or multifilament types. Some marketed fibers, in fact, are sometimes obtained from a polyethylene/polypropylene mixture. Polypropylene is remarkably resistant to the

majority of aggressive chemical agents: acids and alkalines. It is not sensitive in alkaline environments, which makes it completely compatible with the cement matrix. Its only weak point is a susceptibility to oxidation. This is why the marketed polypropylene fibers are stabilized against this reaction. Using these fibers also makes it possible to be freed from facing defects related to possible surface corrosion, as with metal fibers. Whatever the results, these defects are only superficial and are therefore primarily esthetic.

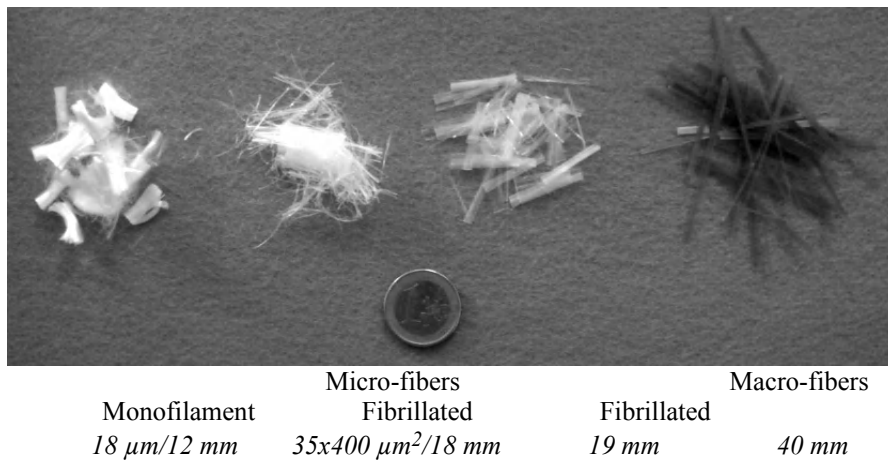


Figure 21.2. *Some types of polypropylene fibers available on the market*

21.3.1.2. Using polypropylene fibers

The main interests in using polypropylene fibers in cementitious materials are, on the one hand, an important reduction in plastic shrinkage (replacing the anti-cracking steel mesh) [BAN 06], [HAS 99] and on the other hand, an improvement in fire resistance [FER 06], [KOD 03]. We will also mention for some quite particular cases, limited in France but widespread in the Scandinavian countries for example, the development of structural applications related to using polypropylene macro-fibers as an alternative to metallic fibers [FIB 07], [GUI 07]. Lastly, other properties of concretes and mortars in fresh or hardened state can be improved. As examples, we will cite: limitation of bleeding and an improvement in the stability of fresh materials, an increase in ductility when hardened without necessarily modifying the mechanical characteristics, an improvement in shock and abrasion resistance, and sometimes, a moderate reduction in total shrinkage.

The modification of the performance of cementitious materials by using polypropylene fibers obviously depends on their dimensions, their presentation, as

well as their dosage. It must be noted, however, that even weak dosages may already lead to significant modifications of the cementitious materials' performances. Thus, micro-fiber dosages in the order of 1 to 3 kilograms for 1 cubic meter of concrete (i.e. 0.1 to 0.3% in volume), are sufficient for improving the fire resistance and, more particularly, that of a high performance concrete. [KAL 01]. Larger dosages, in the order of 3 to 9 kg/m³ are, on the other hand, necessary when using macro-fibers in structural applications [GUI 07], which nevertheless corresponds to dosages approximately 4 times weaker than for metallic fibers, where the number of fibers is still the essential parameters to be considered. In addition, the rather average fiber/matrix adhesion may be compensated by a significant improvement in the fiber anchorage, by using fibrillated micro-fibers or macro-fibers with non-straight shapes, according to the application considered. We will, however, prefer to use monofilament type micro-fibers type for improving fire resistance, where the action mechanisms are different [KHO 08b]. It should also be noted that using polypropylene fibers may lead to a loss of workability more or less significant, depending on the fiber dimensions used and above all for high dosages. This loss of workability can nevertheless be compensated for by modifying admixtures.

21.3.1.3. *Manufacture and main characteristics*

(Monofilament) polypropylene fibers are manufactured from the polymer which is extruded and stretched, which fixes the crystalline phase at approximately 55% and the total density at 0.91. The crystallinity depends on the polymer's molecular weight and the thermal history during extrusion. A second stretching phase means that the crystals can be directed and the tensile strength increased, thus the fiber's tenacity. Fibers may also be manufactured as very fine films and cut out – fibrillated fibers – or, the threads are twined into strands to give multifilament fibers.

A thermal rise when exposed to high temperatures (fire, for example) leads to, first of all, a loss of crystal direction and a cancellation of the stretching phase as the main consequences: the fiber retracts and increases in diameter. Any crystallinity is then lost from the moment when the fiber reaches the melting point, which is around 165°C. Temperatures ranging between 350 and 475°C then lead to hydrocarbon vapor formation (very noticeable reduction in molecular size) which burns around 550°C when oxygen is present, and from 350 to 400°C if they are directly exposed to a flame [KHO 08a].

Polypropylene fibers are generally covered with a dispersing agent which allows a good fiber distribution during concrete mixing. However, with only a small affinity to water and the cement matrix, the fiber/matrix adhesion remains quite moderate.

Polypropylene is a visco-elastic material. Polypropylene fibers have a very low elastic modulus, around a few gigapascals at room temperature. This means that,

according to the type of aggregate used, the concrete's elastic modulus is from 5 to 30 times higher than for polypropylene. The tensile strength is approximately 30 to 300, or even 500 MPa, i.e. approximately 10 to 100 times bigger than for fiberless concretes.

21.3.1.4. *Using micro-fibers in structural applications*

Fiber dimensions are selected according to the products which are to be manufactured, the formulation and the granulometry of the aggregates (length of 30 to 50 mm, and diameter of 100 μm to 1 mm). According to the desired performances, their dosage may vary from a few kilograms to a little less than approximately 10 kg/m^3 .

Macro-fibers allow for an improvement in behavior under flexural tension. Indeed, the material's ductility (aptitude of material to deform without rupture after crack growth) can be increased. These macro-fibers may also improve hard shock resistance, and consequently, reduce risks of bursting and fragmentation of the concrete elements. They can be used to replace steel mesh and provide an alternative to metallic fibers for pavements, tunnels, vaults, etc. Concretes can be *a priori* pumped or sprayed.

In shotcrete applications, these fibers allow limiting the risk-related to rebound during direct spraying. The rebound may be also limited and the projection output improved from approximately 20 to 30%. Moreover, when posing a waterproofing film, using these fibers can help to avoid the risk of perforation and therefore the implementation of usual precautions: increasing the thickness of the protective geotextile, and spraying of a non fibrous concrete layer [GUI 07]. Finally, the wear and tear of the projection machines and the risks of clog formation are less prominent than with metallic fibers. Such fibers have already been tested for implementing temporary supports in tunnels (Bocognano and Chavannes tunnels) or for final coatings in safety galleries (Grands Goulets tunnel). These experiments which are still very limited in France, however seem to very encouraging and open up interesting prospects. Questions are still being asked on the long-term deformations of such concretes, and therefore on the limitations of the use when these deformations may be damaging to the structure.

21.3.1.5. *Reduction in plastic shrinkage in concretes*

Monofilament or fibrillated micro-fibers are used for reducing plastic shrinkage. Studies on the influence of the fibers' geometry and dimensions have often led to contradictory results [BAN 06], [BRA 02], [MA 02]. It is nevertheless true that the quality of fiber anchorage, their smoothness and their specific large surface are important parameters with regard to the impact on shrinkage. The majority of tests carried out up to now (flexion, localized punching, etc), show that these fibers,

generally in doses of less than 1 kg/m^3 , can be used to replace the steel anti-cracking mesh, whose positioning is not always easy [HAS 99]. Fibers are uniformly distributed in the mass and simplify implementation. Certain fibers or rather certain products or processes are often the subject of technical reports. Characteristics such as: free shrinkage, porosity, mechanical strength, etc. are generally not significantly modified by fibers, but cracking tends to be finer and better distributed. Lastly, strength under flexural load and punching under a localized charge of fiber slabs are generally slightly lower, but close to the strength of slabs with a traditional welded steel mesh. Residual post-crack growth resistances are higher, on the other hand. These fibers also play a large role with regard to the quality of the end product, and probably to later drying processes.

21.3.1.6. *Improving concrete fire resistance*

21.3.1.6.1. Spalling and consequences for the structure

Spalling within a concrete structure element can be defined as a detachment, either violent or not, of concrete layers or pieces from the face which is exposed to fast and important increases in temperature. This last phenomenon occurs particularly during a fire. However, under certain conditions, spalling may be observed for thermal phenomena with a much less amplitude than those occurring during a fire.

According to the nature of the mechanisms involved, we can generally distinguish two kinds of spalling [KHO 05]. This distinction has its own limitations, however, and remains purely conventional insofar as the prevalence of one or the other implied mechanisms is not always quite obvious. When we refer to spalling, we are generally talking about “explosive” spalling, which is considered to be more damaging during a fire.

As a result of the combination of the two main mechanisms, there is an increase in the pore pressure due to water evaporation, and an increase in thermal stresses due to differences in thermal strain between the aggregates and the cement pastes. [KAL 01], [KHO 00], [KHO 08b] (Figure 21.3). This spalling leads to a violent and progressive expulsion of small, low thickness concrete scales (a few millimeters compared to a few centimeters in other directions). This expulsion may appear as soon as the fire begins, and may continue if the fire is not controlled. This leads then to a progressive reduction in the concrete element’s thickness. Using reinforcements does not change spalling, except possibly to perpendicular steel bars with strong diameters or densities, which may act as obstacles to the expulsion of concrete scales [COM 05].

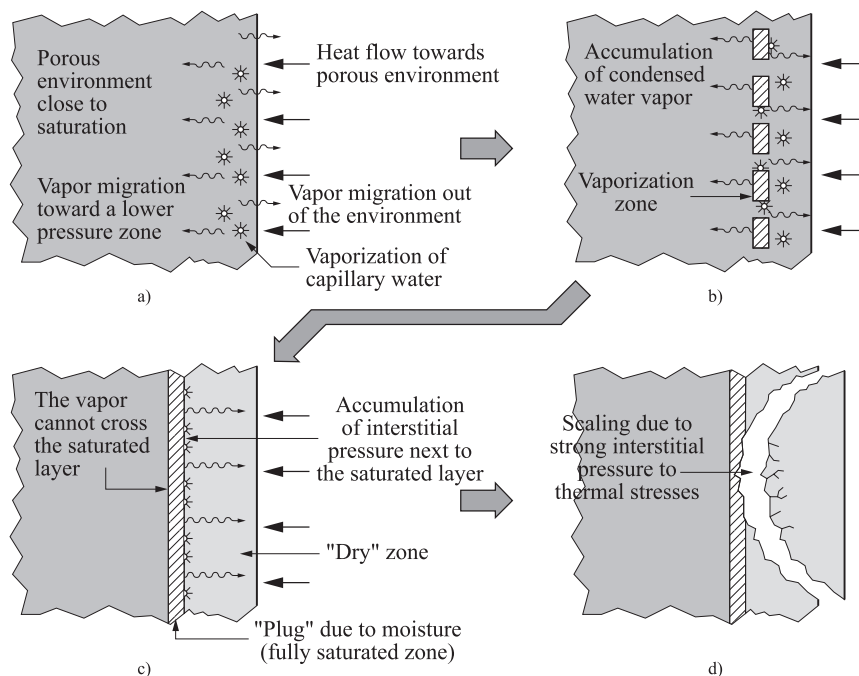


Figure 21.3. Mechanisms responsible for spalling according to [ZEI 06]

In addition to the deterioration of the concrete's mechanical properties due to physico-chemical modifications during temperature rises [KAL 01], [NOU 05], [XIA 06], [ZEI 06], explosive spalling may turn out to be damaging with respect to the structure, insofar as it may lead to a loss of insulation for a separating partition, by partial destruction of the partition, or even by a loss in its supporting capacity.

Indeed, on the one hand, the concrete section supporting the compressive forces decreases and on the other hand, the disappearance of the concrete's surface coat (which ensures thermal protection of steel) leads to excessive heating, and a loss in their mechanical properties. Therefore, there is an increase risk of damage through buckling.

21.3.1.6.2. Factors likely to influence scaling

Regulation defines two principal thermal stresses (time-temperature curves) which are considered to be the envelope curves for all fires that are likely to be encountered in tunnels. These standard curves called, respectively, the CN or ISO

834 curve (low envelope curve in tunnels, also used in buildings) and the HCM curve (hydrocarbon modified curve, high envelope curve in tunnels) allow to specify the level of fire resistance required for the various elements of a tunnel, according to their function and their exposure risks (Figure 9.4). Fire resistance is, then, the capacity of an element to preserve its role despite the development of a fire. The objectives for sufficient fire resistance are to allow self-evacuation of users, the intervention of emergency services according to an acceptable risk level, the construction's strength so as to ensure the safety of surrounding structures, and possibly the durability of the structure so as to minimize the repair costs and time to re-opening of the tunnel [COM 05].

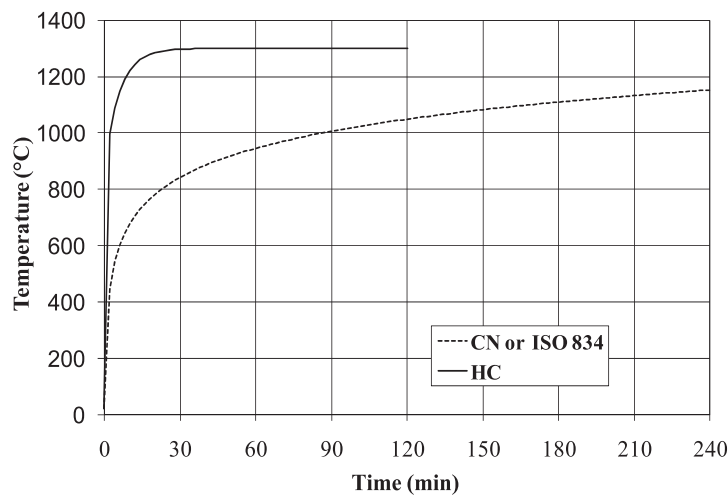


Figure 21.4. Standard thermal stresses called CN or ISO and HCM (hydrocarbon modified) curves

Spalling risks, then, depend on a certain number of external factors, including thermal stress itself (heating velocity, maximum temperature reached and process duration), structure element loading or even environmental conditions. The latter particularly determines the concrete's drying, and thus its residual water content. It also depends on internal factors related to the concrete's very composition: nature and dimensions of the aggregates, binder type, mineral additives, or the use of air-entraining agents or polypropylene fibers. It is generally considered that there is a spalling risk for HPC (compressive strength higher than 60 MPa) as soon as a CN type thermal stress occurs, and for all other concretes with a HCM type stress. The strong risk of HPC spalling compared to concretes with lower mechanical strength can be explained by the very low permeability levels of these concretes. Pressure in the pores which is greater and nearer to the exposed surface is then generated and

leads to the gradual detachment of very fine concrete scales [KAL 01, KHO 00] (Figure 21.5).

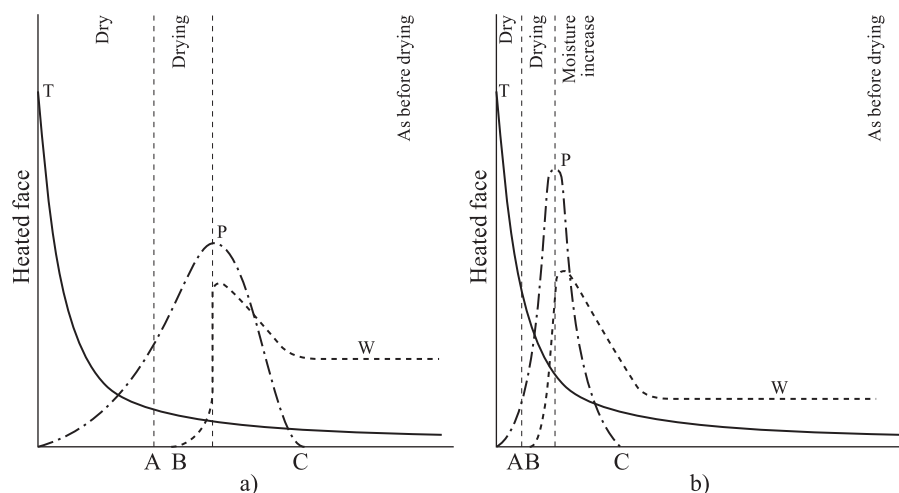


Figure 21.5. a) Conventional concrete; b) high performance concrete temperature (T), water content (W) and pore pressure (P) in concretes heated on one face, according to [KHO 00]

21.3.1.6.3. Action modes of polypropylene fibers

Using polypropylene fibers is one method of considerably reducing the risks of spalling in a concrete formula [FER 06], [FER 08], [KHO 00]. Fiber action mechanisms are not yet fully understood or modeled [BEN 00], [KHO 08a], [KHO 08b]. Experiments have shown that they primarily act by reducing pressure in the pores [KAL 01]. This reduction in pressure seems to take place by creating of two vacuum types in the concrete's microstructure [KHO 08b]. On the one hand, this is related to isolated "reservoirs", and on the other hand, to a continuous network of "channels" which are created due to the progressive pyrolysis of polypropylene fibers, at temperatures ranging between 350°C and 475°C. The isolated vacuums consist of air bubbles which are entrained when the polypropylene fibers are mixed, as well as microscopic cracks generated around fibers when being heated, and are used as surge tanks for the vapor. These vacuums act in the same way as those which would come from using air entraining agents. As for the network of vacuums created by the transformation of polypropylene fibers into hydrocarbon vapor, in addition to its own continuity related to the dosage and dimensions of the fibers used, it also allows for an inter-connecting in the capillary porosity of concretes with moderate water/cement ratios, or even an inter-connection in areas with higher porosity around the aggregates. It will be noted here that for low mechanical strength

concretes (high water/cement ratios), the capillary porosity which is already connected only allows steam evacuation by itself, and it is therefore not necessary to use polypropylene fibers.

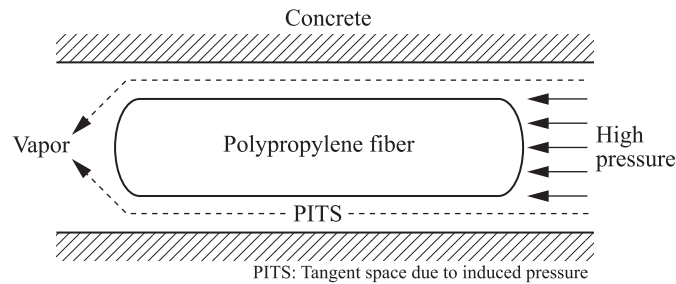


Figure 21.6. *Simplified representation of the fiber/matrix interface rupture, under steam pressure influences according to [KHO 08b]*

However, explosive spalling occurs very early under the combined effect of pore pressure and thermal stress. Pore pressure depends on the heating velocity, the concrete's permeability and its water content. It has been noticed that the pressure peak appears near the heated surface for temperatures around 150 to 250°C, i.e. when the polypropylene is melted (around 165°C) but not yet transformed (Figure 21.5). The channels, then, are not yet released to allow steam evacuation. In addition, the strong viscosity of melted polypropylene means that a flow across these channels is unlikely, except maybe if it is in the immediate vicinity of the surface. Therefore, for lower temperature ranges, one of the possible fiber action modes would then be to create a rupture zone at the fibers/matrix interface [KHO 08b]. Indeed, the adhesion between the cement matrix and the polypropylene fibers is weak, and a sufficient steam pressure may generate interfacial rupture, and creating a zone around the size of 1 mm. This zone would then allow steam evacuation even before fiber melting (Figure 21.6).

The effectiveness of such a mechanism obviously depends on the characteristics of the polypropylene itself, but also on the specific surface of fibers and the connected network which they are likely to generate. The use of monofilament type fibers compared to fibrillated fibers is preferred. The fiber's diameter must be low, and the length suitable so as to obtain a good level of dispersion (not too long) and a good connectivity (not too short). In practice, if we also take into account the limitations related to the fiber manufacturing techniques, fibers with a diameter of 10 to 50 μm and a length of 6 to 18 mm with dosages of 1 to 2 kg/m^3 of concrete, are generally used.

21.3.2. *Plant fibers*

12.3.2.1. *Wood fibers*

Certain countries were able to anticipate the replacement of asbestos by using natural fibers. This is the case in Australia, where motivations within the industry were initially economic and strategic. Effectively, asbestos was imported there in its entirety. As of the 1960s, certain products such as roof plates integrated up to 50% wood fibers in order to replace asbestos fibers with completely satisfactory performances. one could not at that time completely replace asbestos because wood fibers were not able to retain cement particles in the same efficient way as asbestos. Later research and finally, the prohibition of using asbestos for health reasons this, meant that as of the 1980s, the Australian industry was seen to be able to replace asbestos fibers with wood fibers in all plate or tube type products. The preliminary and mechanical treatment of wood fibers means that the fiber's structure can be modified, to make it more flexible and improve its bond with cement during the manufacturing process: internal or external fiber fibrillation sometimes accompanied by filler formation [COU 05]. Chemical treatments using chlorine means that the lignin which creates problems of compatibility with cement may be eliminated. The success seen for this type of application remains, nevertheless, greatly related to specific manufacturing processes.

From then on, it has been looked to extend the range of natural fibers which can be used to replace asbestos fibers in cement/fiber composites [COU 95], [KHE 00] and generally in cementing materials according to fibers available in the various countries, and always in relation to given applications and processes, either in terms of manufacturing and treating the fibers, or in terms of the finished product.

21.3.2.2. *Hemp fibers*

Hemp fibers were also studied as a strengthening agent for cement-based materials. They have high tensile strength (approx. 900 MPa according to Beaudoin, quoted by [LIZ 06]) as well as a good strength level in alkaline environments. These properties mean that hemp fibers are excellent strengthening materials for shotcretes, for example (Table 21.4). Finally, their low density (1.5 t/m^3) gives composites whose density decreases in a linear way, with a growing percentage of fibers. The “wet” or “dry” manufacturing methods influence the material's mechanical properties by modifying the adhesive properties between the fibers and the matrix. Indeed, the “wet” method seems to give a better adhesive strength between the fiber and matrix, and therefore increases properties such as flexural strength. However, independently of the manufacturing process, the compressive strength decreases when compared to traditional concrete. Finally, the fiber dosage seems to be the main parameter which influences the properties under compression and flexion, whatever the manufacturing process [LIZ 06].

Fiber type	Density (t/m ³)	Moisture Absorption (%)	Water absorption (%)	Tensile strength (MPa)	Elastic modulus (GPa)	Fracture elongation (%)
Hemp	1.5	9-10	85-105	900	34	
Bamboo*	0.9			340-500	20-36	1.4-1.7
Coconut	1.15			500	2.5	20
Banana	1.35			600	18	3.4
Sisal	1.45			570	10	5.5

* values obtained according to two different processes of extraction: mechanical and chemical.

Table 21.4. *Properties of plant fibers according to several sources [LIZ 06] and [RAO 05]*

Insofar as they use binders which are different from cement, concretes known as “hemp concretes” which are undoubtedly more well-known, will not be discussed here. The binder used is made up of a hydraulic and air lime mixture. Applying these materials comes directly from the compromises between mechanical, thermal and acoustic properties during their formulation [CER 05], as well as their capacity to control moisture in buildings. Methods of production and implementation must be adapted [ELF 08].

21.3.2.3. *Bamboo fibers*

Contrary to the majority of plants, bamboo only presents axial growth, which gives the hollow stem an almost constant diameter over the entire length. The full radial section is very homogeneous and displays a very good level of fiber coaxality. There are two types of these fibers: packet fibers whose diameter can reach one millimeter and filling fibers, whose diameter is around a few hundredths of a millimeter. Fiber stacking is also denser here than in other plants. These characteristics as well as good mechanical properties, great lightness, a fast growth rate associated with low production costs, make bamboo a quality plant which may be used in construction as an alternative to traditional materials, such as wood, concrete or steel [LUG 06], or even for reinforcing concrete elements [GHA 95], [GHA 05]. We will note, for example, its use in Asia for scaffolding constructions [LUG 06]. More recently, bamboo has been used in industrial applications in Western countries, including for temporary structures [LUG 06]. In addition, bamboo seems to be a completely renewable resource, which grows quickly and simply. We can count approximately 1,500 species, varying in shape and size. They

grow mainly in tropical areas: Asia, Latin America and Africa, but certain species adapt very easily to other climates.

Bamboo shows better characteristics compared to other plants. This means that the resultant fibers can also be interesting, in terms of strengthening composite materials. The fibers can be used alone or as a strengthening agent in soils [GHA 06] or cement materials [CAB 92]. With bamboo filaments, we are distinguishing from applications intended for other plant fibers, and which are, nonetheless, generally a way of simply lightening the material and improving its thermal properties. The fibers can be manufactured by successive splitting. Crushing by hammering will remove the fiber from the plant, and thus obtain fibers with a diameter ranging from between 0.1 and 1.5 mm [CAB 92].

The notion of replacing wood fibers by bamboo filaments when manufacturing cement/fiber composites (alternatives to asbestos fibers) has also been studied. Bamboo may appear more interesting from an economic point of view, and it constitutes a more abundant natural resource in some countries. This replacement involves a study on the impact of pre-treating fibers and of the manufacturing process on the composite's properties. In this case, the fibers coming from the paste required an elimination of "fillers". The fiber dosage, however, had to be slightly increased (12 to 14% in mass) compared to generally used wood fibers (*Pinus radiata*) (8 to 10% in mass) by replacing asbestos fibers to get the same properties [NECK 95].

21.3.2.4. *Other plant fibers*

Plant fibers are natural fibers which can be taken from the stems, leaves, roots, fruits and seeds of various plants (Figure 21.7 and Table 21.4). We will particularly make note of coconut, sisal and banana fibers here, but many other plant fibers could be exploited [RAO 05] together with cement matrix, particularly to develop light products and materials intended for detached housing.

With regard to this last point, answering the increasing demands for housing is a major concern for developing countries, and strong demographic growth. Vegetation, agriculture and forests are therefore important potential sources for extraction fibers which are still not being exploited enough, just like recycling residues from the paper industry [SAV 00]. Fibers which can be extracted by a wet mechanical process are inexpensive, and offer good properties compared to more established plant fibers such as banana, sisal, or coconut fibers. Attempts to develop cement material applications have generally ended in failure, which was generally due to not fully knowing the relatively average and very variable mechanical properties of plant fibers, as well as a generally bad reaction to ageing when crude.

From now on, it is clear that using plant fibers with cement materials (or with polymeric matrices) is of great interest for enlightening the subject of sustainable development. Their use necessarily involves controlling fiber production and transformation [RAO 05] as well as the development of technologies adapted to production, i.e. mixing and implementing the composite product [AGO 05], [SAV 00].

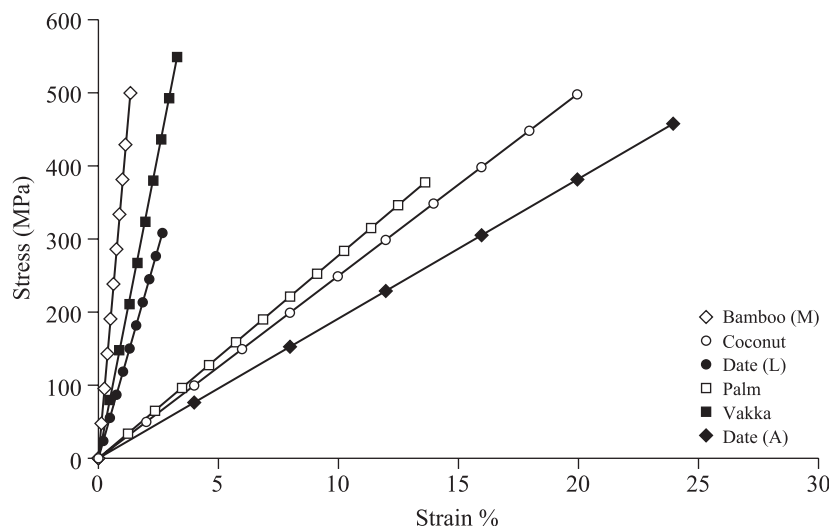


Figure 21.7. Behavior under tension of various plant fibers [RAO 05]

Sisal, banana and coconut fibers have particularly been studied in countries like Brazil, Australia or even Mexico. We will note the important sensitivity of sisal and coconut fibers to alkalinity and relative humidity variations. One of the main solutions consists of pre-treating fibers before use. Juarez *et al.* [JUA 07] compare several solutions for sisal fibers and retain paraffin whereas Filho *et al.* [FIL 03] have had recourse to impregnating of sisal and coconut fibers by a “slurry” of silica fumes. It is also possible to decrease the alkalinity of the environment while having recourse to fly-ash, slag or pozzolanic materials as a substitution for cement [FIL 03], [JUA 07], [SAV 00]. Lastly, carbonating the matrix also improves its durability [FIL 03].

21.4. Contribution of organic fibers to recycling

Recycling can be considered from two different angles. The first relates to recycling organic waste in the form of concrete fibers, and the second corresponds to

improving material properties by using fibers when it contains other products obtained from recycling.

With regard to the first aspect, we will mention some attempts, such as valorizing worn tires into concrete fibers [LIG 04]. The concrete's ductility is improved *a priori* and its susceptibility to crack growth decreased. However, producing fine fibers from worn tires consumes energy and has a certain cost. This can greatly damage this potential source of valorization. We need, then, to find a compromise between the less "costly" production of coarser fibers by using worn tires, and the performances of the finished product which must be suitable for use in applications. Associations with other synthetic organic fibers such as polypropylene fibers are also a way of reaching this compromise. We will also quote another attempt, which consists of recycling bottles made from PET in the form of concrete fibers [OCH 07]. Here, also, it is a question of evaluating and including the economic and environmental impacts of the fiber production processing by using PET bottles, in the analysis of the suggested solution. Applications already exist for shotcretes in underground galleries, and offer certain advantages: good behavior, absence of crack growth after 1 year, etc.

Regarding the second aspect, we will cite the reduced susceptibility to crack growth in concretes made with aggregates taken from destruction waste by using fibers. Effectively, the aggregates produced from destruction waste have a very high absorption coefficient which involves a strong level of shrinkage, and thus an important risk of cracking. The recourse to polypropylene fibers, or better still in this case, to metallic fibers, allows reduced cracking [MES 99], [OCH 02].

These few examples illustrate the attempts to valorize organic waste as fibers in cementing materials, or even the recourse to organic fibers to help to recycle other waste in cement materials. For the moment, the results are still very limited. However, they are particularly interesting and promising in the current context, which puts forward the concerns related to sustainable development. It is also clear that economic and environmental assessments must take the impacts of transformation processes and pre-use waste treatment into account. This is not always easy if we acknowledge that adequate tools are not always available, just as for the set of economic and environmental data.

21.5. Conclusion

The use of organic fibers in cement materials is much less widespread compared to metallic fibers, except for quite specific applications. Indeed, the elastic modulus of organic fibers is still generally lower than that of concrete. Products incorporating organic fibers are not generally part of dimensioning methods. However, the advantages

of resorting to this type of fiber are varied. In particular, according to the nature and dimensions of the fibers and according to its dosage, we will retain the more or less important quality of a limited crack-growth due to plastic shrinkage and an improvement in ductility. Other properties can be also improved, such as fire resistance, shock resistance or even stability when fresh, and the quality of the end product, in terms of esthetics as well as durability.

Polypropylene fibers are undoubtedly the most used organic synthetic fibers in civil engineering. Using micro-fibers can particularly improve the concrete's fire resistance while limiting, or even preventing, spalling. Thus, the structure's integrity may be preserved over a certain time, and allows emergency services to intervene in a tunnel fire, for example. Evacuating the users is then possible, as well as a being able to put the construction back into use quicker, after diagnosis and possibly repair. Here, we are directly referring to user safety and a quick restoration of the construction's function which dominates other aspects. This is still true even if economic considerations related to the expense of studying concrete formulation cannot be completely denied. At any rate, this expense is still rather lower than for a passive protection on the surface of a concrete without polypropylene fibers.

Reinforcing cementing materials by natural organic fibers such as wood, sisal or even bamboo, sometimes manifests disadvantages, due to a strong dispersion of the plant properties, their strong sensitivity to moisture and often their negative behavior in alkaline environments. The majority of these problems can, nevertheless, be solved by pre-treating the fiber and a good choice of the binder. The composite's durability then is greatly improved. The recourse to natural organic fibers has seen a renewed interest today, because of a new interest in taking sustainable development into account. Indeed, using such fibers gives lighter composites and generally presents good thermal and acoustic properties. These products, of average quality but nevertheless sufficient, can answer the increasing demand for detached housing. This request is a major concern for developing countries with strong demographic growth. It is, then, an interesting alternative in terms of local management of resources with an often favorable environmental impact. In terms of health, wood or bamboo fibers also constitute an alternative to asbestos fibers, in light of the more developed production of thin, plate type elements. In this last example, it is clear that the recourse to organic fibers for reinforcing cementing materials is strongly related to the simultaneous development of adapted production and implementation methods.

Lastly, organic fibers can be interesting from a recycling point of view. Indeed, experiments carried out in this field show that some synthetic organic fibers can facilitate the recycling of concrete demolition waste. In addition, certain organic waste can also be recycled in concretes as fibers. Residues from the paper industry

can also be used as a source for plant fibers. It is clear that these experiences have been carried out so as to be developed in the very distant future.

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PART 7

Problems Specific to Organic
Materials: Adhesive Bonding
and Characterization Methods

Chapter 22

Adhesive Bonding, a Method for Construction

22.1. Preliminary thoughts

“Assembly technique known since the most ancient times, and developed in all sectors of human activity, adhesive bonding is not yet considered as being reliable in the fields of civil engineering and building, particularly in France: whether they are engineers or architects, this technique does not instill them with confidence.”

“Some lines of thinking, from a physicochemical approach, may be advanced to try to reopen up the debate on the use of adhesives in construction. The engineer’s work always consists of looking for the best combination of existing techniques to obtain more comfortable and economic constructions. Adhesive bonding is part of these techniques, and should find its place there.” [MOU 99].

These lines, written over ten years ago, hoped to see adhesion techniques better recognized as a constructive method. The message was sent out in various directions [BEN 03, MOU 06] and particularly taken into account by the LCPC (Laboratoire Central des Ponts et Chaussées, Paris, France), which launched a wide research program on the subject [BRU 06, CHA 06]. The knowledge obtained from this research program has been used as the base for writing the following chapters.

The 1999 article [MOU 99] still contains some ideas which have not lost their relevance today.

Chapter written by Thierry CHAUSSADENT.

“It is possible to solve virtually all these problems (acquiring effective adhesion and good durability of the adhesive bonding), either in terms of formulation, or constructive devices adapted to a precise problem (fire-protection, for example). Chemists know how to formulate adhesives which can meet all requirements, but under the condition that the demands are not contradictory: the wonder product does not exist”.

Here, it is advisable to note the importance of *constructive devices* and therefore the role of the architect (or of the designer, in general). This is an aspect which is not often clarified. Nature is generous, but it is always preferable to ask it to make materials that work to their best possible ability.

Finally, this text discusses cultural aspects.

“The general problem raised in this talk is not only of a scientific, technical, or economic nature, but it is also cultural. There is no universal assembly method, in construction, or in other fields. Adhesive bonding is one of the possible methods, and must find its place amongst construction processes, along with other techniques. For this, it is necessary for cultural problems which stand in the way of this technique to be taken away. Studies and researches which prove necessary in order to deal with technical obstacles must be carried out, by both producers and users. But first, it is essential for all those involved in building to accept that old habits must be questioned”.

Knowledge is advancing, but there is still a very vast field of action for researchers and contractors.

22.2. Introduction

The possible users of adhesive bonding methods in civil engineering often lack objective information with regard to the technique's potential. Sometimes biased due to negative experiences in their private lives (self-adhesive product which cannot be repositioned without breaking, but which end up becoming detached by itself) or in their professional lives (a technique which initially functioned perfectly, but which is impossible to reproduce under other conditions), this absence of specific recommendations, both for implementing and following up its performance, leads contractors to use this technique moderately with regard to its potential. It should be recognized that the success for adhesive bonding methods often mainly relies on empirical knowledge of the materials used and their properties. Current applications in civil engineering aim especially to repair or reinforce existing constructions [QUI 11]. Adhesive bonding is a very widespread technique in many industrial applications and its development in the world of civil engineering offers

many advantages compared to other modes of mechanical joining, such as bolting or riveting:

- it is an economic and fast technique to implement for which several mechanical connections can be simply replaced by an adhesive joint;
- there are many types of adhesives and their characteristics can be adapted, according to the application and the implementation process considered;
- the stresses are uniformly distributed on the adhesively surface, which means that local stress concentration can be avoided;
- an adhesive bonding solution can generally decrease the mass of the structure compared with other methods;
- the risks of corrosion are reduced.

The objective of this chapter is to briefly present the basic theories of adhesion, and the main adhesive products used in civil engineering, as well as to specify some principles to optimize a long-lasting adhesive bond, and finally, to give ways of progress in the use of this assembly technique.

22.3. Theory of adhesion and practical conclusions

22.3.1. *Microscopic aspects of adhesion*

Although adhesive bonding has been used for more than thirty centuries, the mechanisms which control the adhesion between two joined materials remain complex and partially unknown. Several theories have been developed in order to describe the various processes.

This part presents the main theories of adhesion, in the general case of two materials put into contact with adhesive product. These theories are approached briefly and for more details, it could be referred to [BRU 06], [HUY 00], [MOU 06], [POC 97].

22.3.1.1. *Theory of mechanical anchoring*

The mechanical theory suggested by McBain and Hopkins [MCB 25] essentially results from a mechanical anchorage phenomenon, related to the adhesive penetration in the pores and the asperities of the substrate. Monternot *et al.* [MON 78] showed that an important roughness of the substrate promotes mechanical anchoring, by increasing the contact surface area at the interface. However, this is only valid if all the asperities of the support are well wetted by the liquid. This wetting depends both on the geometry of the asperities and on the rheological

properties of the liquid adhesive. If this adhesive does not fully fill the asperities, it forms air bubbles which generate excess stresses and then degradation of the adhesive bond. Therefore, an optimal roughness of the substrate should be found.

22.3.1.2. Adsorption theory

This theory is based on inter-atomic and/or intermolecular forces at the interface of two materials in contact. The most commonly encountered forces are the Van der Waals, hydrogen bond, and chemical bond forces. These interactions may be classified according to their bonding energy (Table 22.1):

- the strongest interactions are the *primary bonds* which group together the ionic and covalent bonds;
- the weakest interactions are *secondary or intermolecular bonds*.

Bond type	Energy (kJ.mol ⁻¹)
Primary bonds	
Ionic bonds	600-1 000
Covalent bonds	60-700
Secondary bonds	
Hydrogen bonds	up to 40
Van der Waals bonds:	
Permanent dipole-dipole interaction	4-20
Induced dipole-dipole interactions	less than 2
London dispersion forces	0.08-40

Table 22.1. Bond energy for adhesion forces, according to [COG 04]

In theory, together these forces give adhesive bonds which can reach around hundred MPa. But the presence of any other heterogeneities, geometrical singularities, defects, or air bubbles in the material leads in practice to a decrease of adhesion strength.

In many cases, only the secondary interfacial forces are concerned. The simple formation of hydrogen bonds makes it possible, for example, to improve the adhesive level in a very important way.

22.3.1.3. Thermodynamic model or wetting theory

This model, developed by Sharpe and Schonhorn [SHA 64], relies on the wetting phenomenon, which characterizes the adhesive's aptitude for establishing a close

contact with the substrate, and defines the formation of secondary bonds with the substrate (Van der Waals bonds, or specific interactions like hydrogen or Lewis acid bond). Although they have a weak energy and on short ranges, these forces more or less compensate for the disappearance of the adhesive's internal cohesion forces when the contact surface area increases.

22.3.1.4. *Model for layers of low cohesion*

This model deals more with a theory of interfacial rupture than with a theory of adhesion. For strong bond cohesion, breaking does not generally occur at the interface, but in a layer close to this interface. Bikerman [BIK 67] then introduced the concept of interphasing between materials. This low cohesion layer, due to the presence of imperfections after implementation (air bubbles, etc.) and to the discontinuity between the phases, makes a transition zone which is defined by property and structure gradients. This model can be used to define the adhesive assembly at a very fine scale since it describes the interface in terms of molecular interactions.

22.3.2. *Macroscopic aspects. Adhesive strength and mechanical properties of adhesive bonds*

Each theory previously presented gives a description of particular phenomena, but alone cannot describe all the different adhesion mechanisms. However, it can be considered that the adhesion process takes place over several stages, which use these different adhesion mechanisms (Figure 22.1):

- substrate put into contact with the adhesive;
- formation of more or less strong bonds, which will maintain the cohesion of the assembly.

Then, it is also useful, or even essential, to approach adhesion from the mechanical characterization of adhesive bonds on a macroscopic scale, the properties on this scale being the desired practical objective.

Generally, breaking relates to the separation of two initially interdependent bodies. Crack growth generally starts from a notch or a preexisting defect. Its propagation speed and its aspect depend on the properties of the material(s), on the internal stresses and those exerted from outside (temperature, applied forces, etc.), and on the geometry of the assembly.

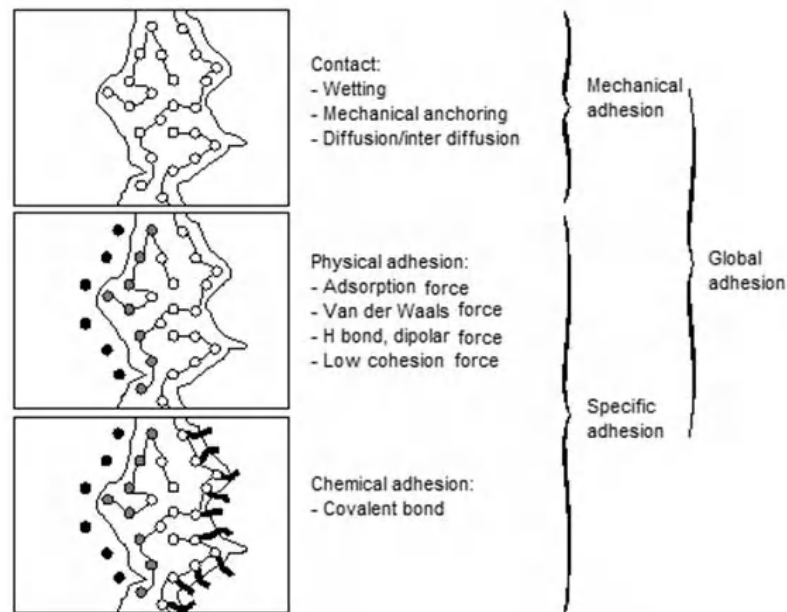


Figure 22.1. Adhesion process, based on the main adhesion mechanisms discussed (according to [SCH 92])

For adhesive bonds, different rupture modes can be distinguished according to the area where crack growth initiates:

- rupture can be confined to one of the two substrates or in the adhesive, which means that the cohesion of one of these materials is weaker than adhesion between components. It refers to cohesive rupture;
- rupture can intervene at the interface, and it refers to adhesive or interfacial rupture. However, the rupture does not always *stricto sensu* occur at the interface, but very near to it. In this case, it refers to “interphase” rupture, because the proximity of an interface can be synonymous with property gradients;
- rupture may also be mixed if it is cohesive in some places and adhesive in others.

The adhesive bonds can be stressed in various ways: strain, shearing, peeling, flexure, cleavage. There are various techniques which allow evaluating the level of adhesive strength, and the mechanical properties of the adhesive joints. In the majority of cases for using adhesives on concrete, the limiting factor is the concrete’s resistance, which is up to ten times lower than the adhesive (strain or

shearing solicitation) and it is, then, often necessary to define special tests, such as in [BEN 07] with a cleavage experiment to test the concrete/resin interface.

22.4. Adhesive formulation and implementation

In this chapter, the few families of adhesives which can cover the majority of civil engineering demands are introduced. Specificities concerning implementation conditions and physicochemical properties of these materials are also discussed.

22.4.1. *Adhesives used in construction*

Adhesives, whatever their state (liquid, paste or film), are polymeric materials and belong to one of the three following categories:

- thermosetting resins, with a 3D structured network. They present high rigidity levels and good mechanical properties;
- thermoplastic resins, made of linear chains. They are generally less rigid, but present good shock properties;
- elastomers, flexible and not very resistant, they have very strong adhesive properties.

A study on adhesive bonding [CAR 02] showed that the construction sector was the second largest adhesive consumer in 2002, and alone represented 17% of the global market (€3.6 b). In France, a proportion of this sector was even higher (27% of the adhesive market, for an amount of €400 m).

Epoxides and polyurethanes make up the great majority of adhesives used in construction (90% in 1999). This chapter will limit itself to presenting some of the aspects relating to epoxidic adhesives, which are mono or bi-component, thermosetting resins with a liquid or paste consistency. Polycondensation between the epoxide base (prepolymer mix, containing at least two epoxy or oxirane groups) and the hardener, the cross-linking agent (in general, an amine with a functionality equal to at least three) gives a 3D network.

Generally, epoxide adhesives are adapted to creating structural adhesions intended to be subjected to high mechanical solicitations (for example, shear strain > 7 MPa). They show some very interesting characteristics:

- excellent adhesion on all types of substrates;
- good mechanical properties: high rigidity (Young's modulus $E \approx 3$ GPa), high strain strength ($\sigma_r > 30$ MPa) and shear strength (> 10 MPa);

- good resistance to chemical aggression (oils, solvents) and moderate water uptake properties.

Formulations of epoxy systems intended for civil engineering may be very different from compositions used in other industrial sectors (aeronautics, electronics, etc.). Indeed, it must fulfill precise specifications [MAY 92, MOS 75], controlled by the building site's conditions and the type of application for which the resin is intended. These specifications concern:

- implementation parameters, such as viscosity, the resin's aptitude for wetting the solid, the workable life, which defines the time when the mixture is sufficiently fluid to allow implementation, and the time of in situ cross-linkage, which specifies the needed time for the bond to reach a given mechanical resistance;
- usage properties after cross-linkage, which may be mechanical resistance, stress/strain behavior, moisture resistance and behavior under fatigue, creep.

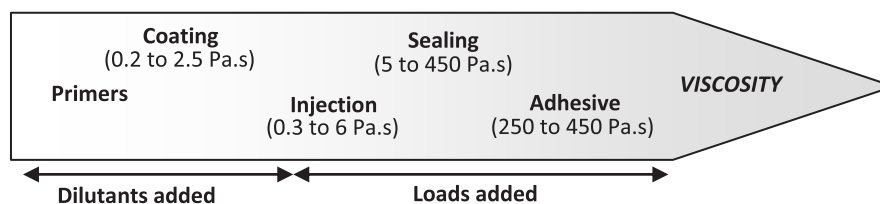


Figure 22.2. *Magnitude values of viscosity required for different civil engineering applications*

Properties of implantation and then service life performance can be adjusted by introducing specific additives (see Figure 22.2), such as inorganic or organic, inert loads (sand, calcite, etc.), dilutants, flexibilizers, etc.

22.4.2. Implementation of adhesion techniques

The implementation conditions of adhesive bonding greatly depend on the nature of the adhesive and the characteristics of the solid surface.

The specificities of civil engineering materials (concrete in particular) can justify using particular techniques, such as surface preparations or adhesive primers.

22.4.2.1. *Surface preparation*

Surface preparation methods aim to optimize the polymer's adhesion to the substrate, via:

- increasing the substrate's roughness, promoting mechanical anchoring;
- eliminating the substrate's weak cohesive layers;
- improving the substrate's wettability.

Many methods are available (chemical, mechanical, electrochemical treatments, plasmas, etc.). Taking into account the particular limitations of civil engineering (dimension of the structural elements), the following treatments are the most widely used:

- Mechanical treatments such as abrasive blast-cleaning, abrasion by sanding or high pressure cleaning. It is interesting to note that a too thorough mechanical treatment may lead to the creation of micro-cracks or local stress concentrations, particularly when the solid is brittle.
- Chemical treatments (mainly for metals) which may eliminate non-adhesive oxide layers, for example, but can also degrease the surface.

22.4.2.2. *Use of adhesive primers*

After the solid surface preparation, it may be interesting to apply an adhesive primer. This type of product has several functions:

- protecting the surface against stains (moisture, dust, etc.);
- wetting the surface and its asperities better than with the adhesive, which is often more viscous;
- for concrete surfaces, it can plug the pores and prevent the adhesive from being completely absorbed by capillarity;
- promoting chemical bond creation when it contains coupling agents (silanes or titanates).

Adhesive primers often consist of a solution with 10% of the adhesive used for bonding. Specific additives can be added to control wetting, penetration, polymerization kinetics or to inhibit corrosion (metal surfaces).

22.4.2.3. *Adhesive implementation and polymerization*

When the substrates have been prepared correctly, the adhesive bond implementation can then be carried out. This often takes place in two stages:

- The adhesion stage, made more or less difficult by the adhesive's viscosity, and by the need to prepare correctly the resin /hardener mixture for bicomponents.
- The bonding and hardening stage, where the elements to be bonded together must be well maintained. In this stage, it may also be necessary to verify the applied pressure, the temperature, and the thickness of the adhesive.

The techniques used depend on the type of adhesive or substrate used.

For thermosetting resins, bicomponent adhesives used in civil engineering, such as epoxy systems, the implementation consists of several stages:

- producing of the liquid component mixture (resin and hardener) in the proportions recommended by the manufacturer;
- adhesion and installation of the parts to be joined;
- adhesive hardening by polymerization, giving a 3D polymeric network. The setting time generally depends on the temperature and the presence of catalysts.

For thermofusible/thermoplastic adhesives, the initially solid adhesive is softened by a heating process, so it can be deposited on one of surfaces to be joined, which is also preheated. After having performed the adhesion process, the join is left to cool and it gradually solidifies.

In all cases, whatever the adhesive and implementation technique used, it is necessary to wait long enough before allowing the join to be subjected to solicitations. In many cases, systems which allow to maintain good position of the pieces to be bonded must be put into place.

22.5. Ageing of adhesive bonds

Generally, and in the domain of civil engineering adhesion applications in particular, an important adhesive parameter is the vitreous transition temperature T_g , which acts as a boundary between vitreous and viscous states. This characteristic temperature depends on the nature of the monomers used and the polymerization process. Indeed, incomplete polymerization often performed at room temperature does not give a high cross-linkage density, and leads to a relatively low T_g . This can be prejudicial, given that the working temperature stays close to this T_g . This aspect promotes the adhesive's physical ageing, which corresponds to an evolution in the thermodynamic properties of macromolecular chains, and is accompanied by important variations in the adhesive's properties (mechanical properties, for example). Recommendations currently exist in France to take the parameter T_g into account [AFG 07].

This chapter thoroughly discusses another aspect of the degradation of the adhesive bonds, which are ageing processes in moist environments (or hygrothermal ageing), by dissociating the mechanisms on a microscopic scale and the effects on macroscopic properties. Literature on this subject provides relatively little information concerning the ageing of adhesive bonds, achieved with cementitious substrates, but there are many studies on metal carrier bonds. Studies on the durability aspects of adhesive concrete/epoxy resin bonds and related investigation methods are currently in progress (see [BEN 11]).

22.5.1. *Microscopic aspects*

Water penetration in an adhesive bond induces several ageing processes:

- The first is related to the micro-structural evolution of materials and, in particular, of adhesives. Water penetrates into the adhesive bond, inducing the network to plasticize, and causes a total drop in the mechanical properties. For under cross-linked adhesives, an increase in molecular movement may also promote the recovery of the polymerization process.
- The second is related to the localized damage at the interfacial zone between the polymer and the substrate, where physical and eventually chemical bonds initially exist between the two phases. This leads to various phenomena.
 - The interfacial area may act as a preferential way for water diffusion by a capillarity phenomenon [IVA 00]. Indeed, the substrate's surface energy may be high enough so that the interaction between the water and the substrate is formed, to the detriment of the polymer/substrate interactions. This effect is particularly noticeable when the substrate's surface presents hydrophilic polar sites [BOW 96, COG 04, TUL 96]. The kinetics of water penetration at the interface may therefore be rather different from that which is observed in the mass polymer.
 - A critical concentration C_c seems to exist, beyond which the water molecules at the interface may cause the rupture of secondary bonds between the adhesive's chemical groups and the substrate (hydrogen bonds, Van der Waals bonds, etc.) [PAR 94, WAT 90], or possibly the hydrolysis of covalent bonds (Figure 22.3). The degradation velocity associated with this phenomenon might depend on the kinetics of the diffusion front advancement from the join's edge towards the core, and would be quicker if the moisture percentage in the environment and the temperature are high.
- Microdefects (air bubbles, porosities) located at the interface may also constitute zones which promote water condensation. Indeed, these defects which are added to the differential inflation between the adhesive and the substrate are responsible for the concentration gradients and high osmotic pressure between the

interface and the resin. This involves a local accumulation of water which may weaken the interfacial zone and increase the risks of decohesion or delamination (Figure 22.4). This phenomenon may be still accentuated when the surface to be bonded is of cementitious type. Indeed, the presence of alkaline ions on the substrate's surface increases the osmotic pressure and promotes moisture diffusion from the substrate's core towards the interface.

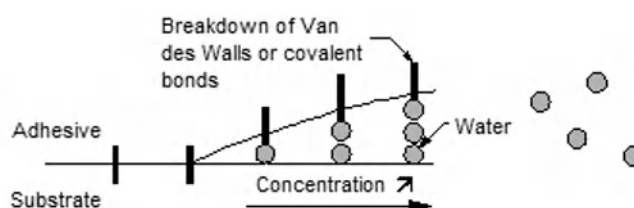


Figure 22.3. Schematic description of induced interfacial damage by water molecules in an adhesive bond, according to [POP 05]

22.5.2. Macroscopic aspects

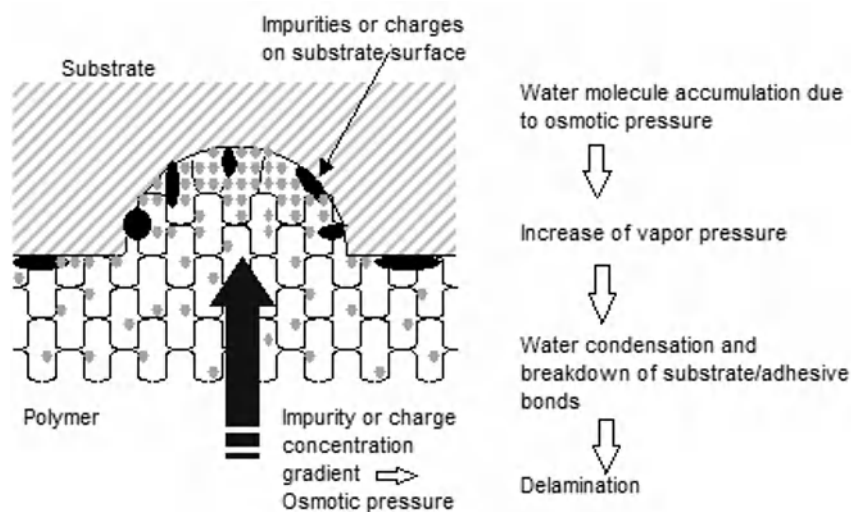


Figure 22.4. Schematic description of blister formation at the interface, according to [BRU 04]

There are only a few studies concerning the influence of hygrothermal ageing on interfacial properties or adhesive strength between adhesives and cementitious

substrates. Literature available on this subject is mainly devoted to the domain of reinforcement by using composite materials (fabrics or plates made from glass or carbon fibers) linked to concrete by adhesive bonding and focuses on the durability of these repairs when they are subjected to accelerated ageing processes. This lack of information can be primarily attributed to the difficulty of evaluating the level of adhesion between the composite material and the cementitious substrate by simple experiments.

Among the available studies, Frigione *et al.* [FRI 06] evaluated the impact of water ageing on the mechanical properties of assemblies made of concrete prisms linked together with various epoxide resins, by means of indirect shear tests. They observed an initial increase in the bond's resistance, which was attributed to a relaxation in the adhesive's residual stresses after water penetration, then to a reduced resistance reaching 20 to 35% for longer ageing durations, and according to the used adhesive type. After a month of immersion, the bond's rupture mode is mainly adhesive to the interface, which would imply substantial damage to the polymer/substrate interface.

22.6. Paths for progress in the development of adhesive bonding techniques in civil engineering

The two fundamental questions asked by all users (real or potential) of adhesive bonding techniques are related to the bond's quality during service life and the possible ways of monitoring it. It is, then, advisable to really define which aspects must be dealt in order to obtain a long-lasting adhesive bond. These various aspects will be described by specifying (when it is possible) the advantages of adhesive bonding techniques, with the view of using adhesives in civil engineering in an innovative way.

22.6.1. Limitation of mechanical stresses

Raising this issue may seem to have little relevance to the current subject. This may be partly true in the strict framework of replacing a mechanical connection by an adhesive bond, but the development of adhesive bonds as a construction method firstly needs to undergo a redefinition of what a construction is, and what the ways of implementing it are. Using adhesives must be perceived of as a technique for improving the total performance of a construction, and for optimizing the choice of the structure, insofar as possible, by simplifying the implementation process.

The construction of bridges made from a steel/concrete mix may be considered as an example, where casting concrete on steel beams with mechanical links could

be replaced by adhesive bonding of prefabricated concrete elements to these beams (this subject is dealt with in the French national project MIKTI [MIK 00]). In this case, improvement relates to a better control over the quality of the concrete which is prefabricated, and over the management of construction stages less subjected to climatic issues.

Besides these innovations which require a realization on behalf of architects, and a thorough reflection in order to limit mechanical constraints across particular constructive techniques, much research has been carried out, related to improving adhesion processes. For example [HAD 01] defined a model to quantify the stress limitations within adhesive bonding process, and to therefore better apprehend the adhesive bond formations.

22.6.2. Adhesive choice and implantation management

Epoxy resins are the most widely used structural adhesives in civil engineering. Generally, and this is also true for epoxy adhesives, adhesive formulations are continuously evolving to fulfill new use requirements, and it is often impossible to refer to older applications to make a choice on the nature of the adhesive. In this case, it is essential to consider the recommendations defined by the manufacturer, for usage but also for implementation. In addition, it may be useful to carry out some preliminary tests in order to check certain mechanical properties for the desired bond.

Besides this essential adhesive choice for a given application, advances are still necessary to answer the question of the reversibility of adhesive process, which is an important parameter, both for restarting an unsatisfactory adhesion operation, but also in terms of destruction and recycling various materials at the end of the structure lifetime.

It is also useful to specify that in many industrial applications, adhesives have secondary functions (for example, conductive adhesives for electronics) which could also be used in the field of civil engineering, in particular to ensure the follow-up of some essential properties linked to durability.

With regard to implementing adhesives, there are two limitations in civil engineering: preparation of the surface and environmental conditions during the hardening process. For preparing the surface, great improvements can be made by controlling some of the construction stages based on the aforementioned ideas (see section 22.5.1). For environmental conditions, there are some possibilities offered by rapid hardening techniques (UV, HF, IR induction) which already exist, but which could also be developed on building sites.

22.6.3. Predicting durability and in situ monitoring

As specified in the introduction, this is one of the key points which limits the use of adhesive techniques in civil engineering. In general, and with a minimum of precautions in the choice of adhesive and its implementation, adhesive bonding gives immediately satisfactory results, but there are still unanswered questions relating to the control over the lifespan and in situ monitoring to avoid brutal degradation and risks for users.

Literature on the subject provides some phenomenological models which can help users with satisfactory descriptions of the effect of ageing on the adhesive's properties alone. With regard to mechanical modeling of adhesive assembly, other useful models are available. The essential point which needs to be resolved relates to defining a model which takes into account the mechanical behavior of the adhesive bond when subjected to an environment which is likely to generate degradation of the adhesive bond. Significant progress has been made in this respect, with studies carried out by the LCPC [BRU 06, NGU 08]. It was shown that a model based on damage can also describe the behavior of a healthy bond as well as a bond exposed to hygrothermal ageing, by introducing an evolution of the model's parameters according to ageing time.

With regard to in situ monitoring of an adhesive bond's behavior, it is necessary to define the parameters, of the adhesive as well as the adhesive/solid interface, which could be easily and continuously measured. There are currently no methods to deal with such problems, but it is reasonable to write that some of the secondary properties given to adhesives (see section 22.5.2) could act as possible paths for development and innovation.

22.7. Conclusion

From this non-exhaustive study, it can be concluded that the choice of adhesive, the substrate preparation and the polymerization conditions directly affect the performances of adhesive bonds. In the field of the civil engineering, other problems intervene, particularly in terms of durability, which are primarily related to environmental conditions. In addition, an important criterion for developing adhesive bonds in this field involves controlling the adhesive assembly's ageing process, or at least controlling an in situ follow-up of its performance.

This chapter has specified some paths for development, which would certainly constitute solutions for developing adhesive bonding methods in civil engineering for long time durability.

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Chapter 23

Strengthening Concrete Structures by Externally Bonded Composite Materials

23.1. Introduction

The construction industry initiated its industrial transformation by gradually putting stone and wood to one side, and replacing them with modern construction materials, such as concrete and steel. However, if the controlled use of these new materials allowed for an unprecedented development of housing and infrastructures, at the same time it led on to the emergence of new pathologies specific to using these materials (reinforcing steel corrosion, alkali-aggregate reaction in concrete, etc.). These pathologies, which in some cases can cause major structural problems and sometimes necessitate complete demolition of the structure, are particularly prejudicial as the degraded structures may have been built to fulfill an essential function for civil society, which would maybe not cope well with interference (bridge supporting strong traffic, river dam, hospitals, etc.). This leads to major difficulties in managing the construction's heritage. For example, replacing a damaged structure by a new one is not compatible with the potential obligations for service continuity, when there is only one rational location for the construction, and the new construction can only be built when the old one is still working.

The frequent occurrence of this type of scenario, associated with an ageing construction park, to a quick change in road traffic (for example, an increase in the frequency and loads due to heavy trucks) as well as a strong desire from public policies to limit the construction of new road infrastructures, led the civil

Chapter written by Marc QUIERTANT.

engineering community to develop new methods of monitoring and evaluation, but also new ways of repairing and strengthening existing structures.

Among these methods, repair (or strengthening) techniques by externally bonded composite materials have known a large development for many years, due to the high mechanical properties of these materials (in particular immunity to corrosion, excellent strength to weight ratio, longitudinal rigidity, fabric and pultruded plate flexibility allowing conditioning adapted to handling, etc.) as well as their speed and simplicity of installation (little disturbance to traffic during repair on a building site). Although the materials used in strengthening composite systems are relatively expensive, the ease of handling and installation result in reduced construction time when compared with conventional repair techniques. It is now possible to find numerous examples of applications of composite materials for the strengthening of many types of structures, from collections of construction and civil engineering structures such as bridges, supports, reservoirs, collectors, air-cooling towers, oil rigs, or buildings (supporting structures) as well as historic buildings (Figure 23.1).



Figure 23.1. *Strengthening of a masonry arch by externally bonded carbon fiber fabric (source: IIFC)*

Let us note that composite materials may also be used for the construction of new concrete structures. Composite materials bars then ensure internal reinforcement (as opposed to reinforcement by composites bonded to the structure's external faces). These bars, which replace classically implemented steel in reinforced concrete (RC) structures, have the advantage of being corrosion insensitive (expression *stress corrosion* when applied to this material class corresponds to a misuse of language, referring to creep rupture). We will find them mainly in maritime environments and therefore are aggressive to steel. For this type of application, the composite is presented as a direct competitor for stainless steel. Due to their low weight, composites present

fewer disadvantages for handling and storage than steel bars, but must be shaped during their manufacturing phase because they cannot be folded on the building site.

In a more marginal way, internal reinforcement of concrete can be ensured by composite bars in certain structures which shelter equipment sensitive to electromagnetic traces (military buildings, magnetic imagery, radars) due to the electromagnetic neutrality of these materials.

In short, it is possible to distinguish three families of application using composite materials for RC structures:

- repairing damaged structures, where adding composite materials allows us to restore the structure's initial load carrying capacity;
- strengthening an *a priori* non-degraded structure, but where either the initial structural function has been changed (increase of the initially designed service load, creation of openings), with deficiencies in initial design or where mistakes have been made during the construction (miscalculations, coating defects, under-strength concrete, etc.), or even, upgrade structures to satisfy new standards (for example, seismic retrofit of an existing building);
- building of new RC structures whose internal reinforcement is guaranteed (at least partially) by composite material bars.

The first two application cases consist of using composite materials as extra reinforcements (often external) whereas in the last case, the composite material acts as traditional reinforcing bars of RC structures. In the rest of this chapter, the focus is on the first two application families since the use of composite materials for building new structures being dealt with in another chapter.

23.2. Composite materials for repairing and strengthening concrete structures

The class of composite materials used for strengthening civil engineering structures is that of fiber-reinforced polymers (FRPs), also known as *advanced composite materials*. FRPs are materials made from of high-strength fibers embedded into a polymer matrix. Many material combinations can be envisaged to create a FRP. However, for structural strengthening techniques (which will be described in more detail in the following sections) it is mainly thermosetting resins which will be used with carbon (graphite), glass and, to a lesser extent, aramid fibers (the most well-known being Kevlar® fibers, produced by Dupont de Nemours). Due to their impact energy absorbance and damage tolerance properties, aramid are more specifically suitable for strengthening application which aim to increasing impact, explosive or abrasion resistance. Properties of FRP materials mainly depend on the type of fibers, on the fiber volume content and on matrix type. The diversity of

mechanical characteristics of FRP used in construction can be illustrated by the tensile test results, presented in Figure 23.2.

For the majority of FRP used for concrete reinforcing applications, the matrices consist of epoxidic or vinyl ester resins, while epoxies are the most widely used structural adhesive in field applications. These resins have good thermal stability to working temperatures, good chemical resistance, as well as a weak creep rate.

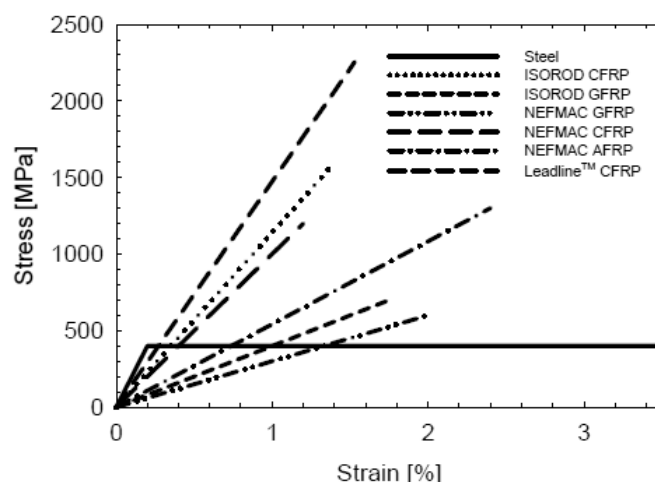


Figure 23.2. Tensile stress-strain curves of FRP materials used for the strengthening of concrete structures (source: ISIS-Canada)

There are various installation procedures for these materials, adapted to the field conditions and the intended applications. For each procedure, specific products have been developed. Among those, four following varieties can be distinguished:

- *Dry fabrics*, whose weaving following the chain and the weft means that the anisotropic characteristics can be adapted to desires uses. They come from simple fiber weaving and only become FRPs after application and curing of a saturating resin. They are bonded on to the concrete substrate by using epoxy resin, with the adhesive resin generally being simultaneously used as a matrix. Dry fabrics are then saturated and cured in-place. This process is described as *wet lay-up* process (or hand lay-up or contact molding). For reinforcement applications, the majority of fabrics are manufactured from using carbon fibers laid out in one direction (“unidirectional” fabrics). However, there are some exceptions, such as TFC® [CST 08] which is a bidirectional carbon fabric, where 70% of the fibers follow the chain direction, and 30% follow the weft direction. In the last step of its production, the

fibers can be covered with a protective material called *sizing*, that will promote the chemical adhesion with the matrix. Moreover, sizing permit to easily wet the fabric by the resins. One of the main advantages of fabrics resides in their flexibility of use, allowing for an application on curved and complex surfaces (Figure 23.3), such as the bond nodes, the curve changes and to wrap beams and columns. In field they are supplied in roll (Figure 23.4a), easy to cut and very light;

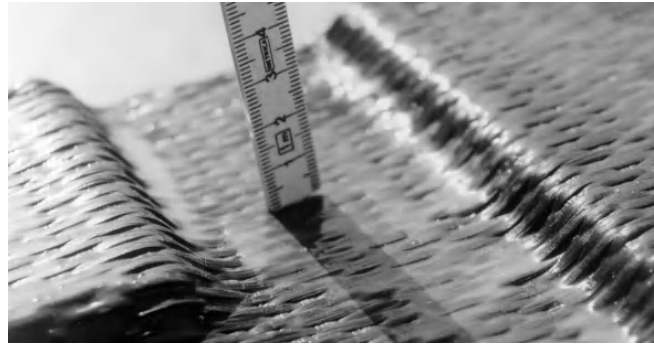


Figure 23.3. Carbon fiber fabric bonded on a complex surface
(source: Freyssinet)

- *pre-pregs (or preimpregnated composites)* are fabrics which are impregnated off-site (with a relatively high fiber volume fraction) with a flexible polymer. They are generally presented as self-adhesive sheets. These products need to be stored in a cold chamber. They are cured in the field by hot polymerization (80 to 150 °C for 1 hour) and with the application of pressure. These installation conditions currently limit their use in civil engineering;

- *pultruded plates (or laminates)* are FRP plates which are more rigid than fabrics. They take their name from the industrial manufacturing process (pultrusion) which consists of impregnating fibers in a resin bath and then curing resin-impregnated fibers in a heated die. The fibers are continuous and aligned along the entire length of the FRP plate. It is then a unidirectional FRP type finished product (dieing is already performed) which only needs, to reinforce the structure, to be bonded to the substrate. The fully automated manufacturing process permit to obtain a component with a high fiber ratio and which is therefore mechanically powerful. The price is competitive and the product is generally sufficiently flexible to be delivered to the site in the form of thin ribbon strips coiled on a roll (Figure 23.4b).

Typically, the volume fraction of fibers in FRPs is about 50-70% for pultruded plates and about 25-35% for FRPs fabricated with the lay-up process. There is no fixed rule as to whether dry fabric or pultruded plates should be used for RC structure strengthening applications. However, usually economical or technical

considerations dictate the choice of one system or the other. For example, plates can only be applied to plane surfaces; therefore fabrics can be used on curved surfaces

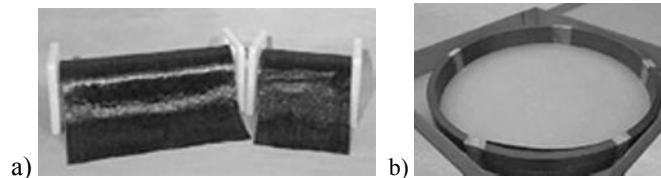


Figure 23.4. Carbon fiber fabric and carbon pultruded plates conditioned in rolls (source: Sika)

– *FRP bars*, which are pultruded materials, whose manufacturing process is derived from offshore platform carbon anchor cables, and carbon cables of cable-stayed bridges. Among those, we can find:

- *tendons* used as an internal and external pre-stressed reinforcement for beams, slabs and bridge decks;

- carbon rods used as reinforcement elements or joins, and whose adhesion to the concrete substrate is achieved by cutting a groove, into the surface of the element which needs to be strengthened; FRP rods are then inserted into the groove along with a structural adhesive grout. Such technique is referred to as *near surface mounting*;

- carbon fiber reinforcement bars (Figure 23.5) which are installed in a similar way to steel bars. The bond between FRP reinforcing bars and surrounding concrete can be increased with a surface treatment applied to the FRP reinforcing bar during manufacturing.

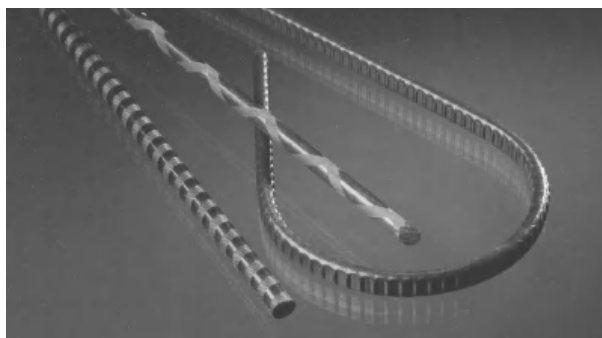


Figure 23.5. Examples of carbon FRP reinforcing bars (source: ISIS-Canada)

23.3. History and background of structural strengthening techniques by externally bonded composites

For more than fifty years, car and aeronautic industries have manufactured specific “all-FRP” mechanical parts and structures but Japan was a pioneering country in applying FRP in civil infrastructures. First, FRP materials were used to replace conventional steel bars and tendons for concrete structures in the early 1980s in Japan [ZHI 07]. It should be mentioned here that at this initial stage, external bonding of FRP sheets in strengthening fields were limited. From 1989 and 1990 onwards, this technique was applied for repairing cracks found in certain refineries, belonging to a company which was one of the primary carbon fiber manufacturers. From 1992 onwards, the first bridge reinforcements using carbon fiber fabrics were achieved. However, the number of applications increased steadily for seismic retrofit purpose after the Great Hanshin Earthquake in 1995. In 1997 Japan had multiple structures having been strengthened by bonded carbon fiber fabrics (generally pre-pregs), such as tunnels, chimneys, electric poles, electricity factories, stations, water reservoirs, hangars, etc.).

In Europe, FRP systems were developed as alternates to steel plate bonding. It is in Switzerland, as a result of precursory work by the EMPA (*Swiss Federal Laboratories for Material Testing and Research*, for construction, arts and trades in Dübendorf) that first structural reinforcements were achieved by using bonded carbon fiber-reinforced polymer (CFRP) systems [MEI 95].

Using these “new generation” materials only really developed in France in civil engineering domains at the end of the 1990s, following the experimental repair work on a highway overpass, where some cracked beams were repaired by bonded carbon fiber based fabrics [FRE 97]. This application gave way to the label IVOR in 1997 (*innovations validées sur ouvrages de référence*/French award for innovations on major structures) for this process [IVO 97].

Essentially used at the initial stages to ensure the serviceability of structural elements, these processes have extended their application scope to the improvement of the behavior of structures at ultimate state, within a logical framework for ensuring the safety of users with respect to extreme or accidental conditions (earthquakes, shocks, explosions).

The process has never stopped progressing on the technical front and, benefiting from reduced costs of FRP, never stopped winning over parts of the market in the domain of repairing concrete structures. From this, it has established recognition in international scientific and technical communities, as well as in the civil engineering profession, as some of the many publications of technical guides and design codes can attest to [ACI 99, ACI 08, AFG 07, EBR 01, JSC 97,] as well as works intended

for training future users [BIS 06a, BIS 06b, BIS 06c]. However, depending on the country, the technique meets different acceptance. It is estimated that a surface of one million of square meters of FRP are installed each year in Japan, for structural reinforcement purpose when only 40,000 square meters of carbon fiber fabrics are used in France.

23.4. Mechanics of externally bonded FRP

In construction, a structure can be defined as a set of elements (or members), qualified as structural, when they balance a load. The function of a structural element generally influences its geometry (for example: walls, beams, ties, columns, slabs, etc.). Among structural elements where bonded FRP strengthening is commonly performed, and by referring only to mechanical function, it is possible to distinguish two main groups (other groups exist): the elements subjected to flexural load (mainly beams and slabs) and those subjected to compressive load, like columns typically used to transmit the weight of the structure above to other elements below. For each of the two groups of element, a specific strengthening scheme must be followed, as will be described in the following sections. Estimating the quantities of FRP necessary, as well as designing particular points associated with the selected type of strengthening systems (such as the anchorage length), should be done in accordance with existing recommendations or design codes (for example [AFG 07]) and are not detailed in this chapter.

It is not recommended to rely on externally bonded FRP systems to resist compressive stresses, due to the risk of microbuckling of fibers or buckling of FRP itself when debonded from the substrate. Then, in the following examples, bonded FRP strengthening systems will be installed as parallel as practically possible to the direction of tensile stresses.

23.4.1. Flexural strengthening

A beam or a slab is a structural element which deforms by bending when a transverse load is applied on it (Figure 23.6). The objective of this chapter is not to describe precisely mechanical behavior of elements under flexure, but to clarify the role of FRP when strengthening such elements. It is then necessary to point out that in a horizontal element supported at the ends and loaded downwards, the over-side of the element is compressed while the underside is stretched (Figure 23.6a). Considering that concrete exhibits a much higher compressive strength than tensile strength, bending of a concrete element under service load systematically results of the cracks initiation and growth at the tension face (Figure 23.6b). The design of flexural strengthening is then usually addressed at controlling the crack growth.

Consequently, in classical RC elements, steel reinforcing bars (rebars) are embedded in concrete zones which are known to undergo tension strains. The steel bars, aligned in the direction of tensile stresses (see the case of a beam in Figure 23.7a), are more rigid than concrete and then absorb an important part of tensile forces.

⌞ Compressive Stress

↔ Tensile Stress

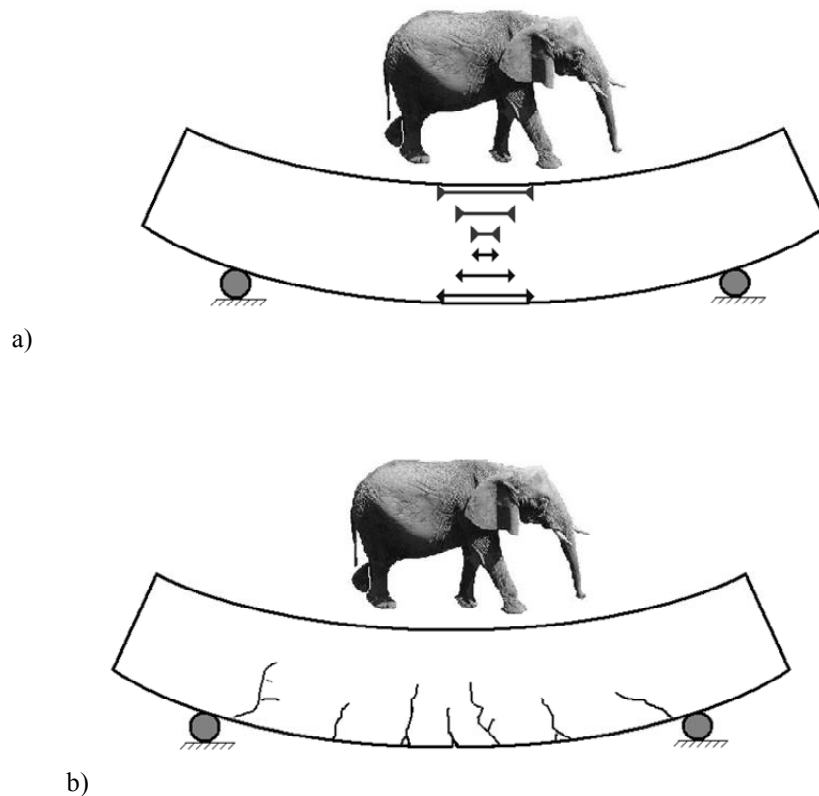


Figure 23.6. Bending of a beam: a) stress distribution at mid-span cross-section; b) crack pattern in tensile zone

By ageing under aggressive environments, the rebars corrode and the effective area of the steel reinforcement decreases leading to a loss of load carrying capacity, stiffness and finally service life of the structure. As the steel corrosion progresses, the premature failure of the whole structure becomes possible, due to the risk of yielding and rupture of steel reinforcement subject to increasing tension stress. It is then

necessary to carry out a rehabilitation permitting to counterbalance the loss of steel reinforcement by steel plate bonding, external post-tensioning or by bonded FRP. As discussed, the later repair material provides efficiency and ease of application. It should be mentioned that various pathologies, others than those relating to steel corrosion, may damage a RC structure (alkali-aggregate reaction-induced expansion of concrete for example). All this pathologies and their causes have to be identified and repaired before carrying out structural strengthening operations.

The FRP reinforcing material used as additional tensile reinforcement may be bonded to either the concrete surface or within slots cut in the cover concrete. Then, FRP reinforcement experiments tensile stress to resist to external loading. Tensile stress is transmitted by the concrete substrate through the shear load path provided by the adhesive. As the tensile and shear strength of the adhesive is usually higher than the tensile and shear strength of concrete, failure will normally occur in the concrete. Consequently, it is obvious that FRP systems should not be used when the concrete substrate exhibits poor shear strength.

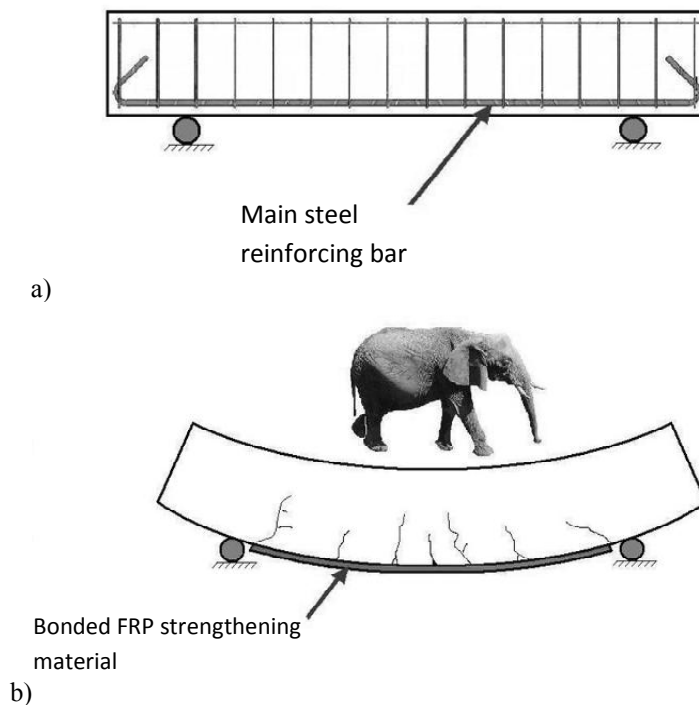


Figure 23.7. Similar principle for the flexural strengthening: a) internal reinforcement, with main rebars on the lower part; b) FRP strengthening material bonded on the lower face

One conventional technique for repairing or strengthening RC structural element consists of externally bonding a steel plate on its tensile face [THE 90]. Bonding is achieved with an epoxy resin that cures in field due to a chemical reaction in two component bonding agent. This technique has its origin in South Africa in the mid-1960s [DUS 74, CAR 03]. The plate thickness varies between 2 and 5 mm. They can be superposed two times. Steel plates are often heavy and an external pressure needs to be exerted during the curing. Consequently, installation of steel plates requires the use of heavy equipment. However, due to the risk of corrosion of steel plates (Figure 23.8.) leading to the bond deterioration, difficulties to apply steel plates to curved surfaces, handling problems, difficulties of on-site installation, relatively important added dead load on the structure and susceptibility to fatigue, the technique of structural strengthening by externally bonded steel plates was not completely satisfactory.

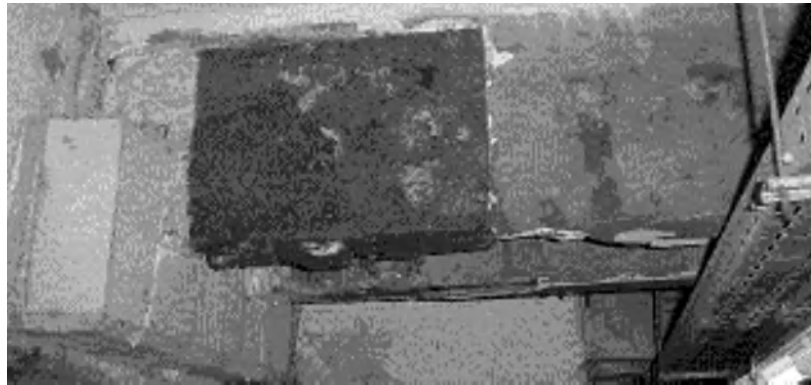


Figure 23.8. *Corrosion of a bonded steel plate (source: Sika)*

Due to the disadvantages described above, replacing the steel plates with FRP strips for external strengthening has rapidly emerged as a particularly adapted solution. FRPs represent a relevant alternative because of their high mechanical properties, their ease of installation and their excellent fatigue and corrosion resistance. Moreover, they are lightweight and particularly flexible, which greatly facilitates their installation (Figure 23.9) and reduce the labor and equipment costs. Although FRP materials are more expensive than steel, installation costs of FRP systems are often lower. In addition, installation of FRP systems generally induce limited disruption to traffic.

Mostly, CFRP systems are used as externally bonded reinforcement for structural strengthening. Nevertheless, it should be mentioned that glass fiber-based FRP (GFRP) are less expensive and are consequently widely used in structural

applications, but most of the time as internal reinforcement. However, there are disadvantages associated with glass fibers strengthening. Glass fibers are less stiff than carbon fibers and damage may be caused to GFRP by the intrusion of moisture into the resin. Moreover, glass fibers are susceptible to failure modes like creep rupture and fatigue failure. GFRP comes in two types: E-glass and AR-glass. E-glass is the most common form of glass fiber used in GFRP but are attacked by the alkali in fresh concrete. AR-glass is alkali resistant and then overcomes this difficulty.

While aramid fibers have stiffness that is intermediate between glass and carbon, they are very occasionally used due to their sensitivity to creep and their propensity for moisture absorption. They exhibit relatively low shear strength and are particularly sensitive to ultraviolet radiation.



Figure 23.9. On-site girder strengthening by externally bonded FRP plate (source: Sika)

23.4.2. Shear strengthening

During flexural loading, a beam experiences shear stress parallel to the applied load plus complementary shear stress on planes perpendicular to the load direction. This can lead to produce sliding failure of the concrete along diagonal planes roughly inclined at an angle of 45 degrees. The shear cracks generally initiate near the supports and extend upward (Figure 23.10). To prevent shear failure, conventional (internal) steel reinforcement of RC elements includes transverse reinforcements called stirrups (Figure 23.11).

However, when these steel reinforcement are deficient (corroded or under-designed) it is possible, according to a similar principle to the one described for flexural strengthening, to increase the shear strength of the RC member with FRP laminates bonded on the sides of the member and oriented transversely to the section (Figures 23.11 and 23.12). The fibers mostly work under tension and then, resist shear forces and shear cracks opening. Three types of shear strengthening schemes can be used: completely wrapping of the FRP system around the section, bonding FRP on the two sides of the member or using U-jacketed laminate bands (Figure 23.11). The later solution, due to its ease of installation and efficiency is the most commonly applied technique.

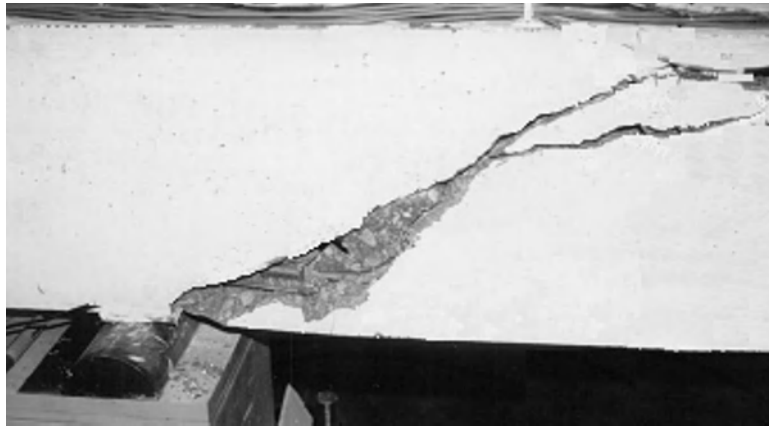


Figure 23.10. *Shear failure of a beam (source: LCPC)*

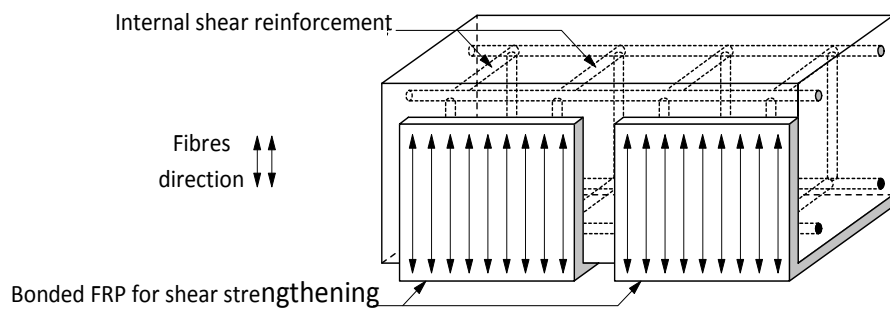


Figure 23.11. *Illustration of the shear strengthening of a beam by bonded FRP (internal reinforcement represented by dashed lines)*



Figure 23.12. *Example of a shear strengthening of a beam by bonded U-jacketed FRP (VSL-France)*

23.4.3. Strengthening of compression elements

The corrosion of steel rebars and concrete deterioration lead to, as for bended elements, a loss in the load-carrying capacity of RC columns (Figure 23.13a). One technique to restore or increase this initial capacity consists of confining the column in a composite jacket whose fibers are orientated transverse to the longitudinal column's axis (Figure 23.13b).

In situ impregnation of the fabric bonded around the compression element forms the FRP jacket. Tensile strain of hoop fibers resists to the lateral expansion of the compression member caused by Poisson's effect (Figure 23.14). By restraining transversal strain of the column, the composite jacket generates a lateral pressure that increases as the lateral expansion of concrete increases under axial load. This lateral pressure is called *confining pressure*. The confining pressure leads to increase the axial compression strength and stiffness of the column.

Moreover, this technique favorably influences the structural safety of the whole structure as confinement results in increased ductility of the columns. Equilibrium of forces in a half-section of the column allows calculating the confining pressure generated by the composite jacket [BIS 06b] and then resulting strength enhancement.



Figure 23.13. Rehabilitation of columns by wrapping: a) example of severely deteriorated column, (source: ISIS-Canada); b) application of FRP sheets using the wet lay-up technique, (source: LCPC)

Installation of FRP jacket must be carried out by following some particular construction details, including:

- sufficient overlap that is required to continuously transfer the tensile stress of hoop fibers all around the external jacket. The overlapping must be applied over each rings of the jacket when the wrapping is achieved by a series of discontinuous rings

(Figure 23.15c), or by a additional transverse FRP layers bonded at the column ends when the wrapping is achieved by a continuous spiral (Figure 23.13b);

– preparation of the corners of rectangular cross sections that have to be rounded to a minimum radius (about 15 to 25 mm depending on the specifications [EBR 01]) to prevent premature failure due to stress concentration.

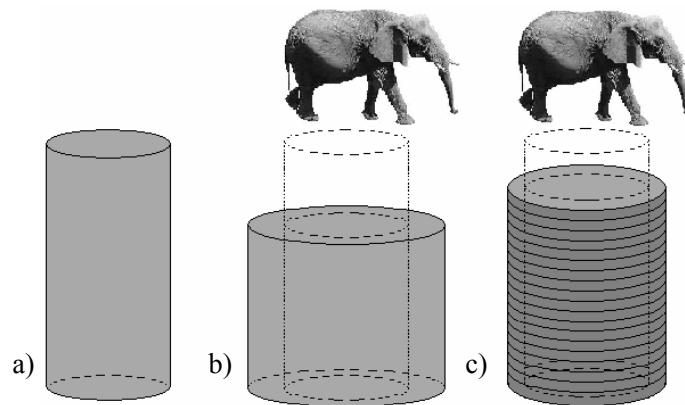


Figure 23.14. Illustration of the confining action of FRP jacket: a) unloaded column; b) column under compressive loading; c) column subjected to a similar compressive loading but confined with a FRP jacket

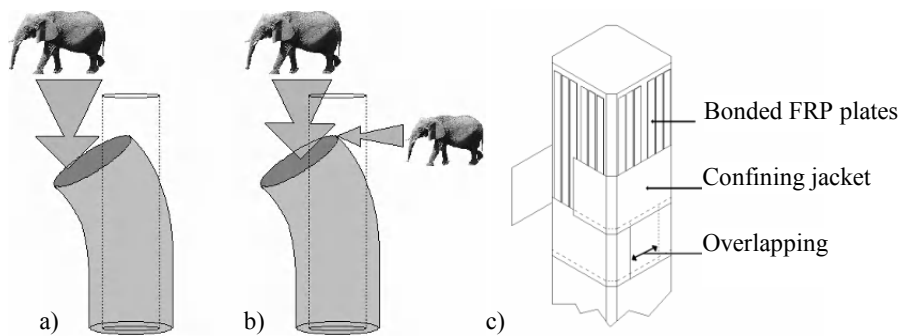


Figure 23.15. Columns experimenting combined axial-flexural loading and corresponding external strengthening: a) eccentrically loaded column; b) column submitted to axial and flexural loading; c) FRP strengthening scheme adapted to combined axial-flexural loading

For jacketed members, a perfect bonding between FRP and the concrete substrate is not a predominant parameter while providing sufficient overlap is a critical construction detail that can govern the failure of the jacket by debonding of

the overlapped laminates if not long enough. Then, unlike for flexural strengthening application, the condition and strength of concrete substrate do not need to be checked when using a jacket. Tests conducted at the technical University of Gent [CLE 05] on wrapped columns where only the FRP lap zone was bonded gave identical results to those obtained with full-surface bonding. However, even if such partially unbonded schemes, as well as pre-stressed FRP confinements were successfully tested [CLE 05], real field applications are not common.

In practice, concrete columns perfectly axially compressed rarely occur. The eccentricity of the loading generates a combined flexure-compression load (Figure 23.15a). Consequently, the column deflects laterally. Such combined loading can also result from the addition of a concentrically loading with a flexural force (Figure 23.15b). Rectangular columns subjected to flexural moment in addition to axial loading are commonly referred to as *beam-columns*. The bending moment can also result from heavy vehicle impact or from seismic activity. For this later, it is important to keep in mind that seismic action is directly proportional to the acceleration imposed on the structure as well as its mass. Due to their light weight, FRP materials allow retrofitting columns with a very little increase in mass and are then highly suitable for seismic rehabilitation. Then, for the strengthening of columns that experiment bending moment, design departments now propose to associate a flexural strengthening, achieved by axially bonded FRP, coupled with a confinement by wrapping (Figure 23.15c).

23.5. Installation of FRP strengthening systems

The retrofitting of RC elements by bonded FRPs, is generally accomplished when severe degradations are observed. Before proceeding to the bonding of strengthening materials, it is then necessary to repair damaged concrete, inappropriate concrete substrate or corroded steel and to address all causes of these problems. All necessary repair and protection operations have to be carried out before structural strengthening by externally bonded composites. Then, FRP strengthening system is applied on sound substrate in accordance with the system manufacturer specifications. Although procedures for installing FRP systems may differ slightly between systems, the following is a general outline of main steps in externally-bonded FRP strengthening application. In all cases, the FRP system has to be installed by an approved contractor.

23.5.1. Control of the strength of the concrete substrate

As mentioned above, the existing concrete substrate strength is a key parameter to allow FRP strengthening to be fully functional. Consequently, the condition of the

concrete substrate should be verified. As shearing strength is very difficult to measure in field, the capacity of the concrete is then usually evaluated by testing its tensile strength by pull-off tests. The pull-off test is performed by bonding a loading fixture (generally a steel disc) on the surface to be tested. Then a testing apparatus is attached to the loading fixture and apply a tensile force normal to the surface to be tested up to failure (Figure 23.16). The pull-off test must be conducted in accordance with existing standards (for example [AST 04] or [AFN 99]).

It is generally accepted that a minimum substrate tensile strength of 1.5-2 MPa is required to efficiently strengthen a concrete structure by externally bonded FRP systems.

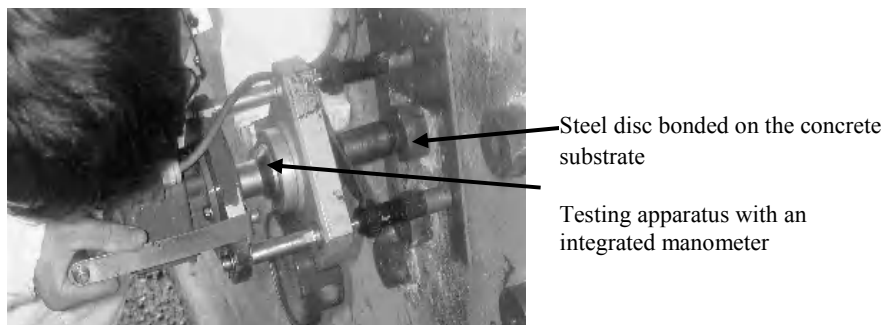


Figure 23.16. *Pull-off test*

23.5.2. Surface preparation

The concrete surfaces to which the FRP system is to be applied should be flat or convex to promote proper loading of the FRP material. If surface leveling operations are required, involving concrete removing or leveling by filling materials, these operations have to be carried out in accordance with national standards (for example [AFN 93a] and [ACI 04]). Pultruded plates are generally best suited for plane surfaces, whereas sheets or fabrics are more flexible and can be applied to complex surfaces (see Figure 23.3).

An other aspect of surface preparation deals with the necessity of profiling the surface to a specific roughness to promote optimal bonding. Surface preparation can be accomplished using abrasive or water-blasting techniques. After completion of surface preparation, the concrete is freshly-exposed, sound, dry, exposes a chemically active surface and exhibits the desired roughened texture. Then the surface has to be cleaned before FRP installation.

23.5.3. FRP installation

Bonding is generally realized through polymerization of a two-part cold cured adhesive. The adhesive is usually epoxy-based. Before bonding the strengthening material, preliminary operations have to be completed:

- marking the contours of the areas to be reinforced on the concrete substrate and specifying fiber direction;
- cutting the fabric or plates to the desired length;
- cleaning the pre-cured plates with acetone using a white rag;
- preparing the resin, usually by mixing the two adhesive components (uncured resin and hardener) just before application (installation must be achieved within the specified pot-life of the resin). Uncured resin and hardener are generally supplied as factory proportioned kits comprising the correct quantities of each component.

Certain field conditions are required:

- ambient temperature must be within the interval recommended by the FRP system manufacturer (typically not less than 5 - 10 °C nor above 35 - 50°C);
- temperature and moisture of the concrete surface should be within the limits specified by FRP system manufacturer;

Two-step bonding is the preferred method for most structural bonding situations. Bonding operations start by applying uniformly a first layer of adhesive onto the concrete substrate. This first step is known as *undercoating*. The first layer is generally applied with a roller brush when using a low viscosity resin (in the case of the wet lay-up process) or with a spatula (when bonding plates). The second step of the bonding depends on the FRP system:

For pre-cured plates, a layer of adhesive is also applied on the FRP plate with a spatula. The adhesive coated surface of the plate is then placed on the coated concrete surface. The FRP plate is pressed against the substrate using a rubber roller until some adhesive is forced out on both sides of the plate. The pressure is applied going from the centre to the outer to ensure that no voids are formed.

For dry fabrics, the resin ensure both bonding and impregnation. The dry fabric is applied onto the coated concrete surface and is pressed with a roller brush to promote a partial impregnation and prevent voids introduction (Figure 23.17a). Then, supplementary adhesive layer, called *saturant layer*, is added on the top of the fabric with a brush to complete the impregnation (Figure 23.17b). This process is called *overcoating*. The heaviest fabrics are saturated in a resin bath or in a saturator machine that control the resin rate, before being laid to the concrete surface.

Thanks to the thixotropic properties of the adhesive and the lightness of the strengthening material, the installation of FRP systems does not require a prolonged application of a pressure against the strip (or sheet) to hold the strengthening material and substrate to be bonded together until the adhesive curing is completed.

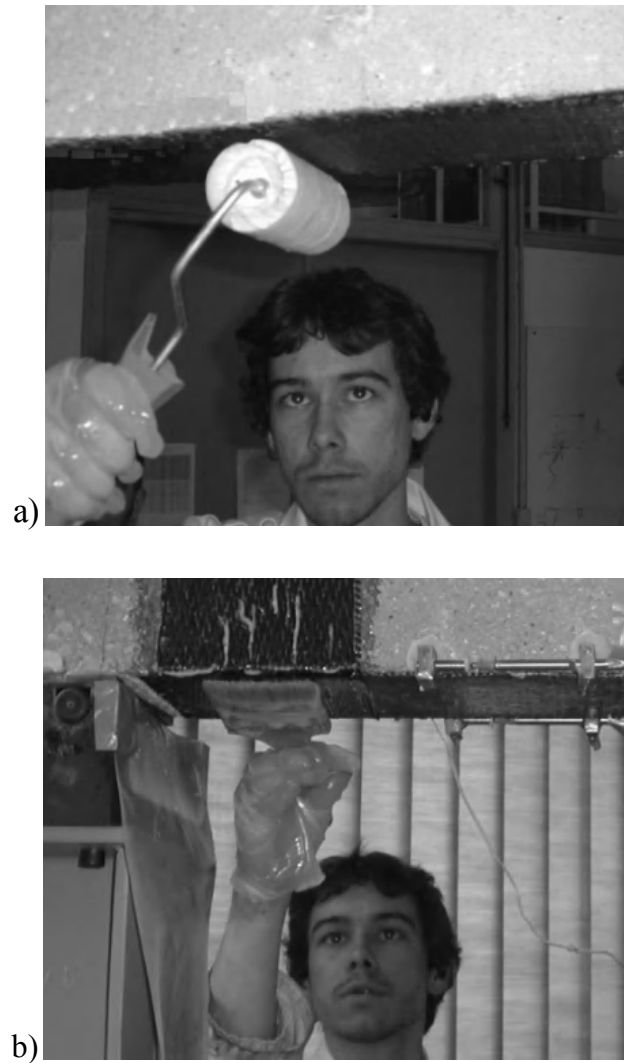


Figure 23.17. *Wet lay-up process for bonding: (a) pressing of the fabric; (b) application of the saturant layer*

It is possible to install multiple layers of FRP bonded together, to achieve the reinforcement ratio allowing the strengthened structural member to carry the design loads. For FRP systems using precured plates, an adhesive layer must be applied on the outer face of the in-place plate and an other adhesive layer must be applied on the plate to be installed. Then, the two plates are bonded together. If the wet-lay up process is used, the uncured saturant layer of the previous (in-place) fabric also serves as the adhesive for the next fabric layer. If saturant layer is cured before bonding of the new fabric, outer surface of the cured layer must be lightly abraded. Then the new fabric must be installed in a similar way as it was described for bonding it on concrete substrate.

During the curing of the resin, it is necessary to limit the vibrations on the concrete/resin/FRP interface [QUI 07]. Sometimes, special measures have to be taken to observe this precaution. For example, if the structure to be strengthened is a bridge, FRP system installation contractors and manufacturers recommended that the bridge remains closed during FRP system installation and epoxy-curing period [REE 05].

A minimal bonded distance is required to transfer the designed force from the concrete substrate to the FRP. This *development length* is a function of the mechanical characteristics of the substrate, of the FRP and of the adhesive. Methods of calculation of the development length can be found in [ACI 08] or [AFG 07]. If the required development length is not possible to provide, various mechanical anchoring systems can be used at termination points (see for example Figure 23.18). Such anchoring systems can balance shear stress concentration near the plate end and then prevent premature FRP plate-end shear failure [EBR 01].

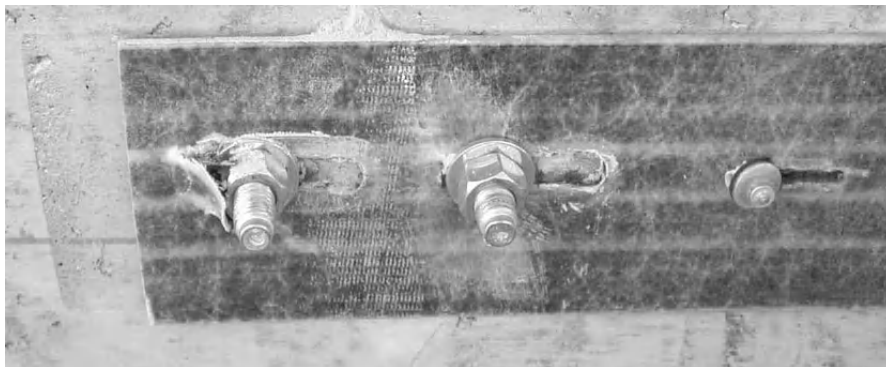


Figure 23.18. Mechanical end anchorage system of a bonded laminate plate (source: IIFC)

It is recommended to bond additional FRP sample in an area of the RC structure where strengthening is not needed. Called *witness panel*, this small strengthened area is installed in a similar way (same system and same procedure) and at the same time as the actual strengthening. The panel can be tested by pull-off test, just after the complete cure of the resin to check mechanical properties of the FRP system, including substrate strength. The tests could possibly be repeated each time the resin is changed for evaluation and acceptance of resin batches. If the panel system is exposed to the same environmental conditions as those of the actual strengthening, pull-off tests can be carried out at different period for durability evaluation of the FRP system.

Many FRP systems are impermeable to moisture. Then, FRP reinforcement that completely encases a RC member may prevent the migration of moisture. For structures where water moisture vapor transmission capacity must be preserved, it is then recommended to limit the total area of bonded FRP.

23.5.4. Finishing or protective coats

For esthetic reasons or to protect from environmental conditions such as UV exposure, salt or water, a *finishing layer* can be applied on the exposed surface of the FRP system. This finishing layer can be a protective coating, a shot-concrete layer or painting. External coatings made of fire resistant material can also be used for structures requiring fire endurance. In all cases, the finishing layer should be compatible with the FRP strengthening system and approved by the FRP system manufacturer.

23.6. Conclusion. Future of strengthening concrete structures by externally bonded composite materials

As previously discussed, FRP materials have demonstrated strong promise in civil engineering applications. They are increasingly used as strengthening materials for RC structures. Worldwide field applications are numerous and varied. However, new resins and new fibers have already been formulated and tested in private and university laboratories (nanostructured adhesives, mineral or ceramic fibers, 3D hybrid fabrics, geopolymer composites, etc.). Those are more resistant, more rigid, less sensitive to aggressive environments, more durable or less expensive.

These recent developments can largely increase the field of applications of FRP strengthening systems, as regularly described in scientific literature: underwater strengthening method (Figure 23.19), reinforcement of elements subjected to high

temperatures, more aggressive pollutants or more severe mechanical loading, prestressing technique with FRP materials, etc.

The rising advantages of FRP strengthening materials associated with the worldwide infrastructure's increasing decay and ever-increasing traffic loads guarantee that recent acceptance in the characteristically conservative infrastructure construction industry is only the beginning of a very promising development.



Figure 23.19. Underwater bonding of a glass fiber fabric (source: IIFC)

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Chapter 24

Durability of FRP Strengthened Concrete Specimens under Accelerated Ageing

In this study, FRP strengthened concrete specimens were submitted to accelerated ageing conditions (40°C and 95% R.H.) and the time evolution of the adhesive strength was monitored using either the pull-off test or a single lap shear test. On the other hand, microstructural evolutions of the polymer adhesive due to hydrothermal ageing were investigated by DSC analyses (differential scanning calorimetry) and tensile tests.

On the basis of these results, effects of accelerated ageing on the adhesive bond properties are discussed, and the influence of the testing method (pull-of and shear tests) on observed evolutions is also considered.

24.1. Introduction

Externally bonded FRP (fiber reinforced polymer) composites are commonly used worldwide for reinforcing and repairing civil infrastructures. In France, these strengthening systems are particularly applied to the rehabilitation and upgrading of deficient structures [LUY 99, HAM 02]. If the effectiveness of this technique is now widely accepted by experts, the long-term durability of such repairs under service conditions is still a matter of investigation.

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Several authors have reported a substantial decrease in the adhesive bond strength at the concrete/FRP interface, when subjected to various accelerated ageing conditions, such as freeze/thaw cycles, immersion in saline and alkaline solutions, or exposure to wet environments [GAN 06], [GRA 05], [KAR 03], [KAR 07], [MAR 08]. The most noxious effect was often obtained by exposure to hot and humid air [GRA 05], [MAR 08].

In this study, testing specimens reinforced by bonded carbon fiber sheets (CFS), or by pultruded composite plates (CFRP), were subjected to accelerated ageing in humid air at 40°C and 95% relative humidity. Changes in the adhesive bond strength during ageing, were evaluated by performing mechanical characterizations using both the pull-off and single lap shear tests. In a similar way, micro-structural changes of the epoxy adhesive induced by ageing were investigated by differential scanning calorimetry (DSC) and tensile tests.

On the basis of these experimental results, the impact of hydrothermal ageing on the concrete/composite adhesive bond is highlighted. The influence of various parameters, such as the concrete surface preparation, the presence of a carbonated concrete layer, or the type of test used to characterize the interface (pull-off/shear tests) is also discussed.

24.2. Experimental results and discussions

24.2.1. *First set of experiments: Investigation on FRP strengthened concrete slabs using the pull-off test*

In the framework of a first experimental campaign, FRP reinforced concrete slabs were prepared in the following way:

- slabs with a dimension of $30 \times 30 \times 5 \text{ cm}^3$ were prepared from a CEM I Portland cement and silico-calcareous aggregates, by using a water/cement mixing ratio of 0.5. After a period of 28 days to reach maturity, the final material had a resistance under compression of 35 MPa;
- the slabs were then divided into two series, whose surface was either treated by sanding or by abrasion (using a rotary diamond bur tool);
- some slabs were then carbonated by exposure to CO_2 at 20°C and 65% relative humidity for one month, so as to obtain a superficial carbonated layer, of thickness 10 mm;
- each slab was then reinforced by one of the two most used composite systems available on the market (Figures 24.1a and 24.1b): half of the specimens was strengthened by bonded carbon fiber sheets (CFS), the other half by pultruded CFRP

plates, using ply in each case. Bi-component epoxy adhesives specific to the two processes were used for bonding. Implementation was carried-out by experienced staff from FRP supplier companies.

Finally, eight types of concrete/composite bonded interfaces were obtained, as listed in Table 24.1.

Type of substrate	Type of reinforcement	
	Carbon fiber sheet (CFS)	CFRP plate
Sanded concrete	X	X
Ground concrete	X	X
Sanded/carbonated concrete	X	X
Ground/carbonated concrete	X	X

Table 24.1. *Preparing the 8 types of test specimens. Interface definitions*

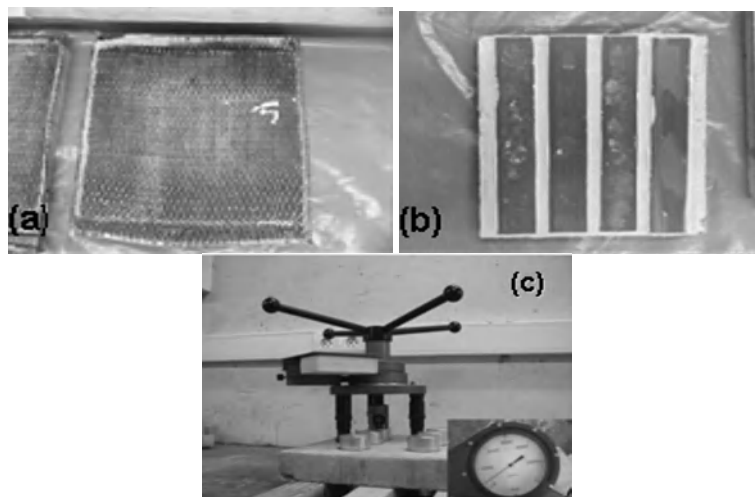


Figure 24.1. *Concrete slabs reinforced by carbon fiber sheets (a) or by composite plates (b), and dynamometric device used for the pull-off tests (c)*

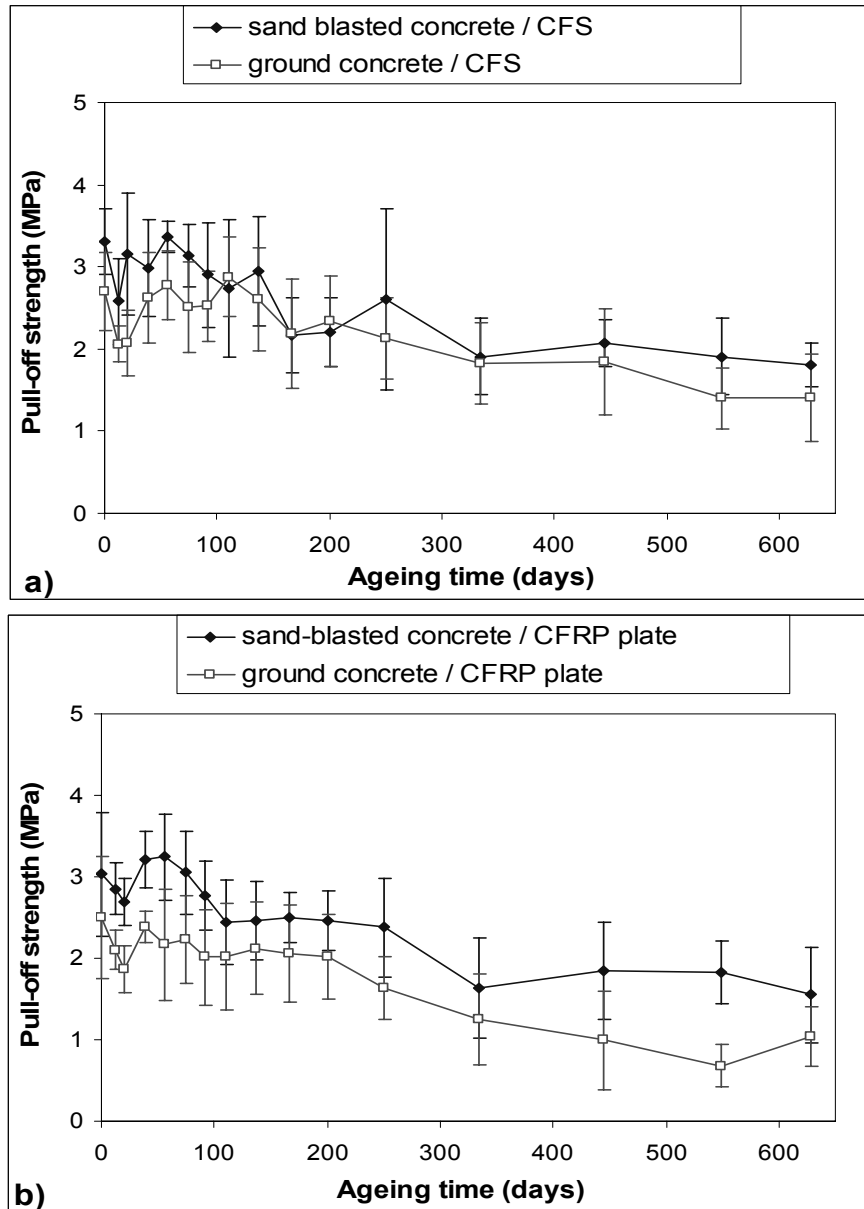


Figure 24.2. Pull-off strength versus ageing time for CFS (a) or CFRP plates (b) bonded on non-carbonated concrete slabs

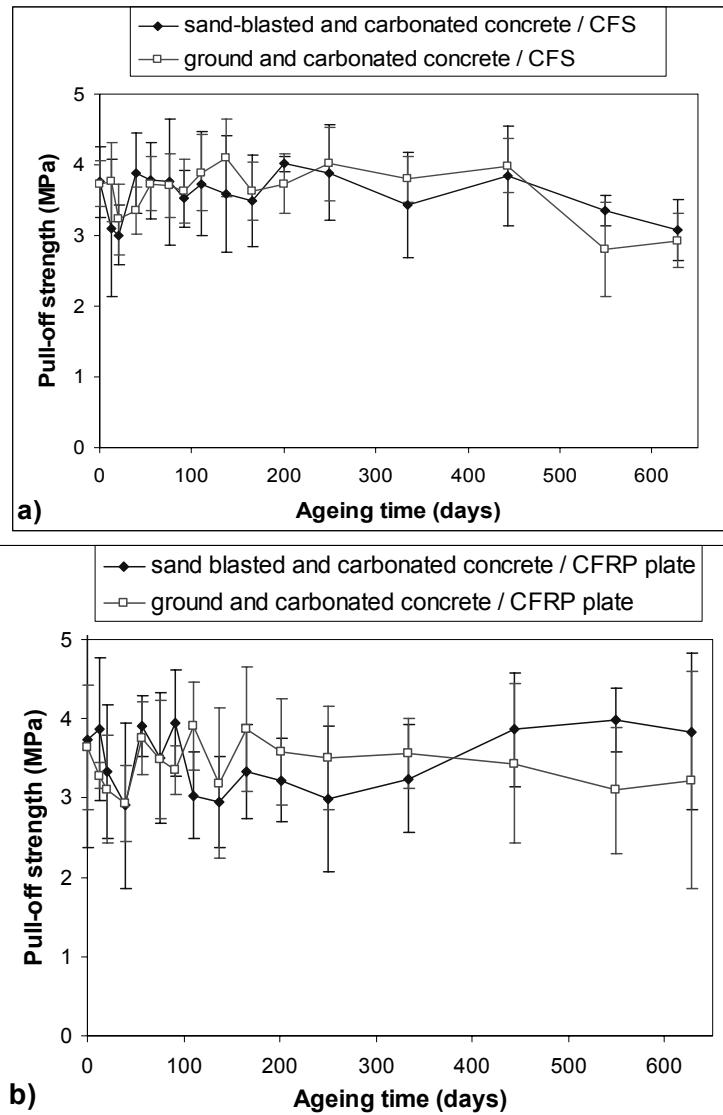


Figure 24.3. Pull-off strength versus ageing time for CFS (a) or CFRP plates (b) bonded on carbonated concrete slabs

All test specimens were then stored in a climatic room with controlled temperature and hygrometry, at 40°C and 98% relative humidity. Mechanical characterizations were then carried out by a pull-off test, according to ASTM D4541

standard [AST 02], and this was performed in regular time intervals until a final ageing period of 628 days. Figure 24.1c shows a photograph of the dynamometric device used to apply the tension force.

Apparent changes in adhesive bond strengths are presented in Figures 24.2a and 24.2b for the CFS and CFRP plate systems bonded on the non carbonated concrete substrates while changes related to the same systems bonded on carbonated substrates are illustrated on Figures 24.3a and 24.3b. The values mentioned correspond to the averages of 6 repeated pull-off tests, and standard deviations are also indicated by error bars.

The histogram presented in Figure 24.4 allows us to compare the pull-off strengths in the original state and after 628 days of ageing for the 8 model interfaces.

A wide dispersion has been observed for strength values, which is an intrinsic characteristic of pull-off tests carried out on concrete specimens. Nevertheless, several trends should be flagged up because they are verified throughout the entire ageing campaign.

With regard to the testing specimens prepared from non-carbonated slabs (Figures 24.2a, 24.2b and 24.4), the following remarks may be put forward:

- The surface preparation of concrete seems to have a slight influence on the resistance values of the bonded interfaces: overall, specimens prepared by sanding give higher strength levels than those obtained for ground concrete surfaces. This effect may be attributed to a better cohesion of the superficial concrete layer or to the roughness of sanded substrates which promote the penetration of the epoxy adhesive, hence enhancing adherence by mechanical anchoring [TOU 01]. In addition, abrasion treatment generally leads to fracture patterns which are smoother than for sanding, which is consistent with the previous comments.

- Accelerated ageing induces a progressive and significant decrease in the pull-off strength values. This phenomenon is particularly noticeable for the “ground concrete + CFRP plate” interface which manifests a loss of strength close to 58% after 628 days of ageing (Figure 24.4.). This result suggests that the adhesive bond of the CFRP plate system may be more sensitive to warm and wet environments than that of the CFS system, which agrees well with the previous work by [GRA 05].

- Whereas, the fracture mode is initially cohesive in the concrete substrate, an increasing number of mixed (concrete substrate and epoxy joint) or even adhesive failures is observed during ageing, as illustrated in Figure 24.5. This is also consistent with a substantial degradation of the adhesive bond or to a decrease in the properties of the polymer joint due to humid ageing.

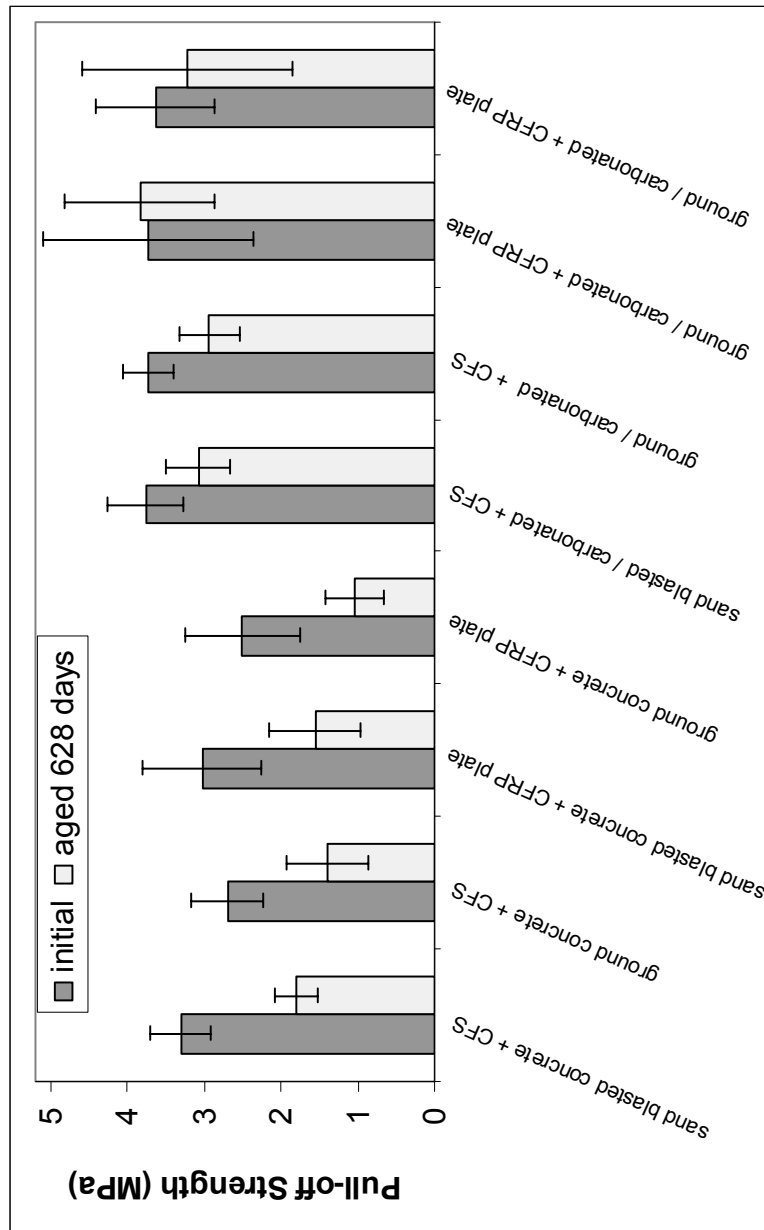


Figure 24.4. Histogram showing the pull-off strength values in the original state and after 628 days of accelerated ageing for the different model interfaces

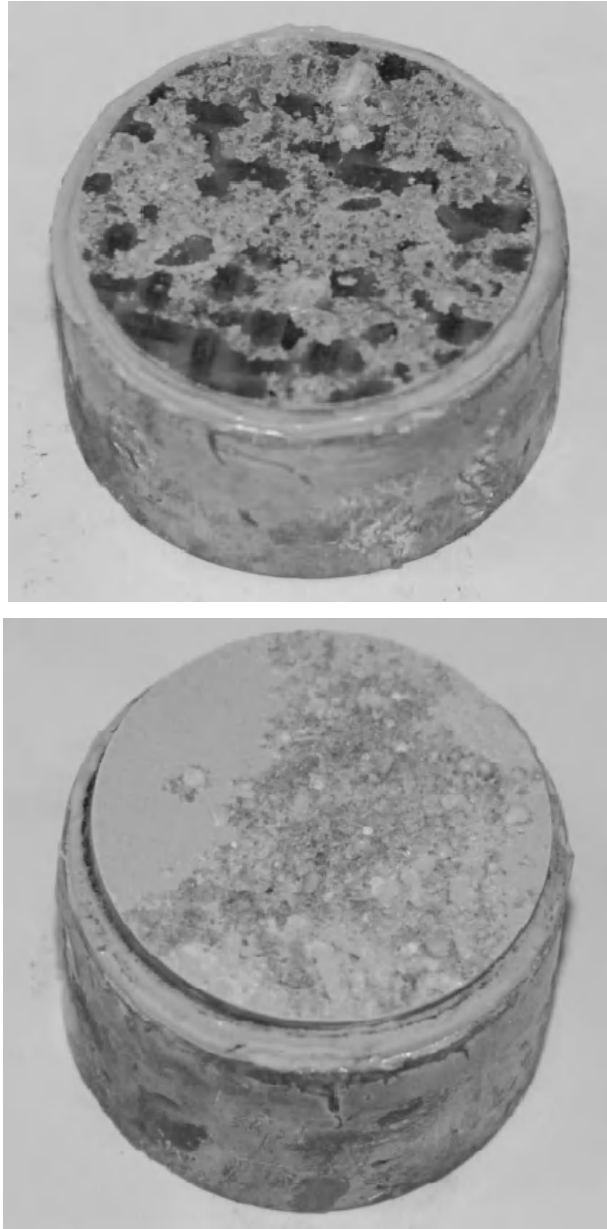


Figure 24.5. *Examples of mixed failure modes observed for model concrete/FRP interfaces subjected to humid ageing (characterization by pull-off test)*

Regarding the test bodies prepared from carbonated concrete slabs (Figures 24.3a, 24.3b and 24.4), the following points are raised:

- Values of the pull-off strength are overall higher than those obtained for the specimens prepared from non-carbonated slabs, in the original state and after ageing as well. This effect can be simply explained by the fact that carbonation tends to close up the porosity of concrete, hence the improvement in the mechanical properties of the superficial concrete layer.
- As the carbonation treatment was carried out *after* the sanding or abrasion treatments, the influence of these surface preparations is no longer discernible in this case.
- The most interesting feature here, is that the reduction in strength induced by wet ageing is rather limited ($< 20\%$) in regard to what has previously been observed for test bodies prepared from non-carbonated slabs (Figure 24.4.). Let us even underline that no variation is observed for the “sanded/carbonated concrete + CFRP plate” interface. This result suggests that the main degradation process involves moisture diffusion from the surface of the concrete substrate towards the bonded interface and the polymer joint. The limited changes observed for adhesive bonding on carbonated concrete slabs may be related to the limited diffusion of porous water through the carbonated layer, whose porosity is lower than that of sound concrete.

24.2.2. Second set of experiments: Investigation on FRP strengthened concrete blocks using both the pull-off test and the single lap shear test

In the framework of a second experimental campaign, the use of two different methods for mechanical characterization was proposed in order to assess the evolutions of the adhesive bond properties during ageing, namely the pull-off test seen previously, and a single lap shear test. The idea here is to obtain comparative data so as to be able to evaluate the influence (or the sensitivity) of the characterization method.

Here again, two types of specimens were used: these were concrete blocs strengthened either by pultruded CFRP plates or by carbon fiber sheets (CFS) from the market. The main objective was to compare more precisely the ageing behavior of the 2 types of strengthening systems.

24.2.2.1. Preparing the test specimens

The testing bodies were made according to the following stages:

– Concrete blocks with dimensions of $21 \times 21 \times 41 \text{ cm}^3$ were made from a CEM II 32.5 cement and silico-calcareous, with a water/cement ratio of 0.55. After a period of 28 days to reach maturation, the compressive strength was 37 MPa.

– For half of these blocks, sanding was performed on the top face. Then, two pieces of CFRP plate were glued by means of a bi-component epoxy adhesive, called Epoxy A. As illustrated in Figure 24.6, we then created two testing zones, one for the single lap shear test (with a bonded length of 200 mm) and the other for the pull-off tests.

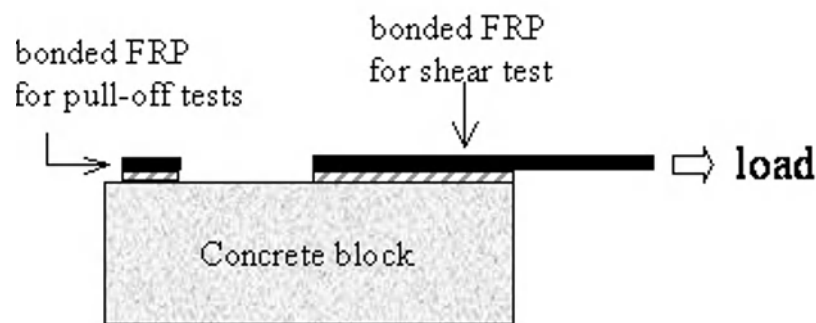
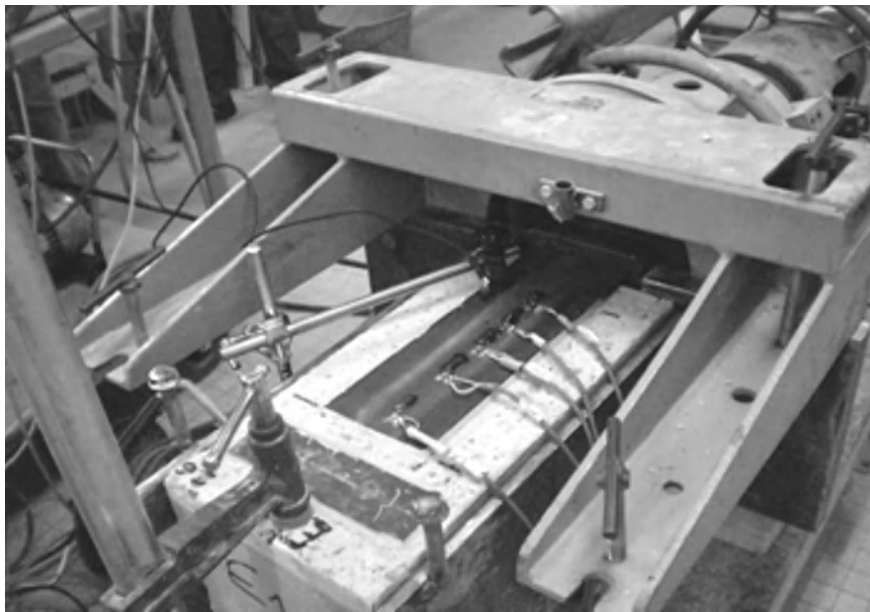


Figure 24.6. Principle of the single lap shear test and picture of the home-made device available at the Regional Laboratory in Autun, France [CUS 05], [C0HA 08]. Two test zones are visible on the testing body, one for the pull-off tests and the other for the shear test

– For the other half of the concrete blocks, an abrasion treatment was performed on the top face using a diamond grinding machine. As before, two strips of carbon fiber sheet (CFS) were bonded in order to obtain two test zones intended for the different mechanical tests. Bonding was carried out by means of a second bi-component epoxy adhesive, called Epoxy B. Again, let us underline that this was performed by professionals from companies specialized in the installation of FRP strengthening systems.

– On each testing body, the test zone dedicated to the shear test was put together by five strain gauges. Locations of the gauges along the lap joint, are displayed in Figure 24.7. This instrumentation aimed at monitoring the strain profiles of the composite along the bonded interface during the shear tests and to evaluate the anchorage length.

Tensile specimens were also molded from pure epoxy adhesives A and B, then polymerized at room temperature. These test-pieces were intended for both tensile tests and DSC analyses (differential scanning calorimetry), so as to evaluate the changes in properties of the bulk adhesives during ageing.

Together, all the testing bodies (FRP strengthened concrete block and bulk epoxy test-pieces) were finally exposed to ageing conditions at 40°C and 95% relative humidity in a climatic chamber. The following sections will successively focus on the behaviors of the bulk epoxy adhesives, the concrete/CFS interface, and the concrete/CFRP plate interface subjected to hydrothermal ageing.

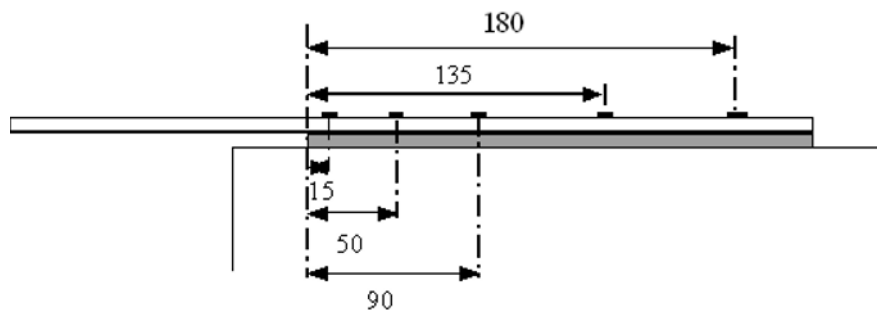


Figure 24.7. Locations of the 5 strain gauges along the bonded interface (15, 50, 90, 135 and 180 mm away from the edge of the adhesive layer)

24.2.2.2. Ageing behavior of the bulk epoxy adhesives

Figure 24.8 shows the evolutions of the glass transition temperature (T_g) for pure adhesives Epoxy A and B. The T_g values were determined by differential scanning

calorimetry (DSC Q100 apparatus from TA Instruments), using a heating rate of $1.5^{\circ}\text{C}\cdot\text{min}^{-1}$ and a temperature modulation. The observed changes reflect the competition between two antagonistic mechanisms, namely the continuation of the cross-linking process at 40°C (or post-curing effect) and the plasticization effect due to moisture diffusion in the epoxy network [MAR 08]:

- an initial increase in T_g is observed for both adhesives, which is attributed to the post-curing effect at 40°C ;
- for Epoxy A, plasticization quickly becomes prevalent and results in a sharp decline in T_g after a few tens of hours of ageing. Afterwards, T_g increases due to the fact that the sorption kinetics slows down and the post curing process then becomes prevalent again;
- for Epoxy B, plasticization involves a slight reduction in T_g , but the value then reaches a plateau at around 63°C .

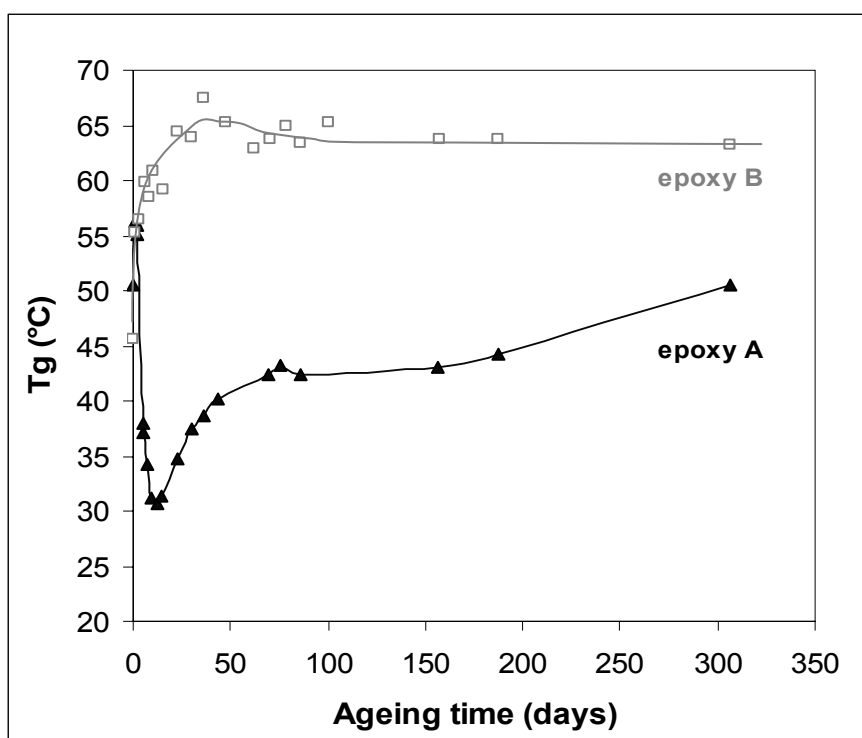


Figure 24.8. Changes in the glass transition temperature (T_g) according to ageing time for adhesives Epoxy A and B (analyses by modulated DSC with a heating rate of $1.5^{\circ}\text{C}\cdot\text{min}^{-1}$)

The two adhesives, then, present appreciably different behaviors, the effect of plasticization being much more noticeable for Epoxy A.

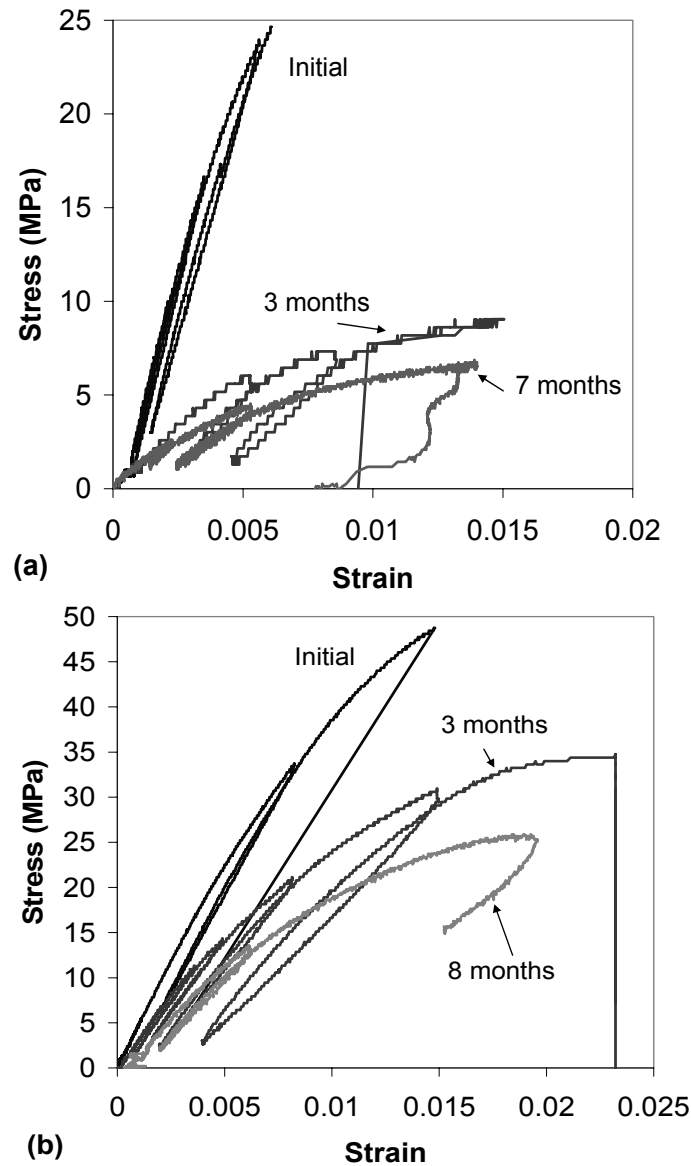


Figure 24.9. Tensile tests for bulk Epoxies A (a) and B (b). Stress-strain curves are presented for initial samples and aged specimens

Figure 24.9 shows the results of the tensile tests for adhesives Epoxy A and B. The stress/strain curves are plotted for the initial test-pieces and for different ageing periods as well:

- in the initial state, the two adhesives both present an elastic behavior, but Epoxy B exhibits higher ultimate properties (stress and strain at failure) than Epoxy A;
- during ageing, the mechanical behavior of the two adhesives becomes elastoplastic, as shown by the observed drop in strength and increase in failure strain. Nevertheless, the properties of adhesive Epoxy A are definitely more affected than those of adhesive B, since the tensile strength is divided by a factor 5 after seven months of ageing (against a factor 2 for Epoxy B). The ultimate strength of aged Epoxy A is then rather close to the tensile strength of the concrete substrate (which is around 2.5 MPa).

Results of these tensile tests are consistent with those of DSC analyzes and show that the impact of accelerated ageing is much more pronounced for Epoxy A, due to an extensive plasticization process.

24.2.2.3. *Ageing behavior of the concrete-CFRP interface*

Concrete blocks reinforced by CFRP composite plates glued with adhesive Epoxy A were then characterized by pull-off and shear tests, after various ageing periods. The shear tests were carried out using the home made testing machine available at the Regional Laboratory of Autun, (France) and whose photograph is presented on Figure 24.6. The process and the conditions of these tests are detailed in the following references [CHA 08], [CUS 05].

Figures 24.10 and 24.11 present respectively, the results of the pull-off and shear test. The following points can be discussed:

- for both test methods, it appears that ageing at 40°C and 95% H.R. induces a gradual evolution of the fracture mode, which evolves from a concrete failure towards a cohesive failure in the polymer joint. This phenomenon can be correlated with the large decrease in the mechanical properties of Epoxy A under the influence of ageing, as we mentioned in the previous section;
- regarding the pull-off tests, a decrease in strength is also observed in agreement with the evolution of the failure mode (Figure 24.10);
- on the other hand, for the shear tests, there is no significant evolution of the maximum shear load, which seems contradictory in light of the evolution observed for the rupture mode (Figure 24.11).

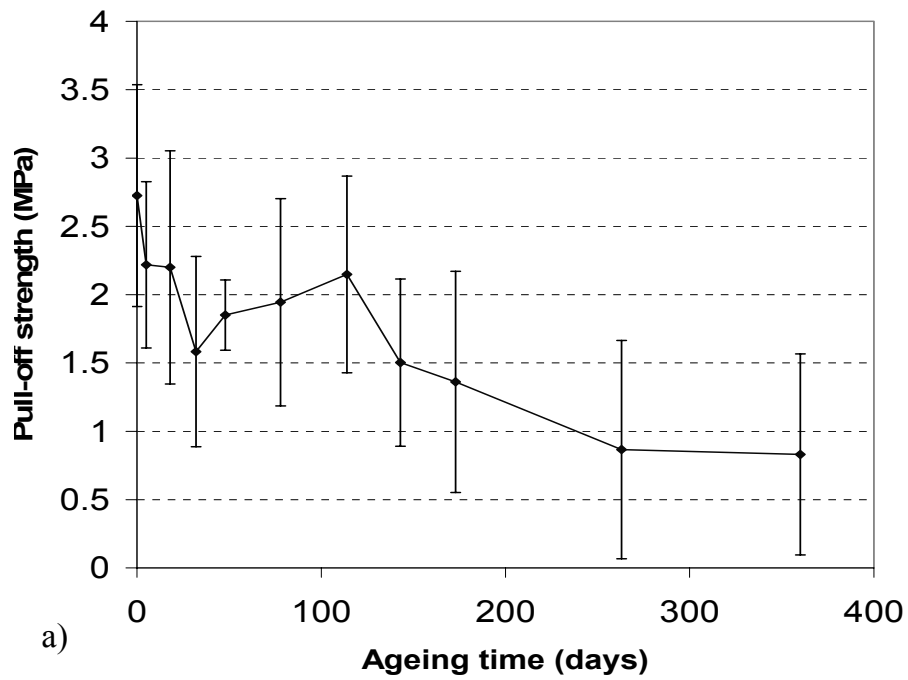


Figure 24.10. Results of the pull-off tests for CFRP strengthened blocks: pull-off strength versus ageing time (a) and pictures of fractured surfaces in the initial (b) and aged (c) states

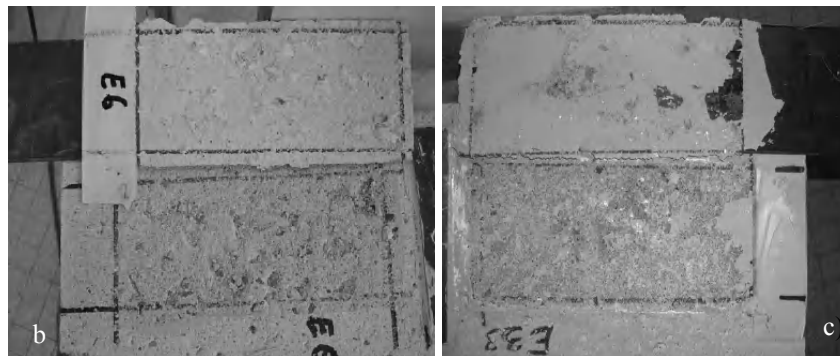
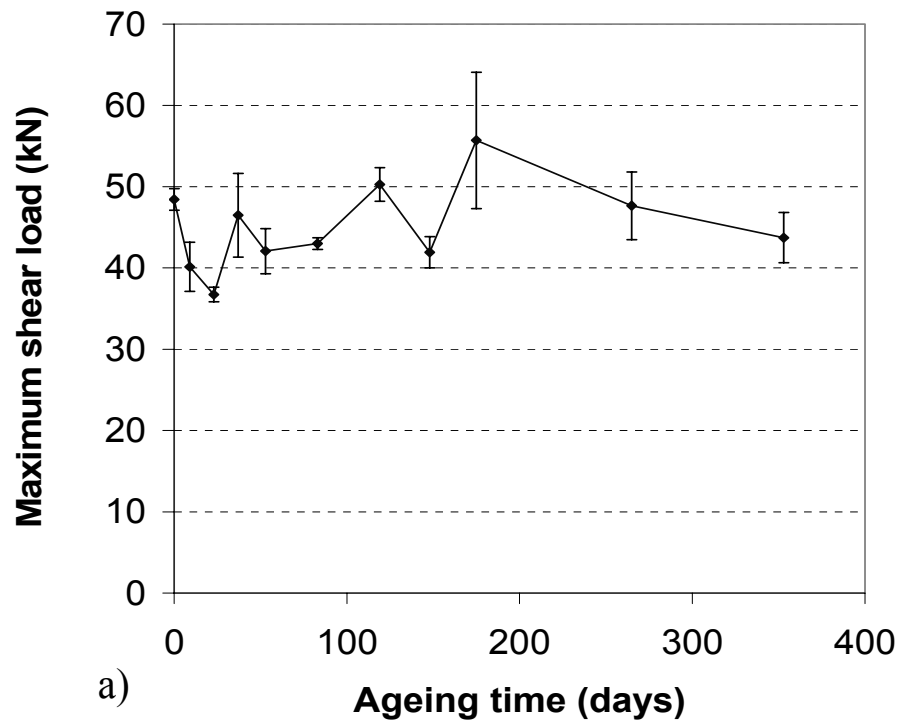


Figure 24.11. Results of the shear tests for CFRP strengthened blocks: maximum shear load versus Ageing time (a) and pictures of fractured surfaces for initial (b) and aged (c) specimens

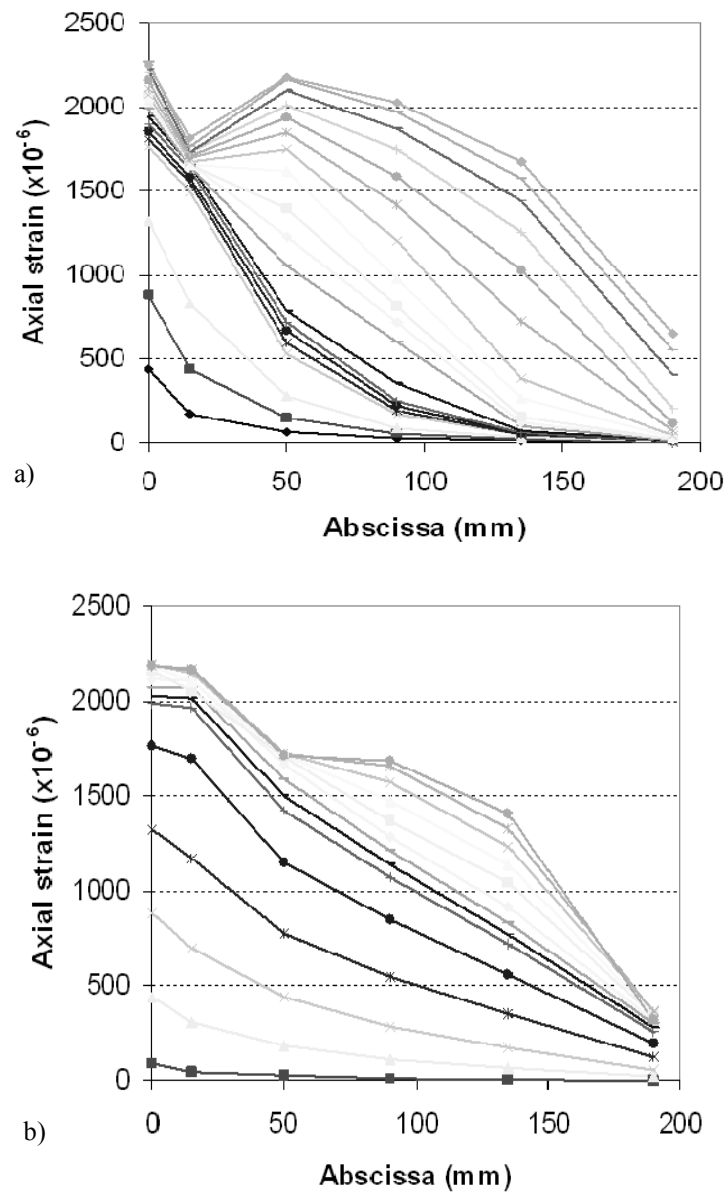


Figure 24.12. Strain profiles of the composite along the bonded interface at various load levels during the shear test, for initial (a) and aged (b) CFRP strengthened specimens

In order to understand why the maximum shear load does not evolve at the same time as the fracture mode, the signals provided by the strain gauges during the shear tests were analyzed.

Figure 24.12 shows the strain profiles of the CFRP plate along the bonded interface, for different load levels. Diagrams are plotted on Figure 24.12 for both the initial and aged states (after 12 months):

- For the initial specimen, the strain profile shows that applied load is mainly transmitted near the edge of the adhesive layer and that the transfer quickly decreases along the interface. We can then determine an anchoring length of 130 mm, beyond which the joint is no longer strained (except at high load levels in the damage domain).

- We may note that hydrothermal ageing strongly affects the strain profile along the bonded interface. A large increase in the anchoring length is observed, which becomes higher than 200 mm. This means that load is better distributed over the entire length of the joint. So, for a given load level (i.e. by following a curve on the diagram), the maximum strain measured at the edge of the joint (with X-coordinate 0) is definitely weaker than in the initial sample. This phenomenon is the consequence of the strong change in the mechanical properties of adhesive Epoxy A during ageing, as shown in the previous section. The major reduction in the elastic modulus and the higher ductility would then promote this redistribution of the load along the lap joint.

Finally, the drop in resistance of adhesive Epoxy A during ageing is compensated by a reduction in the intensity of the stress peak at the extremity of the joint, and the average shear capacity overall remains unchanged. On the other hand, once failure has begun, crack growth propagates within the adhesive joint which has been weakened by ageing. These features can explain why we observe a change in the fracture mode without changing the average shear capacity.

24.2.2.4. Ageing behavior of the concrete-CFS interface

Concrete blocks reinforced by carbon fiber sheets bonded with adhesive Epoxy B were also subjected to the same mechanical pull-off and shear tests, after various ageing durations. The results of these tests are presented in Figures 24.13 and 24.14, respectively.

Analyzing the results brings out the following points:

- After a 13 month ageing period (390 days), the pull-off tests do not reveal any significant variation in the adhesive bond strength (Figure 24.13a), or an evolution of the fracture mode, which always remains cohesive in the concrete substrate (Figures 24.13b).

– Regarding the shear tests (Figure 24.14), the maximum load also remains unchanged during ageing. On the other hand, an evolution in the fracture mode is observed: the failure, which is initially cohesive in the substrate, gradually evolves towards the adhesive/concrete interface (Figures 24.14b and 24.14c). The appearance of such interfacial ruptures seems characteristic of a weakening of the adhesive bond during ageing. The fact that the maximum shear load remains unchanged despite this evolution could result again from a modification of the load transfer mechanism along the lap joint (Figure 24.15), even if this is less obvious than for the previous case.

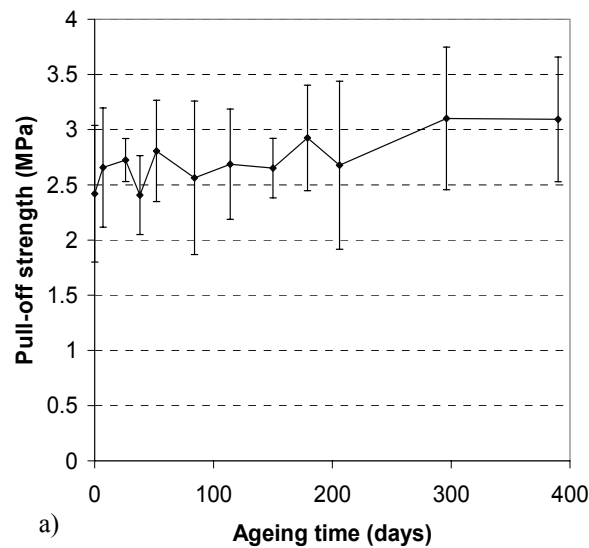


Figure 24.13. Results of the pull-off tests for CFS strengthened blocks: pull-off strength versus ageing time (a) type of substrate failure observed both in the initial and aged states (b)

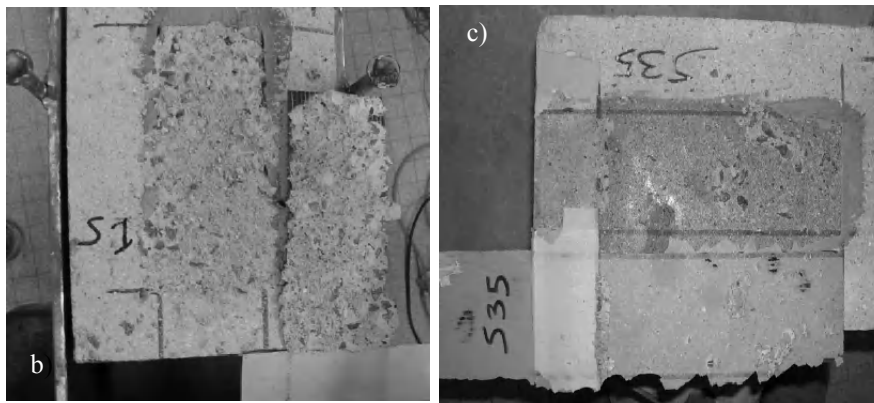
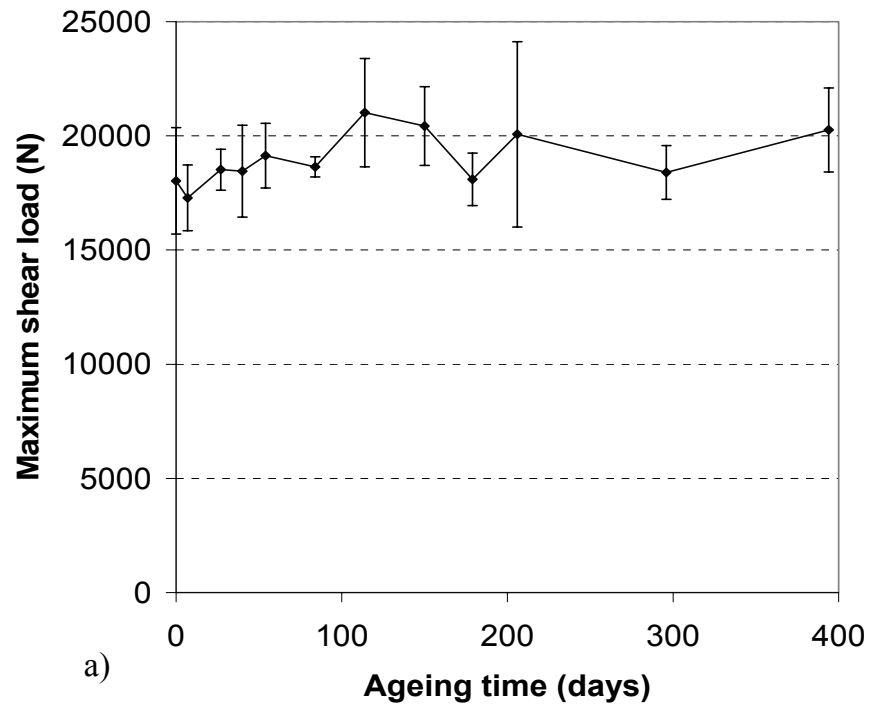


Figure 24.14. Results of the shear tests for CFS strengthened blocks: maximum shear load versus ageing time (a) and pictures of fractured surfaces for initial (b) and aged (c) specimens

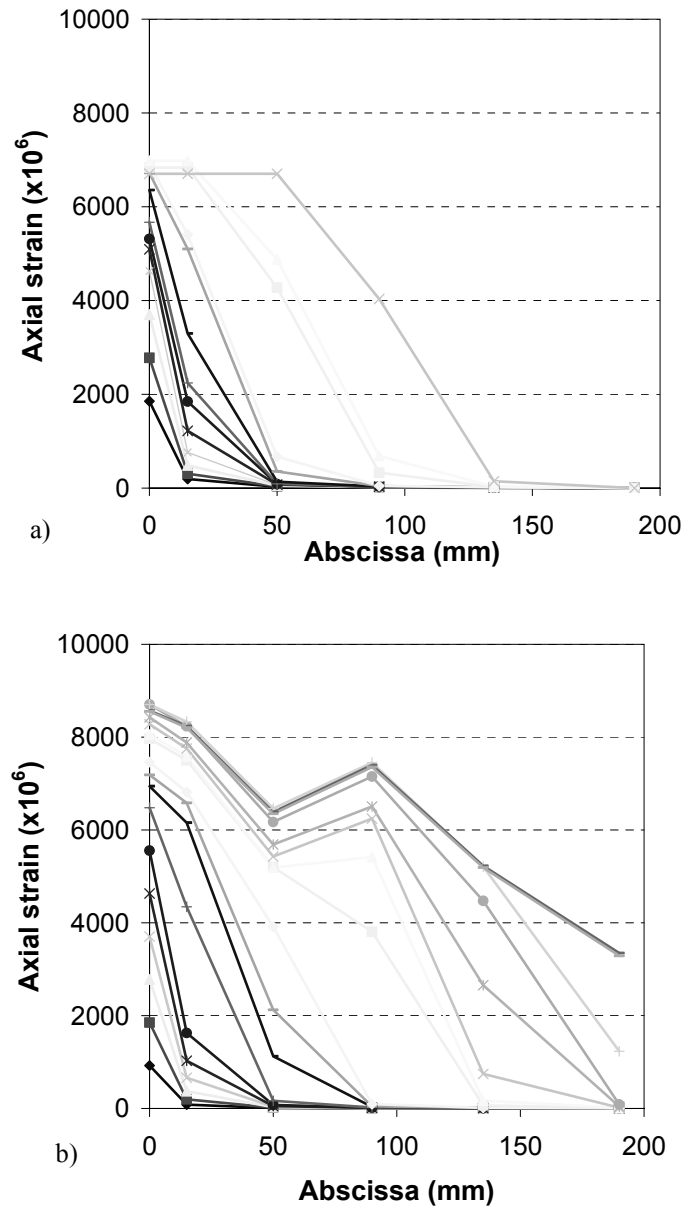


Figure 24.15. Strain profiles of the composite along the bonded interface at various load levels during the shear test, for initial (a) and aged (b) CFS strengthened specimens

In addition, note that the pull-off test appears to be less sensitive than the shear test to variations of the adhesive bond properties, as it does not reveal any evolution of the fracture mode during ageing. In fact, the pull-off test only seems discriminating when there are strong variations in the joint properties, and when the tensile strength of the epoxy adhesive gets very close to the tensile strength of concrete. This was the case for the adhesive Epoxy A in section 24.2.2.2, but this is not checked for Epoxy B which still exhibits high residual properties after ageing (see Figure 24.9).

24.3. Conclusion

The study presented in this chapter illustrates efforts currently being made by researchers to understand the mechanisms which control the durability of repair works with bonded FRP systems. This type of investigation is generally based on accelerated ageing tests which are not always representative of in service conditions, but which rather aim at assessing the influence of specific parameters (moisture, temperature, freeze/thaw cycles, etc.) or coupled parameters on the characteristics of adhesively bonded joints. For this reason, observed changes can only be interpreted within the framework of the chosen ageing conditions, to verify the influence of the given parameters (moisture in this case), and do not necessary predict the lifespan of repair works under normal service conditions.

Moreover, it is noted that additional protective coatings are systematically applied onto the surface of bonded FRP reinforcements in order to reduce the effect of environmental ageing. In these conditions, FRP strengthening systems constitute a viable solution for increasing the lifespan of defective or under-dimensioned works, and should be promoted by experts and civil engineers.

24.4. Acknowledgements

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Chapter 25

Characterization of Organic Materials used in Civil Engineering by Chemical and Physico-chemical Methods

In the field of civil engineering, the organic materials used are very diverse (bitumens, paints, cements, etc.), but the study of their chemical structure and their composition generally uses the same analysis techniques.

Without claiming to be exhaustive, this chapter completes and brings up to date the presentation of chemical, physico-chemical, physico-mechanical and thermo-mechanical properties previously offered [MOU 06] through research studying the chemical structure of basic organic materials and their additives, used in civil engineering. The original aspect of this work primarily lies in adapting methods and analysis conditions, extending their application domain and interpreting their results according to the nature of the material being analyzed (bitumen binders, anti-corrosive paints, organic admixtures used in cementing materials) and the problems presented.

25.1. Bituminous binders

For road technicians, there is no longer any doubt that a good number of setbacks encountered, during the implementation process as well as the bituminous mix lifetime, are related to the physicochemical and physico-mechanical characteristics of bitumens, and more generally, to the used bituminous complex.

Chapter written by Fabienne FARCAS.

Degradations observed are neither systematic nor with the same amplitude for all the bituminous mixes. To try to explain the differences between the offending samples, we tried to precisely define the chemical and physicochemical characteristics of the binders and to formulate the laws of evolution versus time of these characteristics.

In front of the impossibility of characterizing bitumen in its entirety, we had to base on the model of colloidal structure [YEN 71], whose parameters seem sufficiently precise to describe or explain certain problems encountered during implementation, or later during their working life. In this sense, research undertaken on bituminous binders was focused, on the one hand, to a better knowledge of the chemical structure of bitumens whose performances are continuously improved by using new manufacturing processes and/or by adding various compounds and, on the other hand, to a better comprehension of the phenomena involved in various ageing processes of bitumens.

The analytical techniques used for studying road binding agents are:

- silica rod chromatography (IATROSCAN);
- steric exclusion chromatography (SEC);
- synchronous excitation emission fluorescence spectroscopy (UV fluorescence-EES);
- inductively coupled plasma-atomic emission spectrometry (ICP-AES);
- Fourier transform infrared spectroscopy (FTIR).

It is through these analysis techniques and, considering the binders studied according to an increasing complexity of their chemical structure (pure bitumens, “special” bitumens, bitumens modified by polyphosphoric acids), that studies on bitumens are described. For each type of road binder, the chemical structure followed by its evolution during ageing, are presented.

25.1.1. Pure bitumen

25.1.1.1. Chemical structure of pure bitumens

By adapting some analysis methods it is possible to highlight the colloidal structure suggested by Yen [YEN 71].

Silica rod chromatography (IATROSCAN), technique which only takes into account the concentration of the generic bitumen groups, independently of any quality criteria, does not completely explain the mechanical behavior of bitumens.

However, it is admitted that the bitumen consistency also depends on the interactions which exist between bituminous molecules and other molecules involved in the micellar equilibrium. To highlight these interactions, we need to use a more adapted technique: steric exclusion chromatography (SEC) under “high-speed” conditions [BRU 87]. High speed steric exclusion chromatography applied to bitumens allowed to define a classification of three structure types, according to whether the bitumen is constituted by one, two or three populations. Taking into account the diversity and the large number of samples, this technique has shown that bitumens which belong to the same class do not present the same quantities of molecular associations.

In order to better understanding the structure and the molecular reorganizations responsible for the consistency of bitumens, we used the ultraviolet fluorescence spectroscopy (UV fluorescence) and excitation-emission matrix spectroscopy (EES). This technique allows knowing the aromatic compounds, and to follow their evolution during the binder's ageing.

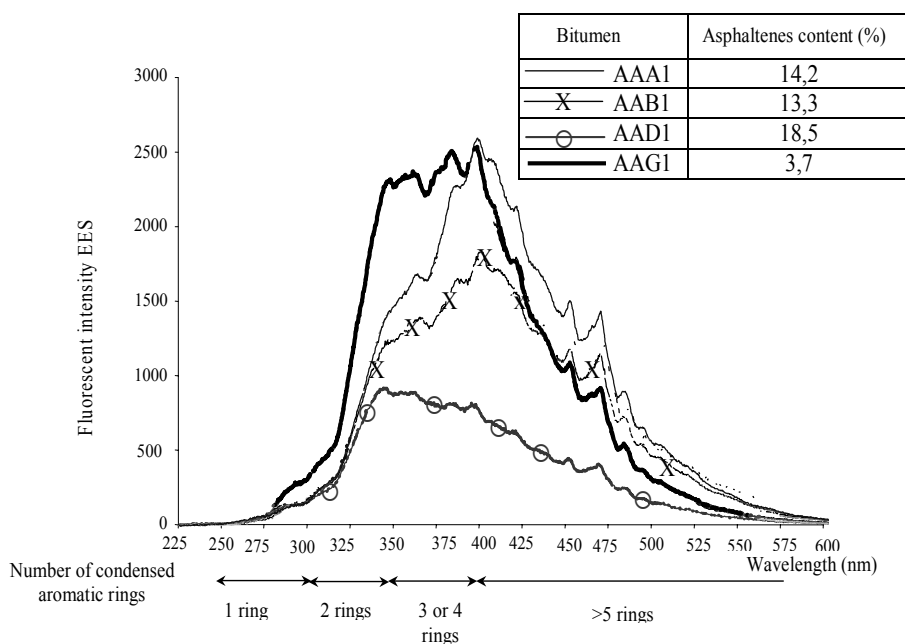


Figure 25.1. Synchronous excitation emission fluorescence spectroscopy spectra of four bitumens from the SHRP

Ultraviolet fluorescence spectroscopy (*UVFS*) in excitation-emission matrix spectroscopy (EEMS) mode was first developed in the framework of research on coals [KIS 92] before being applied to road bitumens [FAR 92a]. The interest of using the EEMS mode for bitumens which are complex mixtures lies in simplifying the spectra, since each molecule is only represented by one single band. The information obtained let us draw some major trends.

The analysis of eight bitumens from the SHRP (*Strategic Highway Research Program*) [BUI 93], [FAR 91], [FAR 92a], [SUC 94] showed that all bitumens had a comparable spectral print ranging from 250 nm to 600 nm with a maximum of 398 nm (Figure 25.1). Considering references to molecules found in relevant literature [VOD 78], it appears that the condensation of bitumen aromatic cycles do not exceed 5 rings.

The diminution of the fluorescent intensity observed when the asphaltene quantity increases can be explained by an extinction effect due to intermolecular interactions between the asphaltene molecules [FAR 92a].

The analysis of the three fractions obtained by “high-speed” SEC (one French bitumen and two Italian ones), shows that:

- the florescence of the population which is eluted under the interaction peak is practically nil;
- the second population’s spectrum corresponds to the fluorescence of compounds composed of 3, 4 and 5 condensed rings;
- the third population, which corresponds to small molecular sizes molecules, displays fluorescence in the zone of aromatic rings which are not much condensed.

This fractionated analysis, allowed to assert that the fluorescence spectral response complies with molecular size distribution. In the majority of cases, the bigger the bitumen’s interaction peak, the weaker the florescent intensity is.

25.1.1.2. *Pure bitumen ageing*

This section describes the evolution of the bitumens’ colloidal structure firstly under the influence of thermal shock during the coating process, simulated by the RTFOT standardized ageing test [AFN 00] and secondly after a long-term ageing (road service) simulated by “oxygen bomb” test, developed by the LCPC and validated by studying bitumens which have aged in situ (A8 highway) [FAR 96].

25.1.1.2.1. Ageing of bitumens during coating

Let us remember that the mainly cause for chemical ageing in bitumens is oxidation due to the oxygen contained in the air. This oxydation makes the bitumen harden [AFN 99]. The chemical analyzes carried out on three grade 35/50 French

bitumens, and eight American bitumens, show that this hardening is a result of colloidal equilibrium evolution [FAR 92b], [FAR 92c], [FAR 96]:

- the analysis using IATROSCAN reveals an increase in asphaltene and resin content, as well as a reduced number of aromatics compounds. The saturated content remains unchanged;
- the analysis using HS-CES shows an increase in the interaction peak, which corresponds to an increase in asphaltene agglomeration;
- the analysis using FTIR reveals an oxidation by the formation of carbonyl functions (increase in the absorption band around $1,700\text{ cm}^{-1}$) and sulfoxides (increase in the absorption band around $1,032\text{ cm}^{-1}$);
- the analysis using UVFS-EEMS undoubtedly shows a general reduction in the fluorescence intensity, in particular in the spectral zone of molecules composed of the most condensed aromatic structures [BUI 93], [FAR 92a], [SUC 94]. This fluorescence extinction probably due to the rupture and/or the recombination of large aromatic rings.

25.1.1.2.2. Ageing of bitumens on the road

In order to be able to predict the road durability, an in situ ageing simulation test was developed by the LCPC [FAR 96]. Its validity, considered from a physico-mechanical and structural point of view, is discussed here.

As road temperatures rarely exceeding 50 to 60°C in France [SUC 95], reproducing ageing effects of bitumens in situ requires a test which privileges oxidation at low temperatures, where the oxidation reactions are accelerated by an increase in oxygen pressure. For this, a standardized method for lubricating greases oxidation, the “oxygen bomb” test [AST 91], was adapted to bitumen ageing: a fine film (4 mm) of bitumen is oxidized in a vacuum at 50°C and 70°C under oxygen pressure of $2.2 \pm 0.05\text{ MPa}$ [FAR 96].

We tried to reproduce the hardening kinetics of two French road bitumens, 35/50 grade. For this, the evolution in the behavior of the bitumen by usual standard tests which tend to characterize its consistency at various temperatures was followed by measuring the Ring and Ball softening point (TR&B) and the penetration at 25°C. Modifications of the chemical and colloidal structures were monitored by IATROSCAN and “high-speed” SEC (HS-SEC) methods.

Laboratory ageing conditions lead to:

- a diminution of penetration and increase of softening point, which is much larger when the temperature and the test duration are higher;

– an increased in the colloidal instability index and molecular associations which reveal an increasing bitumen structuration over the test duration.

In order to validate the accelerated ageing test, the modifications obtained after laboratory ageing tests were compared with those obtained from bitumen samples from A8 highway.

The diagrams of penetration variation according to the softening point for two artificially aged bitumens from the experiment site on A8 highway (figure 25.2), show that the data obtained by oxidation in the laboratory at 50°C and 70°C follow the model (in a satisfactory way) represented by a hyperbolic function suggested by Brown [BRO 57], to describe in situ ageing.

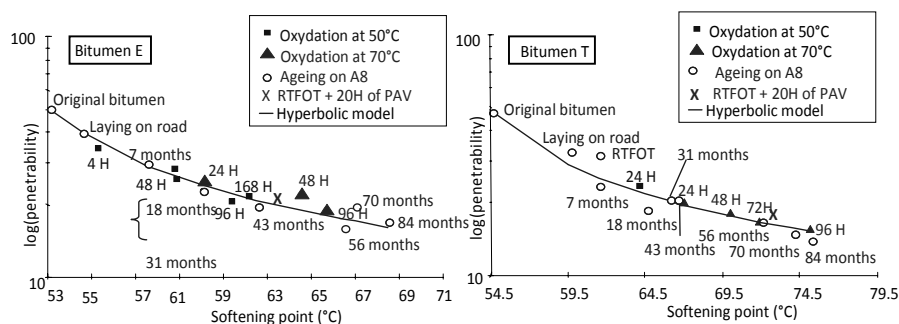


Figure 25.2. Variation of the penetrability logarithm according to the softening point of two same grade bitumens aged on the road and in the laboratory

As all the ageing factors (traffic, bad weather conditions, UV radiation, etc.) are not being taken into account, simulating structural modifications proved to be more difficult.

The comparison of the variation between the I_c values taken from the road and the laboratory ageing have shown that oxidation at 70°C under an oxygen pressure of 2 MPa allows us, for the two studied bitumens, to simulate a structural state corresponding to different ages of in situ ageing. Here we find a difference in reactivity between the bitumens, probably the reason behind the previously shown differences in hardening.

On the other hand, variations in the ratio of the first chromatographic peak surface shows that the increase in the molecular associations induced by an oxidation temperature of 70°C under 2 MPa of oxygen is not sufficient to simulate road ageing.

However, this study has enabled us to show that in the experimental field exploited by SEC, after the oxygen bomb ageing test over 96 hours at 70°C under an oxygen pressure of 2 MPa, the dissociation kinetics of the dissociable asphaltene species when in solution is close to that for the same bitumen aged for 84 months on the road [FAR 96].

25.1.2. *Special bitumens*

In order to prevent rutting, the manufacturers have developed special bitumens. Considering usual consistency criteria (penetration and softening point), the European specifications [AFN 99] leave behind them the fear of premature crack growth on the roadways.

However, the observations carried out on some roads made using this type of binder present a good behavior in the bitumen mix during winter temperatures [MAR 99]. To understand the particular behavior of these bitumens, they were analyzed using the same analytical techniques as for the used pure bitumens.

Moreover, in order to distinguish the different bitumens studied, it was interesting to determine Ni, V, S and P content. Those elements represent a way of distinguishing bitumens according to their origin, or even the method used to make them. The dosage of these elements is performed according to an elementary analysis method developed by the LCPC: ICP-AES performed with a bitumen emulsion solution [DRU 00].

Four special bitumens and a “traditional” bitumen of the same grade (35/50), considered here as a reference bitumen, were studied. The evaluation and the comparison of ageing effects on the chemical structure of the special bitumens were performed by considering various stages of ageing.

25.1.2.1. *Elementary analysis by ICP-AES spectrometry*

The values for Ni and V content (Table 25.1), show that the studied bitumens are made by using three different origin petroleum:

- special bitumens A and B come from similar crude oils;
- special bitumens C and D are made from oils with close origins;
- traditional bitumen R comes from a third oil source.

The sulfur contents are comparable for the five bitumens (Table 25.1). The “anti-rutting” performances of the special bitumens, therefore, cannot be attributed to the addition sulfur, which (by a vulcanization process), gives them a higher modulus.

	Ni	V	S*	P
Wavelength of emission bands	231.60 nm	290.88 nm	181.98 nm	214.91 nm
Bitumen R	67.7 ppm	234.0 ppm	3.0%	Not detected
Bitumen A	18.1 ppm	76.4 ppm	3.6%	Not detected
Bitumen B	14.8 ppm	70.1 ppm	3.2%	Not detected
Bitumen C	32.0 ppm	116.0 ppm	4.4%	0.4 ppm
Bitumen D	31.4 ppm	234.0 ppm	3.0%	Not detected

* The sulfur contents are expressed in mass percentages.

Table 25.1. Ni, V, S and P contents in four “special” bitumens (A, B, C, D) and traditional” bitumen (R) determined by ICP-AES

25.1.2.2. Structure state determination using IATROSCAN

High asphaltene contents lead to high I_c values (Table 25.2), indicating that special bitumens are highly structured, in comparison with traditional bitumen.

Bitumen	Saturated (%)	Aromatic (%)	Resins (%)	Asphaltene (%)	I_c	n-heptane precipitated asphaltenes (%)
R	7	48	30	15	0.28	10.2
A	8	49	24	20	0.39	19.3
B	9	43	26	21	0.44	19.5
C	6	43	25	26	0.48	22.6
D	8	42	28	23	0.45	18.7

Table 25.2. Separation into generic families by IATROSCAN and asphaltene content precipitated by N-heptane

Generally, highly structured bitumens are oxidized bitumens. Bitumen's oxidation level can be evaluated using, IRTF spectrometry. This technique gives information on the nature and the content of existing functional and structural groups.

25.1.2.3. *Determining oxidation state by FTIR spectrometry*

FTIR analyzes show that all grade bitumens have the same chemical functions. The spectra are simple and reveal that bitumens mainly consist of aliphatic and aromatic hydrocarbons. Their functionality is primarily related to the presence of carbonyl functions ($C = O$) towards $1,700\text{ cm}^{-1}$ and sulfoxide ($S = O$) towards $1,032\text{ cm}^{-1}$. These chemical functions reveal the binder's oxidation state. Evaluation of their content represents a way to distinguish bitumens between them and, as we will see further on, evaluate their susceptibility to ageing.

This technique highlights that the structure of special bitumens can be attributed to high carbonyl content. This conclusion lets us consider that the manufacturing process of these bitumens includes a "blowing" stage. The oxygenated functions of bitumens are responsible of molecular associations. They generate complex structures which define the bitumens' colloidal structure. The carbonyl function content highlighted by FTIR induces differences in the colloidal structures, which we try to visualize using "high-speed" SEC methods.

25.1.2.4. *Colloidal structure determination by "high-speed" SEC*

The results of quantification of each chromatographic population (Table 24.3), performed using a program which allows chromatogram deconvolution in three normal distributions, confirm the high structuring of special bitumens. It is important to note here that all special bitumens do not present the same structure (bitumen D is approximately three times less structured), meaning that they are not all manufactured by the same process.

The application of different analysis techniques leads us to conclude that the special bitumens are structured bitumens, obtained by processes which involve oxidation reactions. In order to understand their unexpected mechanical behavior during the ageing, the evolution in their chemical structure, during the coating process and on the road, is studied in the following section.

Modifications of the chemical structure of the four special bitumens during ageing are studied by two artificial ageing tests:

- RTFOT, ageing stage during aggregate coating;
- RTFOT followed by 20 hours of PAV (pressure ageing vessel), in situ ageing stage.

Bitumen	Agglomeration (%)	Micelles (%)	Molecules (%)
R ("traditional")	0.5	8.5	91.1
A	7.2	10.3	82.5
B	5.9	11.7	82.4
C	6.9	21.8	71.4
D	2.0	29.5	74.6

Table 25.3. *Contents of molecular associations and molecules isolated from "traditional" bitumen and from the four "special" bitumens*

The two stages of ageing considered lead to a comparable increase of the asphaltene content of the special bitumens and the "traditional" bitumen. Similarly, the increase of the I_c value is comparable for all bitumens.

Oxidation during ageing results in the formation of sulfoxide and carbonyl functions, more or less important according to the bitumen: bitumens A and B appear to be the most oxidable. We can note that these two bitumens have also the greatest sensitivity to cold cracking. The two other bitumens are less oxidable, and the oxydability of bitumen D is comparable to the reference bitumen.

The formation of oxygenated functions contributes to the creation of molecular associations. However, it cannot be directly related to the bitumens' structuring (formation of molecular associations) because it does not take into account other phenomena, such as polycondensation reactions.

The "high-speed" SEC technique performed at the two stages of ageing, shows that molecular associations of the special bitumens increase much less than those for "traditional" bitumen. This observation is not surprising knowing that a structured bitumen is not very ageing sensitive.

The differences in manufacture processes, and the low contents of metal may be the parameters which lead to differences in modification of the colloidal structure observed between "special" bitumens.

25.1.3. Polyphosphoric acid modified bitumens

Polyphosphoric acid (PPA) modified bitumens are used, particularly in the United States, to improve the properties of bitumens with regard to the SUPERPAVE (*Superior Performing Asphalt Pavements*) reference specifications [ASP 95]. Addition of PPA to bitumens induces a similar effect to the blowing process: lower penetration, higher viscosity. In addition to correct ageing resistance, the advantages of PPA addition, in relation to blowing process, are its low cost and a little incidence on bitumen behavior at low temperatures [DEF 95].

PPA modified bitumens have not only improved mechanical properties, but also a better resistance to stripping from water [ASP 01]. The few elements which we know today on the physicochemistry of PPA modified bitumens [BIS 01], [HO 01] do not enable us to explain these property modification, and the action mode of these acids still remains widely misunderstood. Research on the chemical structure of PPA modified bitumens appears all the more necessary, as some PPA modified bitumens do not display the improvements described above.

25.1.3.1. Basic materials and usual mixture characteristics

In order to get a better seeing of the characteristics of PPA modified bitumens, we have chosen to carry out work on mixtures of bitumens modified by 2% APP – the rates usually used in the USA being around 0.9 to 1.2%. The polyphosphoric acid introduced to the mix is a polyacid with the supposed composition: H_3PO_4 (54%); $\text{H}_4\text{P}_2\text{O}_7$ (39%); $\text{H}_5\text{P}_3\text{O}_{10}$ (7%).

Three bitumens of different origins which respond differently to the modifications were selected for this study (Table 25.4).

Bitumen	Crude bitumen origin	Improvements in mechanical properties by adding 1% APP
Av	Venezuela	Strong
Bm	Mexico	Moderate
Cc	Canada	Nil

Table 25.4. *Origin and behavior with the addition of APP to the studied bitumens*

Whatever the bitumen considered penetration measurements at 25°C show that polyphosphoric treatment induces a loss of one penetration grade. This criterion is more important for the Av bitumen, which distinguishes itself from both the other bitumens by a particularly strong increase of softening point after RTFOT [SUC 03]. Therefore, bitumen Av does not satisfy current European specifications [AFN 99]. In parallel, this bitumen, stated as being larger improved by PPA addition, also seems to be the most reactive in terms of its usual characteristics.

25.1.3.2. *Chemical and structural analyzes*

The elementary ICP-AES analyzes of unmodified bitumens means that we can distinguish bitumen Av by a high vanadium content. Excluding this characteristic, the three bitumens are identical.

Adding PPA results in a large increase in the asphaltene precipitated by n-heptane content (approximately 6%). This increase should lead to hardest bitumen than the one obtained (penetration of 39/10 mm).

As an indication, pure bitumen with high asphaltene content (23%) generally has a penetration lower than 20/10 mm. To explain these contradictory values, we propose the hypothesis that the PPA reacted with the aromatic asphaltenes and the resins to form phospho-aromatic asphaltenes insoluble in n-heptane, but soluble in cycloaliphatics solvents.

Generic groups separation by IATROSCAN reveal:

- for bitumen Av, a decreasing of the asphaltene content by 0.5%; an increase in the aromatic content by 27% and a reduction in the resin content by 2%;
- for bitumens Bm and DC, a decreasing of the asphaltene content by approximately 3%;
- for bitumen Bm, a decreasing in the aromatic content by 3.6% and an increase in the resin content by 0.8%;
- for bitumen Cc, a small variation of the aromatic content, and an resin increase by 3.6%.

The increase in the I_c values of bitumens Bm and Cc leads to a structuration of bitumen after modification. This conclusion is also verified by rheological tests, which show that the elastic nature of the binding agent increases with the PPA content [ORA 04].

IATROSCAN method, used to bitumen generic groups separation, does not reflect the large variation in the content of insoluble asphaltenes in n-heptane induced by modification of the basic bitumen. This means that the compounds

formed by the PPA and bitumen reactions are separated with the other generic families. Therefore the hypothesis of phospho-aromatic soluble asphaltenes in toluene and chloroform seems plausible.

The “high-speed” SEC analyzes of the three bitumens reveals that PPA modification induces a diminution in the agglomerated asphaltene content. Used as an additive, added in the bitumens in small quantity (1%) in the majority of cases, PPA destroyed the bitumen colloidal structure [DEF 95]. The PPA appears to be an asphaltene dispersant. This result, surprising if we takes into account the bitumen structuring revealed by the I_c values and rheological tests, is still favorable to the hypothesis on phospho-aromatic components formation which are compatible with resins and aromatics bitumen compounds.

To conclude this study, the diminution of large molecular sizes species concentration, detected by SEC methods, promotes the formation of phospho-aromatics which disperse the asphaltenes in the maltene environment. The results of separating into generic families and the asphaltene contents support this hypothesis.

25.2. Anti-corrosive paints

The aim of the study presented here was to determine ageing indicators sensitive enough to allow intervention before buildings and structures degradations require heavy and expensive repairs.

Sensitivity of current analytical techniques, applied to the study of a material's chemical evolution, represents a method of detecting paint degradation at an early stage. A bibliographical study showed that infra-red spectrometry (transmission, specular reflection, diffuse reflection, transreflexion and attenuated total reflection (ATR)) [DEF 98], [CHE 00], [IRI 01], [ISA 72], [LEM 98], [NGU 87], [PER 00], [WER 97] is an interesting technique for studying the chemical modifications of polymers during ageing.

This is the reason why we retained this method to detect significant indicators of chemical modifications in the finishing layer of four coating systems (chlorinated rubber, urethane alkyd, polyurethane and acrylic urethane) naturally aged for 12 months in Florida, i.e. under particularly aggressive conditions (UV radiation, heat, moisture and marine environment) [FAR 01a], [FAR 03].

The modifications of the binder's chemical functions are studied by FTIR:

- in transmission mode: this infra-red analysis mode requires a mechanical scraping to recover the surface of the top coat;

– in attenuated total reflection mode (ATR): this analysis mode enables a study on the paint surface in a spectral range 650 cm^{-1} to $4,000\text{ cm}^{-1}$ the depth of penetration of the infrared beam for a sample with a refractive index of 1.5 is between 0.6 and 4.8 mm. [PER 00]. FTIR-ATR microscope allows the analyze of a small surface (infra-red spot size: $60\text{ }\mu\text{m}$). Because of a sufficient contact possible between the internal reflection crystal and the often rough film, especially after an ageing test, this technique is particularly interesting for coat pain studies.

The spectral range of the infra-red spectrum located below $1,500\text{ cm}^{-1}$ is highly characteristic of a molecule, but is sometimes difficult to interpret. Moreover, for products containing mineral fillers, which is the case for paints, the absorption bands of the organic compounds are masked by those of the mineral compounds, which have intense absorption bands below $1,200\text{ cm}^{-1}$ [FAR 01b].

This is why, in the majority of the cases, we were interested in the spectral range of the FTIR spectrum between $2,000\text{ cm}^{-1}$ and $1,500\text{ cm}^{-1}$, which corresponds to an infra-red absorption area whose interpretation is reliable and unambiguous.

The FTIR spectra of different colored top coats of a system from the same manufacturer are identical. The pigments, added in small quantities into the mixtures, do not appear on the spectra. Moreover, for a given binder type, the same FTIR spectra modifications for aged paints were noticed. From this, we can confirm that the pigment does not influence the chemical ageing of the paint resin.

Some paint binders have common infra-red absorption bands. Thus, the FTIR study is conducted by distinguishing two groups of binding agent:

- chlorinated rubbers;
- polyurethanes, acrylic-urethanes and urethane-alkyds.

25.2.1. Ageing of chlorinated rubber binders

The list of the main absorption bands observed on the FTIR spectra for analyzed chlorinated rubber paints is given in Table 25.5.

The comparison of FTIR spectra of chlorinated rubber paint before and after ageing (Figure 25.3) does not make it possible to directly highlight the intrinsic chemical modification of the binder. Indeed, the double characteristic of the C-Cl bonds, between 600 cm^{-1} and 700 cm^{-1} , is masked by talc absorption ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) to 669 cm^{-1} .

Wave number (cm ⁻¹)	Chemical functions in vibration
3,675	v (OH) (talc)
2,966-2,851,	v (CH ₃)
2,923	v (CH ₂)
1,731	v (C = O) ester
1,600	Aromatic cycle
1,444	δ (CH ₂)
1,370	δ (CH ₃)
1,017	δ (Si-O) (talc)
669	v (Si-O) (talc)
534	v (Si-O) (talc)
465 and 451	v (Si-O) (talc)

Table 25.5. Attribution of the main absorption bands read on IRTF spectra, chlorinated rubber paints (v: elongation vibration; δ: strain vibration)

However, we can see a modification in the FTIR spectrum of the aged paint, by an increase in the absorption bands to 1,731 cm⁻¹ and 1,600 cm⁻¹ which can be explained by two phenomena:

- migration of the plasticizer towards the surface, phenomenon behind polymer deplasticization [MAT 96];
- oxidation of the chlorinated rubber binder by photochemical degradation mechanisms [VER 84], [WIL 97].

The FTIR spectrum of the part located at a depth of 10 μm is identical to that of the specimen before ageing (Figure 25.3), which shows that ageing factors are no longer observed at a binder depth higher than 10 μm.

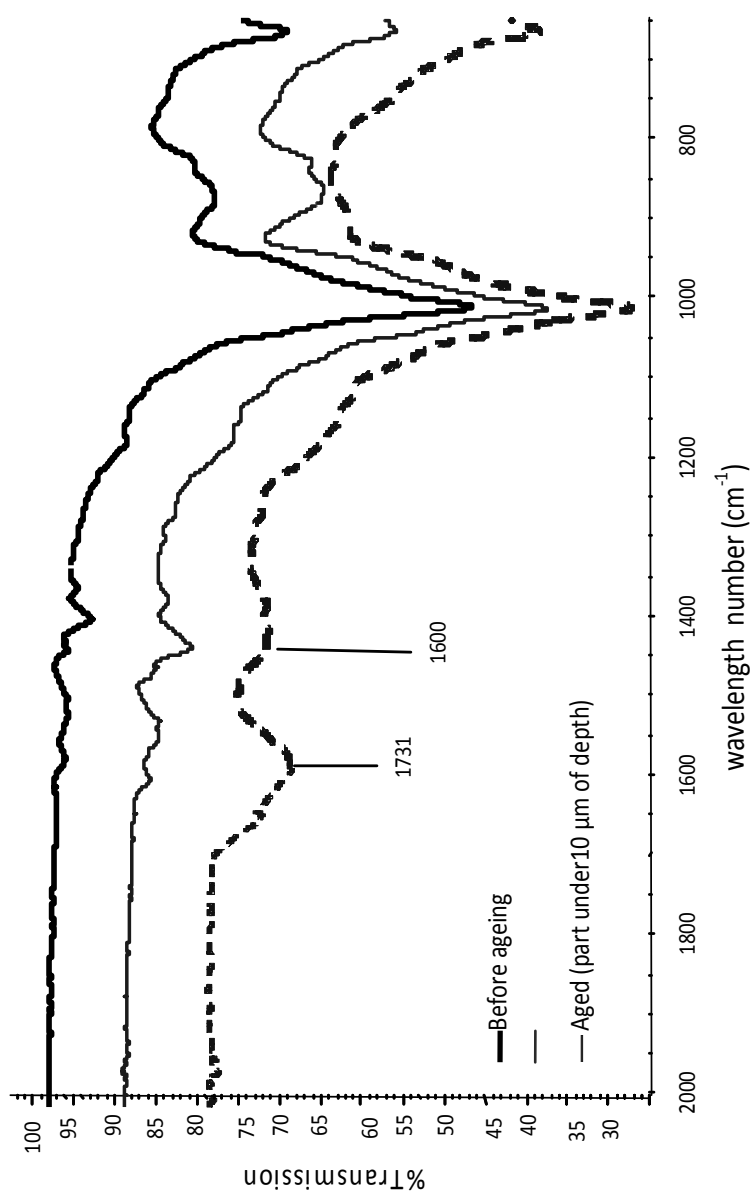


Figure 25.3. IRTF spectra in ATR mode, of surface parts of chlorinated rubber paint, naturally aged for 12 months in Florida and the part located at a depth of approximately 10 μm in the aged system

25.2.2. Ageing of polyurethane, urethane-acrylic and alkyd-urethane paint binders

The main absorption bands characteristic of polyurethane, urethane-acrylic and urethane-alkyd paints are reported in Table 25.6.

Wave numbers (cm^{-1})			Attributions
Polyurethane	Urethane-acrylic	Urethane-alkyd	
1,730	1,730	1,732	ν (C = O) ester
1,689	1,690	674	ν (C = O) urethane
1,634	1,648	1,652	ν (C = O) secondary amide
///	///	1,623	ν (C = O) third amide
1,524	1,520	1,550	δ (N-H) and ν (C-N) secondary amide
Absent	Absent	Absent	ν (C-O) ester

(ν : elongation vibration; δ : strain vibration)

Table 25.6. Attribution of the main absorption bands of the FTIR spectra, polyurethane, urethane-acrylic, and urethane-alkyd paints

The miss of some characteristic absorption bands observed is explained by the differences in the formulation. So the FTIR spectrum of urethane-alkyd binder (Figure 25.4) was used as a basis for describing the induced chemical modifications by the natural ageing on the three types of paints studied. According to the bands present on the spectrum of the paint before ageing, we observed five chemical modifications:

- stretching of the ester carbonyl band towards $1,732 \text{ cm}^{-1}$ with formation of a bump towards $1,800 \text{ cm}^{-1}$;
- decrease of the urethane carbonyl band towards $1,674 \text{ cm}^{-1}$;
- decrease of the intensity of secondary amide carbonyl bands towards $1,653 \text{ cm}^{-1}$;
- increase of the tertiary amide band towards $1,623 \text{ cm}^{-1}$;
- increase of the surface area ranging between $1,500 \text{ cm}^{-1}$ and $1,680 \text{ cm}^{-1}$.

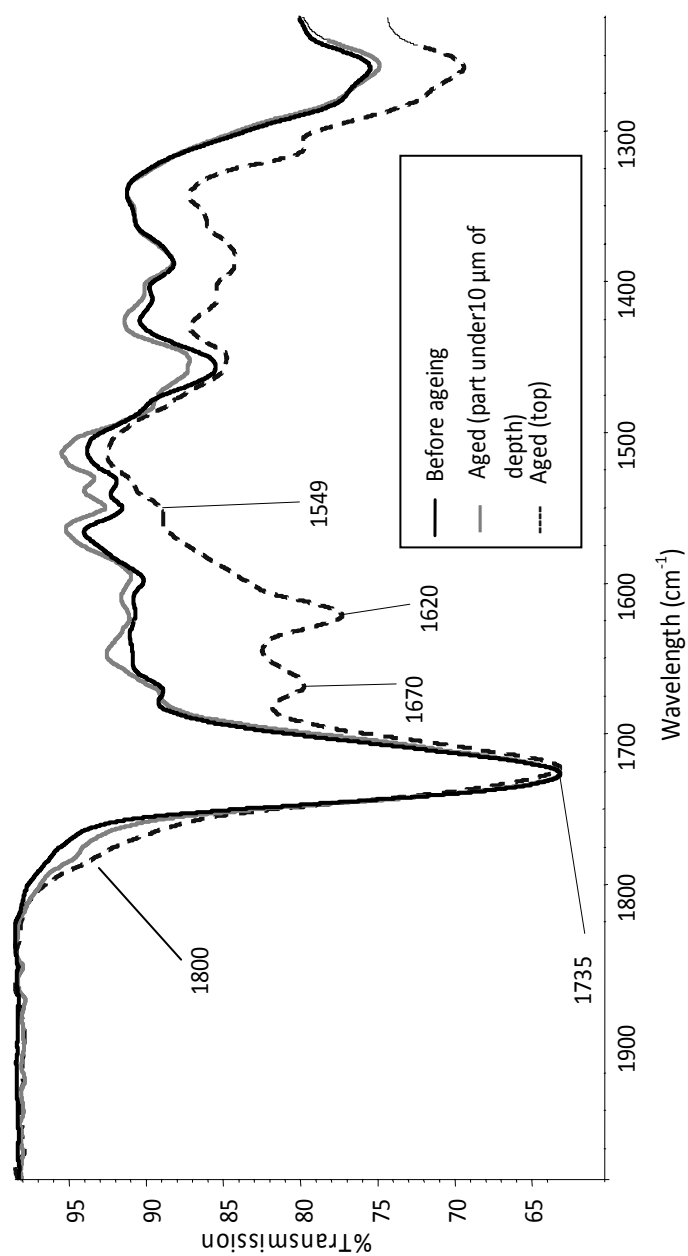


Figure 25.4. FTIR spectra in ATR mode for the surface coats of urethane-alkyd paint aged naturally over 12 months in Florida, and located at a depth of approximately 10 μm of the aged paint

The spectral modifications considered correspond to the photo-oxidation mechanism of the polyester-urethane polymers [WIL 97]. The carbonyl stretching band, and the appearance of a bump at $1,800\text{ cm}^{-1}$ characterize an oxidation in the binder, by the formation of carboxyl, carbonyl and acetyl urethane ($-\text{CO}-\text{NH}-\text{CO}-\text{O}-$) functions. The decrease of the urethane carbonyl band to $1,674\text{ cm}^{-1}$ highlights urethane degradation. The decrease of the secondary amide bands to $1,653\text{ cm}^{-1}$ and $1,550\text{ cm}^{-1}$ are explained by the break of C-N bonds, which leads to the formation of a precursory radical of an amide corresponding to the band at $1,623\text{ cm}^{-1}$ [ROG 85].

The FTIR analyzes for the paint located at approximately $10\text{ }\mu\text{m}$ under the exposed surface show differences according to the binder:

- for polyurethane paint, the FTIR spectrum shows that at a depth around $10\text{ }\mu\text{m}$, the binder tends to regain the same chemical structure as the non aged paint; however, the ester band at $1,730\text{ cm}^{-1}$, still hides the urethane-carbonyl band;
- for the acrylic-urethane paint, we note the absence of the massif, which includes the ester carbonyl bands ($1,730\text{ cm}^{-1}$) and urethane bands ($1,684\text{ cm}^{-1}$). On the other hand, although less intense than on the non aged paint spectrum, the band at $1,798\text{ cm}^{-1}$ (characteristic of calcite), becomes visible again;
- for the urethane alkyd paint, the FTIR spectrum performed at a depth of $10\text{ }\mu\text{m}$ is identical to that of the non-aged sample plate.

In conclusion, the FTIR analyses of five non-aged paint systems (each one in several colors) and aged for 12 months in Florida, showed that:

- the pigment does not influence ageing;
- whatever the nature of the binder, natural ageing causes an oxidation for the constitutive polymers;
- for the four paint systems studied, the FTIR analyzes in transmission mode, as in ATR mode, enable us to highlight ageing indices related to the photo oxidation phenomenon of a polymer:
 - the ageing of rubber chlorinated paint results in an increase in the carbonyl band towards $1,735\text{ cm}^{-1}$ and in the band at $1,600\text{ cm}^{-1}$;
 - the three other types of paint studied have the same chemical functions:
 - esters (towards $1,735\text{ cm}^{-1}$);
 - urethane carbonyls (towards $1,674\text{ cm}^{-1}$);
 - secondary (towards $1,652\text{ cm}^{-1}$ and $1,550\text{ cm}^{-1}$) and tertiary amides (towards $1,623\text{ cm}^{-1}$).

By considering all the chemical modifications detected in those binders made of urethane and ester functions, it is possible to draw off ageing indices which correspond to:

- formation of carbonyl functions;
- degradation of urethane functions;
- degradation of secondary amide functions;
- formation of tertiary amide functions.

ATR – FTIR spectrometry reveals that, for most cases, ageing only affects the surface part of the paint.

25.3. Organic admixture in cementing materials

As previously seen, in the third part of this work, rheological admixtures in cementing mixtures represent an undeniable advantage for implementation of these products, whether it is a question of concretes, mortars or grouts. However, we note problems of premature hardening when using water reducing plasticizer type admixtures, superplasticizer, admixtures for pre-stressing grouts, etc. To understand the reasons for these phenomena, the interactions between the superplasticizer molecules and the cement grains study was necessary.

The studies described here, firstly considered from the point of view of detecting “classic” superplasticizers in hardened concretes and, secondly, from the point of view of “new generation” superplasticizers characterization in the new type of concrete: high-performance concretes (HPC) or self-leveling concretes (SLC), first seen in France in the 1990s.

25.3.1. Evolution of “classic” superplasticizers in hardened cement pastes

Questioning the presence of admixtures in problems which may appear on public works (premature hardening, too long setting times, lack of mechanical resistance, etc.) requires us to establish their responsibility in a univocal way.

The first stage of this work consisted of leading a physicochemical characterization of the base superplasticizers, which is necessary before approaching the study of superplasticizers extracted from hardened cement pastes, in a second stage [MAR 97].

Three samples belonging to the three most commonly used superplasticizer families were studied:

- polynaphthalene sulfonates (PNS);
- polymelamine sulfonates (PMS);
- lignosulfonates (LG).

25.3.1.1. Characterization of superplasticizers

The FTIR spectrum of each admixture, enable us to differentiate the families, without any possible distinction between products belonging to a same family. On the spectra of each family, we will only look for the characteristic infra-red absorption bands reported in Table 25.7.

Chemical family of superplasticizer	Vibration frequencies (cm ⁻¹)	Chemical vibration	Chemical function
PNS	1,600 and 1,500	ν (C=C)	aromatic cycle
	1,444	δ (CH)	ethyl (CH ₂)
	1,356	δ (CH)	methyl (CH ₃)
	1,184-1,120 and 1,034	γ (S=O)	sulfonate
	829, 752 and 562	γ (CH)	aromatic substitution
	682 and 622	γ (S=O)	sulfonates in the PNS
PMS	1,555 and 1,485	ν (C=N)	triazine cycle
	1,360	δ (CN)	amine
	186 and 1,044	ν (S=O)	sulfonate
	810	ν (C=N)	triazine cycle
LG	1,600 and 1,500	ν (C=C)	aromatic cycle
	1,604	ν (CO)	carboxylic (COO ⁻)
	1,210 and 1,040	ν (S=O)	sulfonate
	651	δ (S-O)	sulfonates in the LG

ν : elongation vibrations; δ : strain vibrations; γ : swinging vibrations.

Table 25.7. Infra-red absorption bands characteristic of superplasticizers

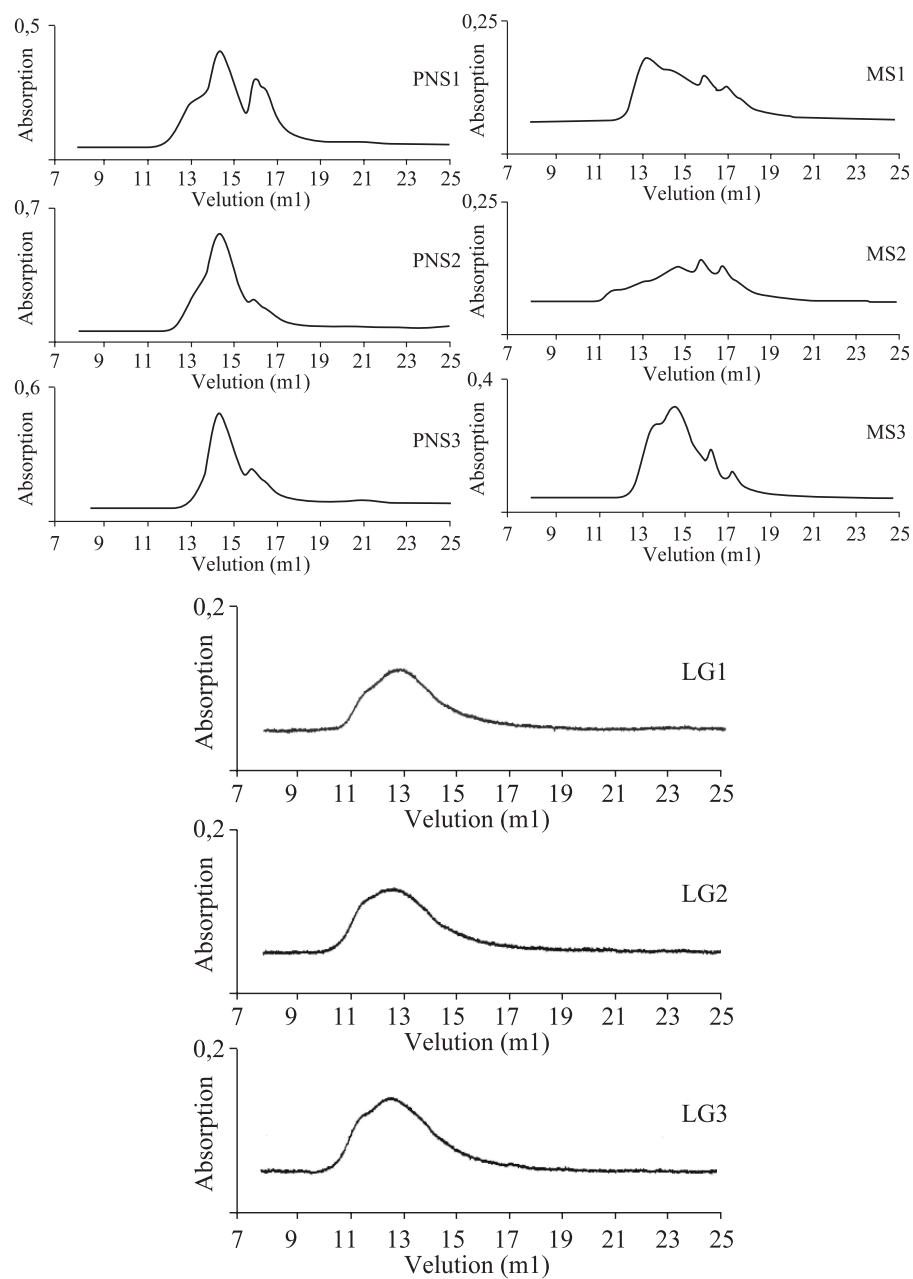


Figure 25.5. Chromatograms of commercial PNS and PMS

The FTIR analyses are not sufficient for a complete chemical characterization of the admixtures. The number of sulfonate groups and the polymer sizes are indeed mainly responsible for cement particle dispersion when in contact with mixing water [AFN 94, BAS 86]. The sulfonate group numbers were therefore determined by an acid-alkaline dosage and by sulfate ash formation, according to the French standard NF T 60-143 [FER 86].

These two methods, which lead to similar results, show that the number of sulfonate groups for PNS and PMS are comparable, with a rate around 60 to 70% which is higher than those for LG [MAR 97].

The best adapted technique for evaluating the size of macromolecules such as superplasticizers is steric exclusion chromatography (SEC).

Considering Basile and Ferrari [BAS 86, FER 86] work, we carried out SEC using two chromatographic columns, filled with a sulfonic divinylbenzene gel type, Shodex Ionpak KS 803 and KS 804.

In order to eliminate ionic exclusion, we used an acid eluent: orthophosphoric acid aqueous solution 10^{-1} M (acid used for extracting admixtures in cementing materials) adjusted to a pH level of 2 (at this pH, the anionic sites of polymers, and the chromatographic gel are in a protonic form). Under these analysis conditions, we did not get satisfactory separation of the LG.

On the other hand, the PNS and PMS chromatograms (Figure 25.5) show that within the same chemical family, the admixtures do not present the same distribution in molecular sizes.

25.3.1.2. *Detection and dosage by SEC of a PNS and a PMS extracted from hardened cement pastes*

Among all the analysis techniques considered (mass spectrometry, NMR, capillary electrophoresis), the steric exclusion chromatography in aqueous phase proved to be most interesting for studying “classic” superplasticizers extracted from hardened cement pastes (HCP) [MAR 97].

Chromatograms of extracted HCPs solutions, aged for 2 years in a laboratory, containing various quantities of PNS and LS, do not show any difference in the molecular mass distribution compared to the pure product. In the same way, the area of the chromatograms highlights that the selected extraction method, followed by a SEC analysis, enables us to recover up to 80% of the admixture mass introduced into the cement paste.

The SEC detection and quantification of the polymelamine sulfonates (PMS) extracted from HCPs, is impossible under the selected analysis conditions. This molecule is hydrolysed in basic medium. The polymelamine formed is insoluble in the interstitial environment [MAR 97]. Indeed, we have shown that the chromatographic response for a PMS solution to a pH level of 13.6 (pH of a young age cement), decreases by approximately 90% in one week. With the PMS being composed of molecules which contain nitrogen atoms, the dosage of total nitrogen by the KJELDAHL method, according to a procedure described in the French standard NF X 31-111, proved to be a relevant method to measure out 75% PMS in hardened cement pastes, after extraction following 21 months of natural ageing in the laboratory.

At the end of this study, we have access to a measuring method for classic superplasticizers in cementing materials [WIT 01] as well as a testing method which enables us to characterize the evolution of these admixtures.

25.3.2. *New generation admixtures*

Since the 1990s, a new type of concrete appeared on the French market: self-leveling concrete (SLC). These special concretes are defined as being fluid concretes, which stay in place just by gravitational effects, without need of vibration, even in very complex formworks. [SED 95]. The installation of such concretes requires the addition of particularly active “new generation plasticizers” which, while being added in low ratios, ensures a good spreading of the material at a young age.

In order to identify the active functions of this new superplasticizer, characterization tests according to standardized procedures were carried out on ten commercial “new generation superplasticizers” [FAR 07]. FTIR spectrometry has proved to be best adapted method to distinguish admixtures according to the functional groups which ensure their fluidifying effect.

This technique, compared to data reported in literature [CAL 98], [HAS 99], has made it possible to characterize superplasticizers, such as methacrylic ester copolymers or acrylate (according to the medium where they are located) on which poly(ethylene oxide) (uncharged) or poly(ethylene oxide) groups are connected. The main absorption bands present on the FTIR spectra of analyzed admixtures are reported in Table 25.8.

Vibration frequencies (cm ⁻¹)	Chemical vibrations	Chemical groups
3,440	ν (OH)	residual water and hydroxyls
2,800-3,000	ν (CH) ν (CH ₂) ν (CH ₃)	methines methylenes methyls
1,731 and 1,729	ν C=O	esters*
1,719	ν C=O	carboxylic acids
1,581 to 1,568	ν (O=C-O) ⁻	carboxylate
1,456	δ CH ₂	methylenes
1,351	δ CH ₃	methyls
1,250	ν CO	ether (ethylene glycol)
1,102	ν C-O	ether oxyde

ν : Elongation vibrations; δ : Strain vibrations

* Only for some polycarboxylates

Table 25.8. Attribution of the main absorption bands of FTIR spectra for (poly)ethylene polyoxide and polycarboxylates superplasticizers

FTIR spectrometry gave prominence to highlight the fluidifying chemical functions of “new superplasticizer” which are ensured by poly(ethylene polyoxide) chains grafted onto a polymer which contains carboxylate groups [CAL 98], [HAS 99], meaning poly(ethylene polyoxide) chains which generate steric repulsions, therefore prolonging the fluidifying effect. The presence of carboxylate and carboxylic acid groups in acrylate and methacrylate in superplasticizers does not exclude the presence of ester groups [DUF 98], [YAM 00]. Indeed, these functional groups are sometimes highlighted by the presence of absorption bands at 1,731 cm⁻¹ and 1,729 cm⁻¹ for admixtures. These absorption bands for the ester functions hide the carboxylic acids characteristic bands.

25.4. Conclusion

Although a direct relationship between the rheological or mechanical characteristics of materials and their chemical structure cannot always be established, undertaken studies show that a modification in material behavior goes always with a chemical structure modification. Therefore the chemical characterizations described in this chapter are important studies for the understanding of the materials' use properties.

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PART 8

Organic Materials, Construction, Architecture,
Creation and Sustainable Development

Chapter 26

Organic Materials and Sustainable Architectural Design

26.1. A context of accelerated evolution

Today, architects and engineers engaged in materials specification see the times of stable progress recede and enter an era of upheaval; a period which cannot simply be envisaged but must be faced head-on.

26.1.1. *Post-war practices*

The idea of our constructed framework is broadly the result of post-war values and practices. The urgency for reconstruction, decolonization and rural depopulation was based a quantitative and collective vision of housing, where the philosophy of the “Modern Movement” gave an architectural coherence. Until the first warnings from the Club of Rome, no one doubted the permanency of this model; optimal solutions were stabilized; and industrialization was presumed to ensure standardization and generalization to each one and everywhere. The economic prosperity of *the glorious 30* could only anaesthetize the internal criticisms of this system. Flagship materials were those which lent themselves to centralized mass production: precast concrete, laminated steel, float glass, etc. in their most elementary form, were considered as a gauge for honesty, in terms of aesthetics. Organic materials – natural or synthetic – if they were available at the scale of furniture, were still marginalized in the building industry: wood was associated with

Chapter written by Michel PAULIN.

regionalism, plastics were relegated to substitution functions. Secondary trades were still operating in ways which conformed to pre-war practices, and related documentation from architect or engineer offices could be held in two or three folders! In the 1960s, only a few held on to developing architectural designs in plastic, inspired by futurist industrial design and organic formalism; this, however, had no real impact on general production.

26.1.2. *The first oil crisis*

The uprising of May 1968, then the first oil crisis, helped to refresh this situation by the combined effects of the demand for individual recognition and the awareness of the fragility of collective systems. In architectural domains, we then dared to return to the baroque period, calling it “post-modernity”: in the urban design stages, we stopped using bars and towers and went back to individual housing, following the leading of the so called *chalandonnettes* (individual housing promoted by the French minister A. Chalandon). The first rules for construction, exceeding the most basic demands for sanitation and safety, seemed to only lightly touch on matters of insulation. It is remarkable to think that, in France at this time, the requirement for open tenders for public projects included the concept of contractual obligation of results for the first time by law.

This contextual turnaround led to the appearance of new products in finishing works to produce coverings, insulation or even walls. This was the explosive appearance of gypsum board, wood particle partitions, expanded polystyrene board, semi-rigid glass wool, etc. and also timber framed houses. Equipment became more complex: all electric heating, double glazing, controlled mechanical ventilation and air conditioning which need more air tightness of facades, etc. Synthetic organic compounds gradually found their place in these new buildings, either as wall components or for equipment. But we must point out that the system was once again fixed on these techniques, that innovative efforts made in the name of “war on waste” began to peter out, and that a number of promising solutions – such as heat pumps, solar collector or parietodynamic insulation – only benefitted disappointing constructions and did not find their place on the market as hoped. The material “hyper-choice”, forecast in the 1970s and which seemed to be natural consequence of industrial development, was finally stabilized (if only a little) in the building sector, unlike others such as the industrial design, car or aeronautic sectors.

26.1.3. *New modernity and heritage*

Nevertheless, the stylistic freedom introduced into architecture by rejecting old functionalist ideals promoted all shapes, expressions and contrasts. For example, the

impossible dream of taking down walls calls more and more upon glass wall structures: the famous “transparency” of facades, partitions and roofs. The relatively low price of oil helped us to accept the enormous heating or air conditioning costs incurred. In the wake of Bilbao, each city wanted to see itself as a symbol of modernity through buildings which were more livable sculptures than pieces of architecture in the accepted definition of the term.

Naturally, in this maelstrom, the need to safeguard our roots, led to a new surge in valuing heritage, sometimes to the point of obsession: this was the notion of “everything is heritage”, which made cohorts of preservation associations rise up against even the smallest projects which may have disturbed the reassuring frames of reference which we had always leant on.

The incidence of one or other of these tendencies on materials utilization is remarkable without being radical. The need for new skins led to some spectacular experiments: titanium cladding, exterior wall panels in ABS, composite shells, etc. But globally, even if wood was to develop, coated or deactivated concrete, and glass last the biggest players on the wall market. Similarly, reconstruction and renovation materials were not as developed as the passion for heritage allowed seeing as regulations and the doctrines of cultural authorities held on to “identical” restitution so tightly.

Thus the contribution of organic building materials was evident in more and more sophisticated wood derivatives, in new adjuvants, paints, coatings, screeds, rigid or flexible structural composites, membranes, sheaths, ducts and pipes, all more and more specific, simple or double glazing windows, not forgetting the progress of glues and mastics, etc. In short, a whole range of visible or hidden products which greatly changed equipment and finishing, but which abounded with no real concern for environmental consequences, for their manufacturing as much as their application, due to the framework of standards having mainly a “zero defect” objective.

26.1.4. The era for sustainable development

Finally, there was a societal shock to make us understand that the new millennium would not turn out to be the hoped for golden age. Globalization, the emergence of new economic powers ramping up consumption; and the impossibility of longer denying mankind’s impact on the environment and climate change changed the order of things. Demands for ecologically sustainable development featured strongly in buildings design, likewise in their components conceiving. From then on, our obligations, both moral and legal – made us to record and report the impact of our choices at every level; on energy consumption, greenhouse gas

emissions, pollutant diffusion, health risks or even balancing economic and local development concerns. Although universal acceptance of this process has been slow (let us not forget the refusal of the biggest consuming powers to adhere to the Kyoto protocol), more and more national and local limiting provisions are being put into place. In France, as the building sector is responsible for more than 45% of primary energy consumption, and more than 25% of CO₂ emissions, this sector must make a particular effort. Regulation exploded, all while changing form and is now more concerned with results than methods; with a noticeable ambition to make up for lost time. Therefore, in 2020, we should be able to produce housing with positive energy! This calls for new practices from designers and a new approach to materials and products.

26.2. New designer practices

Whether working as an architect, as a consulting engineer, or as the numerous creation and control professions from the building sector, the current designer is often subjected to, or adopts, essentially new procedures. First of all, he is committed to forming strong partnerships with others, meaning he is obliged to update his methods with more systemic thinking. Next, he is constrained to define his product in terms of performance, with regard to sampling resources and to demonstrate its longevity, including the construction's end life. Also, he is confronted with an array of materials which are constantly undergoing a process of renewal and update, coming from extremely various production structures. Finally, with free market competition, on the one hand, and a rise in the regulatory compliance requirements on the other, his authority is contested more and more and he must be engaged *vis-à-vis* his responsibility when faced with a lawful and plentiful normative arsenal. All this leads him to consider each project at all angles; from environmental compatibility to how features of each device employed may encourage the user to adopt sustainable practices.

26.2.1. *The revival of the systemic approach*

The legislation governing public contracts, also adopted by many private developers, followed by the introduction of multiple experts, controllers and obligatory consultants, without forgetting the recourse to subcontracting, forces the designer to develop new skills in complex tool-aided communication, for collecting information to be integrated as well as to explain his choices. He, then, rediscovers the virtues of systemic methods whose architectural application was developed by certain research teams in the 1970s; but these must be readapted to integrate different fields, as various as technical devices, energy circuits, user practices or natural environment characteristics. This systemic approach applied to the field of

modern materials – and particularly organic materials – coincides well with their manufacturing processes, which give very wide ranges of specific products coming from relatively very few bases.

26.2.2. Performance design

It is, then, for a large part, this “compound” practice which is known as the development of performance design procedures. In the perspective of sustainable development, benefiting from a large manufacturer reactivity and faced with open, globalised competition, it is no longer possible to prescribe *a priori* a particular product; we must make out a specifications list which emphasizes the expected effects of implementing this product, both short and long term, over its initial characteristics. This presumes a new skill is employed by the designer: a more fundamental understanding of material structure, more attention to environmental effects, greater awareness of time factors (beyond the only duration of legal civic responsibility), and, as always emphasized, the ability to acquire information. This is obviously very complex, because the mass of documentation is high, often blurred or contradictory; or even restricted due to commercial secrecy or from the inevitable ignorance due to the novelty of these processes. The obligation, on an international level, for transparency and traceability on synthetic materials (thanks to the European REACH program), is a testament to this vital need for the products’ visibility. Moreover, the spread of construction-maintenance contracts attests to this need to be engaged during a building’s entire lifespan. Yet, all this is only an additional demonstration of replacing a culture of methods by a culture that yields results for all levels of society.

26.2.3. Responsibility evolution

During this time when it is no longer possible nor desirable to resort to his accustomed material choices, the designer often finds himself having to assume sole responsibility for a new application. The question of guarantees then arises in a crucial way, like a powerful brake on innovation. When the norms DTU and AT are no longer appropriate, ATex procedures and others, or an understanding attitude on behalf of insurers still remains! For this reason, organic materials raise particularly crucial questions. Indeed, contrary to iron, steel, cement or glass production, their broad spectrum extends from composites made from the most complex polymers from petrochemistry to the most crude plant waste; *ipso facto* their manufacturers operate on different scales, from large multinational industrial companies to small artisans, or associations. The levels of information transfer are then extremely distorted and difficult to manage, by a single unit of design. It is therefore normal to see a classification and labeling system developing amongst professionals, as

already exists in companies from the BTP, and new specialties will probably quickly appear in their interfaces. With the question of guaranties, the question of payment must be asked: how can we value a service at the beginning, when it will only be evaluated in time by its results?

26.2.4. *Legal complexity*

As for the legal and normative arsenal, this is increasingly difficult to follow in real-time, despite the expansion of supporting information. This is due to several factors, including the emergence of precaution principles, the multiplication of statutes and their rise on a supranational level. The public tendency is to call more and more on authorities to assume responsibility for risk, at the same time limiting in situ innovation and experimentation. Arbitrating this contradiction inevitably involves multiple inconsistencies, reversals and exemptions. Naturally, in this context, all kinds of intermediate levels of reference texts appear, from all kinds of unequally represented groups, acting in domains with variable ranges. This goes from simple guides to good practices, to decrees and laws, while passing by a whole range of recommendations, approvals, labels, norms and directives. Moreover, such text, purely advisory in nature, will become obligatory within such market, driven by such stakeholder. If we add to this the need for harmonizing regulations on a European or even a worldwide scale, we are faced with the coexistence of different texts with identical purposes, the existence of texts which are transposed or being transposed, the acceptance foreign texts, etc. without mentioning the confusion caused by the certification frauds practiced on large scales in less scrupulous countries. In short, paradoxically, the current designer finds himself having to make more choices when ever more constrained by regulation. In parallel, he must unceasingly record his procedures to demonstrate as well as possible compliance with the plethora of rules which are also quickly being renewed, and to protect himself against enquiries likely to emerge from all parts; hence the appearance of new professions ensuring interface functions, like project management supports.

26.2.5. *NTIC on projects*

Lastly, we should not neglect the impact of new modeling and communication technologies on planning and design procedures. The dazzling increase in computer power and the growing complexity of the systems able to turn data into products, have thrown traditional building design processes and the performance of their components out of the window. From now on, architects can access geometries which have been, up until now, reserved for artists. They can visualize them, test their light, and acoustic qualities. Engineers can handle their mechanical and thermal models; the manufacturer can evaluate their manufacturing processes and the costs;

the operator can anticipate maintenance, operating costs, replacement, etc. Therefore, orthogonality, verticality, modulus, etc, are no longer the basis of such projects. In the same way, the ability of changing instantaneously the project scale promotes new freedom, returning the responsibility for details which may have been overlooked in the past. Of course, this is dizzying, but these new tools may turn against their masters. Living in the virtual can make us lose sight of viability, quality of use, economic profitability; the feeling of complete power can push us to jump through hoops, and exploits which are not related to the matter at hand. But, inversely, it will allow for an amazing renewal of design, aesthetic and environmental concepts, as soon as the decision chain is coherent with the concept of production.

26.3. New approaches to materials and structures

26.3.1. *A new status for materials in society*

Historically, materials have been directly involved in structuring society. As we know, for a long time, corporations have provided the heads of municipal authorities. They were distributed according to trades, each one working on a sole, or at least the main, material, whether gold for goldsmiths or lead for plumbers. This vision of materials is now completely scrambled. Projects must now be based on new images, or even build these images. In addition, constructions call increasingly upon material associations which attribute new performances, and exceed their usual identification. In particular, the spectacular increase of knowledge in physical chemistry makes project choices necessary on microscopic levels, much smaller than for traditional materials. As a result, measurements carried out in laboratories and experiments are becoming normal in project procedures. However, concerns to do with the concept of sustainable development are calling upon other ways of conceiving transfer functions or energy transformation which are of interest, one after the other, to all building structures, and this, over its entire lifespan, is even a matter when the structure is to be modified or destroyed.

26.3.2. *The lack of image for organic materials*

All in all, organic materials suffer from a lack of image. Admittedly, wood is universally identified, but primarily in its natural form. This is already less clear when we are dealing with lamellated, laminated, lathed, plied, pasted, derivatives. As for synthetic materials, they indistinctly fall into the category of “plastics” where only professionals recognize the different classes and families. This irrefutable fact is a serious handicap for the designer. Indeed, these materials are presented via particular finished applications, and not as suitable amorphous potentials for open

applications; so the designer will often find himself powerless to undertake a design problem from the beginning. Therefore, PVC – not to speak only of the most often used building plastics – is identified as being for pipes or window frames, largely catalogued, but not as a granule to be melted, spun, thermally shaped, guaranteeing resilience, more or less transparent, not propagating flames, etc. This is explained, of course, by the vast range of industrial polymers, the relative interchangeability of their appearance and the weak popularization of their production process. Here, we are touching on a fact which is as cultural as it is technical. It is up to the designer (more than the manufacturer's communication department) to contribute to creating this image by diffusing ranges of objects investing in the niches of applications which are familiar to the public, such as electrical household appliances, cars or leisure boats.

26.3.3. The specificity of composite materials

The rise of composite materials, and more generally a “compositional approach” to materials, changes their relationship with the designer as well as the user. Indeed, composites, understood in the broadest sense, rarely exist alone; they are only made in the framework of a particular project. The close collaboration of materials is an important part of the considerations and decision making in the project's process, a process which requires more collaboration and transparency on behalf of the partners. The compatibility of the components, the mixture's operational viability, and predicting resultant properties are factors which are often unknown, not labeled, and may be completely experimental. It is, however, a very promising way of renewing the store of materials, in particular by new associations considered exclusive up to that point, such as organic and mineral, hygroscopic and inert, thanks to glues, welds or binding agents. In parallel, composites – whether coming from high or low technology – are not easily decipherable, precisely because they never show anything but their skin, which hides their internal structure, itself mysterious to the observer. Moreover, they present incongruous properties with regard to their appearance, their dimension or their reaction to strains: a fabric may be perfectly rigid, a pole may support a heavy mass without buckling, a plate will escape your hands, its lightness being so surprising, etc. But still, an education process is underway, which depends on the quality and popularization of the composite items and their applications.

26.3.4. Double approach: low-tech and high-tech

In the context of sustainable development, applying organic materials to architecture is a matter of two radically opposing approaches.

On the one hand, industry is now able to produce very chemically elaborate, synthetic materials – albeit expensively – but with a very high level of efficiency, which leads to important “collateral” savings on the constructions and their associated operations, such as reduction of weight, of thicknesses, of assembly and finishing complexity, reducing maintenance costs, increasing recyclability, etc. On the other hand, we are rediscovering traditional organic materials or industrial by-products of low value; their properties are scientifically reevaluated and we are revising their use ranges, so as to make them perform as well as possible, while weakly resorting to new material and energy resources.

These two approaches go together and, even if their followers are often in conflict with each other, they are contributing to the same goal: maintaining the quality of the built framework, while reducing its environmental and social costs. For designers who are independent of these circles, synthetics are difficult to implement, because, as we stated previously, the domains where these material families exert their control are often impermeable to each other.

26.3.5. Irruption of the nanoscopic scale

Another radical change in the approach to material lies in the fact that nanotechnologies have opened up a field of knowledge which was completely unheard of until recently. We know now that the properties of very small quantities of matter have no correlation with those in large quantities. Hence the development of nanochemistry, the opposite to a traditional chemistry which deals with large masses and makes great use of non renewable resources. By using processes which are often inspired from the living: grafting, germination, sowing, etc. we can produce microstructures, thin layers, filters, etc. with radically new properties. For now, knowing how to use these is more a matter for research laboratories than for independent engineering consulting firms, but the results are available and only need to find their application domain.

26.4. What are the hopes for architectural creations?

Organic materials constitute an immense potential for the architecture of tomorrow, perhaps the most important. They are finding, and will continue to find, their place in each great subsystem of the construction domain, whether it is a question of structure, enclosures, or the associated equipment and supplies. Dealt with correctly, they offer interesting alternatives with regard to sustainable development in relation to traditional mineral materials.

26.4.1. *Organic materials and the structure of the buildings*

Wood is obviously the first renewable organic material for building structures. Its place in the construction industry is increasing. Thanks to the various techniques of decomposing/recombining its fibrous matter and the progress of glue, its performances are improved and stabilized, which has allowed us to extend its use, from great constructions to medium-sized buildings. Its resistance in relation to its specific weight puts it in a good position with respect to other structural materials, such as reinforced concrete and steel; it generally has a gain over foundations and handling. Moreover, being less conductive and less dangerous with regard to fire (in any case, in strong sections) than the other materials mentioned, it can be left visible and therefore lends itself to a set of combinations which are more varied with other walls. Its technical and plastic modes of expression are extremely varied, from strict machining of laminated wood to rough masonries of cordwood. The collaborating structures containing wood are now in use, whether wood plays the part of a compressed mass associated with metal strengthening agents or synthetic materials, or whether itself, it is the tensor associated with various concretes. Research continues in this field. For each one of these applications, it is advisable to choose qualities of wood according to the stresses which they will have to undergo in order to save the noble species, allowing us to manage forest stocks as well as possible. Lastly, it should be recalled, that used in large quantities, wood constitutes a “carbon well”, which postpones the release of CO₂ in the atmosphere.

Organic materials occupy other essential niches in the structural domain. Framework profiles made from composites allow for a complete renewal of the carpenter’s plastic vocabulary, replacing forms coming from industry with the register of organic. The same applies to applications of cardboard – waterproofed or not – in multiplied, self-supporting panels, tube lattices from recycling, etc. We should also not forget that organic polymers make use as components in high performance concrete, such as plasticizers, strengthening fibers, varnishes, anti-tags, etc, giving them more resistance, workability and at the same time, reducing the quantity being used and the need for additional structures.

Multiple kinds of natural fibers are tested, such as “green concrete” matrix strengthening. Taking rubber variants, they are resilient and insulating aggregates for screeds and coating technical soils; these rubbers may come from worn tires, therefore contributing to solving the serious problem of eliminating this type of waste. We are, however, still very far from exploring all the properties which come from the association between polymers and concretes, particularly on a nanometric scale; we are waiting for a new launch in concrete structure technologies, perhaps with consequences for architectural expression as great as those at the very beginning of the 20th century.

Since we no longer only consider the grey energy absorbed by the structure itself, but in fact all the environmental impacts of the building in its location, it is appropriate to put forward the qualities of structural membranes. Their small volumes in work, their very light weight, their continuity on immense surfaces, their multi-functionality make them extremely powerful structures, whether they are made of coated textiles or by membrane films. They permit transparency, can be self-cleaning; thanks to the stability of fluoride polymers their resistance to UV and other atmospheric agents guarantees a durability equivalent to traditional structures. In single or double sheets, according to the required insulation, tensed on masts and ropes or by air pressure, they offer the designer an infinite range of forms, from now on controlled by image and calculation software. Exploitation the tensegrity principle means that it is still possible to reduce the proportion of compressed struts necessary according to their stability, struts which are *a priori* heavier. Their installation and disassembling are fast; recycling their materials is complete. Wiring and chandlery, themselves made from synthetic materials, contribute to lighter structures while avoiding corrosion, specific to steel.

26.4.2. Organic materials for building enclosures

Even more so than the structural domain, the enclosures domain lends itself to well to the expanding menu of organic materials. The heat and phonic insulating sector comes, of course, first of all. Even if expanded polymers still have a long life in front of them, their environmental disadvantages make them less and less preferable to more natural materials. Two ways are offered: insulation blocks, or infillings. The development of insulating supporting blocks associating a plant filler and a mineral or organic binder has already been developed. As for the use of straw or plant pulp, compressed or lightly bonded, such as studwork filling blocks, wall doubling panels, covers and coatings or simply in bulk, it is now current practice, even if its standardization has only just begun. These processes containing renewable matter, often agricultural or industrial waste, mobilize a very moderate amount of grey energy and fit into a short supplying circuit. These materials are more or less hygroscopic, which leads designers to rediscover the advantages of breathing walls, commonly employed in traditional architecture until the arrival and excessive application of artificial cement. They claim bigger thicknesses, which inevitably influence gross floor area of constructions. However, if we prioritize this preoccupation with thinness and high thermal efficiency, organic materials bring another type of response with carbon or carbonated silica aerogels, which, in addition to their extraordinary insulating capacity, also absorb infra-red radiation. Admittedly, these are expensive and brittle products which need to be protected, but they offer, on the other hand, immense prospects for wall applications, including bays, thanks to their relative transparency.

In this vein, we are contributing greatly to a large change in the architecture of bays. Confined for a long time in the window itself in the wall, the function contributing light to construction can now be proportioned and distributed in the whole or part of the wall, in the facade as well as the roof. Admittedly, the generalization of float and tempered glass is behind this evolution, which has not been without problems of heating and air conditioning costs, due to its poor thermal properties. But modern glasses are no longer exclusively mineral. On the one hand, we can improve their quality by the application or interposition of thermoplastic films, which reduce their fragility or their conductivity, making them self-cleaning or non-slip, even electrothermal or electrochromatic. In addition, we are substituting them with organic glasses, classically acrylic and polycarbonate, but more and more we are finding out how to make transparent polymers. The technology of extruding multi-alveolar plates meets the needs for insulation; thermoforming satisfies the wish for curved and soft forms; surface texture ensures control over insolation or simply decoration. PMMAs transparency to UV rays promotes interior plant growth, with associated benefits to air quality.

But the traditional window is not being left behind. It is also evolving thanks to organic materials, towards a better coherence with the performance of the entire wall. As a long-time primary surface for heat loss in winter, and responsible for overheating in summer, its situation is almost reversed when it is insulation augmented glazed and has frames made from synthetic materials. The latter – mainly PVC – was largely criticized for the increase in sections and its poor appearance. With co-extrusion, veneering, differential expansion, and composites, we achieve products which meet requirements for rigidity, insulation, self-cleaning, which have vast ranges of colors and textures. Admittedly, the increasing complexity of these products makes recycling at the end of their life more problematic, and their energy valorization remains the most economic; but the serious analysis of their life cycle shows that their environmental impact is limited and in any case lower than that for imported exotic wood, for example.

External skins also benefit from the qualities of organic materials. Roof waterproofing gains flexibility and longevity, thanks to bitumen and elastomer alloys. Their resistance to UV is increased by gel-coats. The spread of plant roofs – whose environmental virtues no longer need to be demonstrated – was promoted by the availability of membrane or corrugated synthetic underlayers able to retain water, filter, control rooting, while displaying great chemical stability with low thickness. Curtain wall, claddings and clothing make organic materials massively profitable: natural or recomposed wood, synthetic polymers in bulk or in coatings. In traditional implementations, wood aged badly outside, thus we were privileged with split wood and strong sections, or particular exotic wood. Thanks to pressure-sealing, cross-linking and hydrophobation techniques, we now have a local material which is not very sensitive to water and dimensional variations; resulting in new

esthetics. As for synthetic materials, fibrous or not, they allow us to manufacture extruded boards or thermoformed cassettes, which offer the designer a pallet of unlimited shapes and colors. Integrating insulations, on the one hand, and no-drop or anti-tag coatings on the other, limit the tasks of manufacturing and maintenance.

Interior design does not escape this tendency, with the return of panelling, ceilings and parquet floors made from sawn timber, or laminated particle board or extruded thermoplastics; with thin elastomers floor coverings, glued or cast, linoleums, stretch ceilings, aqueous paints, etc, they are all materials which benefit from improvements in their sustainability, their harmlessness with respect to interior air quality and their aptitude for being recycled and biodegraded.

As for cataloguing the organic material applications in construction equipment, there are too many to be listed here. Sanitary and heat piping systems, cable-making, electrical fixtures, optical fibers, etc, are already using organic materials to near totality. Bathroom and kitchen fittings largely rely on acrylics and resins which, thanks to fillers, may reach, and even exceed, marble or ceramic qualities, and can be molded in very large sizes, removing seams and infiltration. Equipment for energy and climatic means is progressively integrating more synthetic material components, amongst other things, thanks to the appearance of castable or injectable refractory materials. All this reduces the weight of structures, facilitates their assembly by adhesive bonding, thermo-soldering at lower temperature than for metals, eliminates corrosion, therefore also coating and maintenance. The difficulties encountered are still primarily due to fireproofing and recycling; the solutions for these two problems are difficult to reconcile, because the first needs the interdependence of their components, and the second their dissociability. But research is advancing nevertheless.

26.4.3. *For the future?*

We hope to go far. Where traditional materials may only have one function, and require to be added together to ensure a maximum total performance, materials to come will be poly-functional. Some of their properties will stay latent as long as external strains do not activate them. We already have electrochromic and shape-memory plastics, but we are beginning to develop self-repairing materials, whose vascularized microstructure releases, once broken, the catalyst which will trigger its re-polymerization. In the same way, in the domains of fixing pollutants or accumulation and controlling heat diffusion, where phase change materials can stabilize a building's interior climate, both summer and winter, without having to move considerable masses of capacitive materials. This should make it possible to reduce the problems of heating and minimize the need for air-conditioning. Architecture will obviously be changed accordingly. In a more general way, it is the

whole approach to materials, mineral as well as organic, which should evolve, taking with it a new relationship to the environment and to buildings. More and more, products should associate mineral and organics, one complementing or fixing the other, even in domains which appeared more reserved. In terms of equipment, users of renewable energy will undoubtedly use organic materials more and more; wind turbines, whatever their new shapes, but also photovoltaics – where we are actively researching a silicon replacement amongst carbon bodied – heliothermals or thermo-electrics.

Chapter 27

Specific Contributions of Viscous Behavior Materials in Construction

27.1. Introduction

Discussion of viscous behavior in the construction industry has appeared in the last fifty years. Indeed, calculations for structures and roadways have been based on elasticity for a long time, and for a large majority, still are. Engineers have previously used words such as creep, delayed strain, or rheology, but always without referring to a constitutive law. For example, if 1D viscoelasticity was present in Jean Courbon's teaching of structural analysis at the ENPC in the 1960s, it is only in Jean Salençon's teachings on viscoelasticity in 1981 that, in this engineering school, 3D viscoelasticity with structural calculations appeared. It also seems rather recent that a connection between the behaviors of extremely different materials, such as concretes, bituminous mixtures and polymers was made, particularly via seminars on rheology.

Let us remember that a fluid or a solid is viscous, or viscoelastic or viscoplastic, if, at least from a certain threshold, the stress tensor applied to an elementary volume of the material depends on its strain velocity tensor. The viscous character of a material, then, only comes to light when it undergoes a displacement velocity gradient, this velocity being either large or small. It has been noted in experiments that a viscous fluid, linear or not, adheres to walls while it flows. This is due to the physical interaction between the fluid's molecules or elements and the solid wall. In the construction industry, as in other industrial applications, the interesting (or

Chapter written by Bernard HALPHEN.

harmful) property of the viscous fluids is either their viscosity, or their adhesive strength, or a combination of the two. We will see further on how it is for solids.

In addition, the strain of a solid or a viscous fluid produces an energy dissipation; this deadens their own movement if they are not constantly strained, or the movement of the element that they are linked to; this property, commonly used in shock absorbers or vehicular hydraulic dampers, is the subject of certain construction applications.

27.2. The viscosity of fresh concrete: a property to be taken into account

Whether a specialist or not, but having seen a building or construction site, everybody knows that concrete is a mixture of water, cement and aggregates, and is poured as a liquid. Cement paste, i.e. the water/cement mix, and the concrete itself must have a sufficient and especially adapted viscosity so to meet the required workability of concrete, while respecting the specifications for the final construction.

Indeed, if the paste was a perfect fluid, without viscosity, the aggregates would instantly fall to the bottom of the formwork, and the additives would be totally separated from the mortar, which is obviously unacceptable.

In addition, the viscosity of fresh concrete, after adding the aggregates to the paste, controls its transport and implementation. It is particularly in this domain, i.e. viscosity, or more generally the rheology of freshly-mixed concretes, that the research of these last thirty years has allowed for true technological leaps. Indeed, if minimal viscosity is desirable, when the concrete is cast between vertical walls and through the reinforcements, the adhesive strength of concrete on walls and steel (a consequence of its behavior) may obstruct its implementation and create vacuums in the final structure; hence the need for choosing a good material for the formwork, to insert formwork oil into it, and to vibrate the concrete. The oil, which acts as a lubricant here, must be well selected in order to obtain the expected result with regard to the quality of the structure facing.

The progress of these last few years in particular has made it possible to work out formulations for concretes known as “self-compacting”. These are not free from viscosity, but this one is mastered and controlled, so that they can fill the formwork without vibration, or be spread out over a horizontal surface without external contributions of mechanical energy. This is only obtained by formulating the concrete in a specific way, whether it is by its main components or its additives (Figure 27.1).



Figure 27.1. Casting self-compacting concrete
(Photo: <http://produits-btp.batiproduits.com>)

We note here that the viscosity of fresh concrete is inescapable and necessary, but it must and now can be controlled according to the technology used for building a structure, which obviously results from comparisons between technical and environmental performances and costs of the various technical solutions considered.

From the first years of the 20th century, the development of reinforced concrete and the first processes of pre-stressing, engineers, such as Eugene Freyssinet, noted that hardened concrete undergoes slow delayed strains under constant compressive stress. It creeps, which is a characteristic of a material which has a certain viscosity. This viscosity, here, does not result from the same physical phenomena as for fresh concrete, and has a much higher value. The physical origin of concrete creeping is not yet completely clarified, and is still the subject of new publications. However it seems primarily related to the presence of residual water in concretes, more precisely to the motion of water at various scales in the matrix made of hydrated cement and various additives. This is, then, how the constitutive differences between traditional concretes and more recent high performance concretes, whose porosity is much lower, can be explained. Let us notice that the difficulties, due to the redistribution of the forces over time, that the first pre-stressed concrete works built by successive corbellings have known, are due to the ignorance or more exactly the negligence of delayed behavior in calculating these structures. Indeed, no one could continue to ignore this phenomenon, brought to light more than half a century

earlier, but it did not become part of the design codes until 1975, either because people were unaware of its amplitude, or because they believed that constructions would adapt to it. Taking this into account allowed to avoid structural problems encountered before. The viscous character of hardened concrete, then, is part of its intrinsic properties, and we know now how to introduce it into structural calculations; it is systematically studied and evaluated for any new type of concrete.

27.3. Viscosity and injection products

The use of injection for reinforcement is an old civil engineering technique. It can already be found in the construction of the Parisian subway at the beginning of the 20th century. A cement grout was injected behind the underground masonry, so as to fill the vacuums created by compactions due to the building process, and to coat the wooden formworks which were abandoned and thus to avoid their rotting. Such grouts are still used today, in particular to plug vacuums and ensure good mechanical continuity. For example, foundations of old structures are reinforced in this way. The rheological properties of grout are important for the good execution of these work. A too fluid grout will tend to run out by the interstices and generally be diluted into in situ water, but a too viscous grout cannot be injected because it will not be able to pass through the porosity. A right balance must, then, be found in the formulation of these grouts, as previously for concretes.

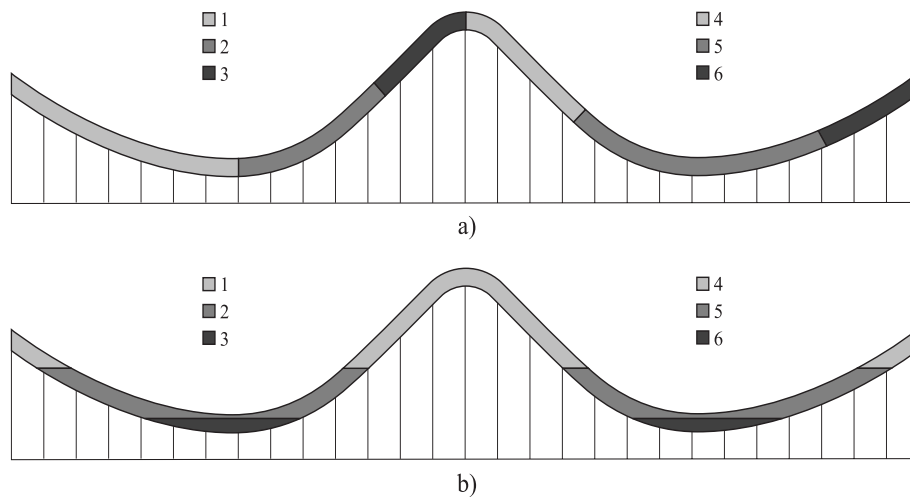


Figure 27.2. Progression (1, 2, 3, etc.) grout in a sheath of pre-stressing (according to [POU 05]): a) good viscosity grout; b) too little viscous grout

Grout injection in the sheaths of prestressing tendons aims to protect those ones against corrosion and, for this, to fill the sheaths by expelling the air and the water which are located there. A grout whose viscosity is too low runs out as a fluid with a free surface in the downward sections of the sheets, and therefore leaves water and air pockets for the future. On the contrary, a sufficiently viscous grout, while coating the tendon correctly, is able to fill the sheath and to expel the air and water (Figure 27.2). However, due to viscosity, the grout flow consumes energy. It should be formulated, then, so that its viscosity lets it be still injected. Here again viscosity is necessary but its value must be controlled.

Epoxy resins are used to repair the structures, in particular to clog cracks, and like glues for adhesive bonding of the segments of bridges built by successive corbelling, or to repair structures by glued plates.

Generally, these products can be considered as linear (or not) viscous fluids, in the liquid state in which they are implemented. Here the polymer viscosity in the liquid state will allow for a good adhesion of the product to the crack wall and a good filling of the crack. Indeed, this adhesion makes it possible for the polymeric liquid product to rise in a crack by capillarity, without the need to apply a large injection pressure. Then, this adhesion, which thixotropy is sometimes added to, allows us to maintain the product in the crack while awaiting its polymerization.

In the case of adhesive bonding, particularly along a vertical face, such as the end of a concrete segment, the adhesive strength and the thixotropy of the resin that is used allow it to hold in situ, while waiting for the second solid face to be glued by applied pressure.

27.4. Viscosity and self-repair

The majority of French roads are mainly made of bituminous mixtures. A vehicle axle locally produces the flexure of the roadway layers, thus creating tensile stresses at their base. Under the influence of traffic, these repeated tensions may cause the appearance of a fatigue crack which is likely to propagate to the road surface. Bituminous materials are, like their matrix, viscoelastic. If a fatigue crack or microscopic crack opens when the axle of a heavy truck goes by, it will be closed again, at least partially, before the next axle goes by. Indeed, if the roadway were perfectly elastic, the crack would be closed again completely; as it is viscoelastic, it does not always completely close up, especially in the small limited time between two axles passing by. The adhesive strength of the crack lips where it closes up again creates new bonds, and the material state then gets close to the way it was before crack growth. This is called self-repair. This property, which was clearly demonstrated in laboratory experiments, creates a lifespan which is far higher than

what we would obtain if axle flow was continuous. On the experimental front, this means that the results from the continuous laboratory tests cannot be transposed directly onto the real roadway. Self-repair is obviously related to the frequency of loads on a roadway, i.e. traffic concentration. This is, then, a parameter which needs to be taken into account in the design of a roadway, not only regarding the repetition and amplitude of the loads, but also their evolution over time, which involves, in particular, an estimation of resting time between loads.

27.5. Viscosity and absorption

In earthquake resistant constructions, the engineer's objective, if a "normal" structure does not resist foreseeable earthquakes, is to control the amplitude of displacements and forces in the structure. For this, a device which dissipates part of the energy transmitted by the ground to the structure is needed. Here, then, viscosity will take place in two different forms: it is either a component of the behavior of the material which makes the structure or its foundations, or it is introduced by means of additional shock absorbers.

First of all, a little viscosity is often present in structures, because of the material's behavior which makes the structure, and the bonds between its elements; this is generally insufficient. The first idea is, then, to separate the construction from the ground so that it does not follow its movement. Engineers then make the construction rest on an elastomeric bearings, similar to the bearings for bridges. This lengthens the system's fundamental period, and therefore moves it away from those contained in the earthquake's spectrum, but the strains are still important. Therefore more or less viscoelastic elastomeric bearings have been designed, including a central lead stud (*Lead Rubber Bearing, Robinson Seismic Ltd*). Lead has viscoplastic behavior and its alternate strain can dissipate part of the earthquake energy. In addition, there are other bearing devices which implement shock absorbers, placed horizontally at the level of the foundations.

In certain industrial buildings, for which there are no questions of geometric obstruction, shock absorbers are placed diagonally in certain wind-bracing planes; this is, then, a way of introducing shock absorption on the level of the structure itself.

For very high building, the solutions proposed above are insufficient. Moreover, it is necessary, in certain areas of the world, to not only guard ourselves against the effect of earthquakes, but also against violent vibrations due to the wind. This is the case, for example, for the highest tower in the world (before the one in Dubai is finished and in use), namely the Taipei 101 tower in Taiwan, finished in 2004: 101 floors and 508 meters high. This area of the world is often subjected to earthquakes,

but also typhoons. To absorb oscillations due to the wind, a sphere of 660 tons is suspended inside the building, between the 89th and 92nd floor. A support welded onto the sphere connects it by cables to the 92nd floor, and the movement of this support, and thus of the sphere, is absorbed by using eight hydraulic cylinders. These jacks dissipate energy into heat. The designers predicted that the maximum amplitude of vibration in the tower would be divided into three. In addition to this system, two absorption devices, 7 tons each, are located on the 101st floor. This system, of exceptional dimensions for this tower of record height, finds, in Japan for example, many analogues, often located high up, in high towers, to absorb earthquake induced vibrations.

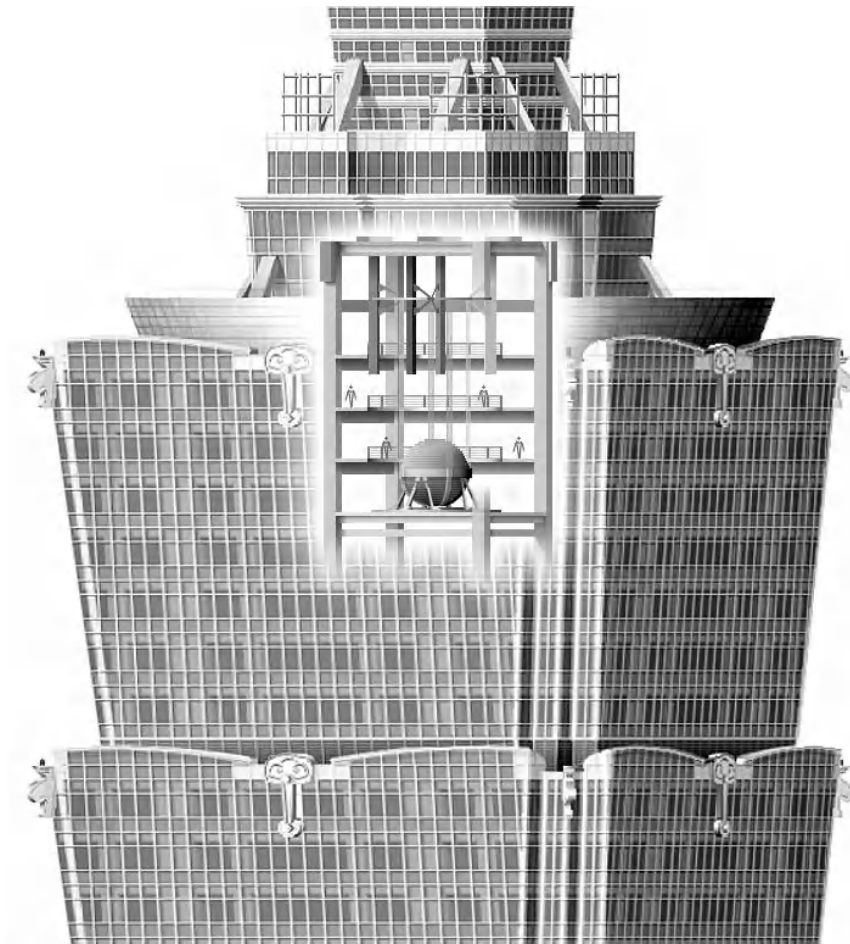


Figure 27.3. *Suspended sphere in the Taipei 101 tower*

The system which works for sky-scrapers is also applied, by adapting it in a specific way, to all high, thin structures, such as the factory chimneys for example, or certain water towers.

To deal with vibrations due to trains or subways in buildings, various insulation methods may be proposed. Among those, we find the installation, in vertical and sometimes horizontal walls at the foundations, of a material which absorbs the vibrations, and displaces their spectrum. This is the case, for example, of Regupol®, which is presented as a set of plates made from rubber granules or fibers in a polyurethane binder, therefore a composite made of viscoelastic materials. The heterogeneous structure of the material in conjunction with the viscosity of its components means that the double objective may be reached.

It is often necessary to absorb vibrations in cable-stayed bridges, when they are, like the Saint-Nazaire bridge, in a location where strong winds may occur; currently this is done via absorption devices similar to those for a vehicle, whose absorbing property is related to the movement of a viscous fluid. The main disadvantage of such a process is its visual obstruction. Could we not find a different and more esthetic solution? For this, it would be necessary to insert the absorbing element inside the cable sheath.

We can conceive injecting a fluid which is solidified at room temperature into the protective sheath of the cables, in the form of a soft solid, with high viscosity, and protective with respect to the cable, i.e. properties of long-lasting filling and adhesive strength, not reacting with steel and protecting it from corrosion, which we may look for among polymeric or bituminous suspensions. It is known that among the first pre-stressed concrete structures, some have external, pre-stressing cables protected by a coat of bituminous product; it is observed that these cables did not suffer any damage. In addition, the composition of the cables themselves is likely to evolve, and it is clear that for non-metal cables in particular, questions of corrosion may arise in other terms, and the protection-absorption coupling would probably be simpler to achieve.

In the maritime domain, it is necessary to protect certain coastal installations against the effects of large swells. Protection against the effects of waves or the modification of its characteristics, currently relies on the construction of rigid, concrete or rock breakwaters. Is it not conceivable to dissipate part of the swells energy through a viscoelastic system transforming the mechanical energy into heat, which is possibly salvageable. Even if it is necessary to refine this idea by calculations, we can imagine replacing a rigid wall by elements connected by a thick viscoelastic joint. Therefore, the structure would not just change the swell, but would also decrease its energy.

27.6. Conclusion

We have been able to see that viscosity plays a large role in construction techniques, as well as in the behavior of the structures. This place, ignored for a long time, which mobilizes all the angles of viscosity, has expanded and will continue to do so, with the evolution of construction materials on the one hand, and with that of techniques, increasingly concerned for environmental protection and control of natural or anthropic risks.

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Chapter 28

Organics in Construction – How Far?

It was now a long time ago that “plastics” invaded the world of design. So much so that Philippe Starck, our uncontested champion for this type of creation, was worried not so long ago about the end of oil, well rather, about its noblest use, for making “plastic”. No more oil, no more plastic thus, at least as we know it. At first sight, there is really a need for panic. Plastic is everywhere. There is not a bathroom, kitchen, dining room, table, chair or “trendy” light which does not use Corian®, PMMA or PU. How could we possibly go without it? Philippe Starck should reassure himself. Despite deafening, alarming speeches, for a long time still, we will have 5% of the oils used for manufacturing this incredibly multiform and multipurpose matter called “plastic”. For the moment, we have no way of looking for alternative sources, to recycle it, or to minimize its impact on the biosphere, particularly on human health.

Can polymer materials in the world of civil engineering, or more generally, in construction, acquire a status as domineering as they have in the world of design? *A priori*, this hardly seems probable. Alone, the volume of concrete used each year in the world (1 m³ per resident roughly) already exceeds the volume of oil produced. Of course, a tense structure made from geotextiles is infinitely more economic in matter than the thinnest concrete veil, and we do not build with one the way we build with another [DRE 08]. But the pressure on fossil energy sources is such that it is fantastical to think about using a very substantial part of these resources for construction ends, at least so much so that alternative energy sources may not be operational on a large scale.

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In these conditions, what developments can we envisage, in light of recent achievements or research in progress, whether they come from architects, builders, industrialists or from laboratories? Upon reflection, and this is the point of view here, the privileged domain for developing polymer materials in construction could well be building envelopes, particularly in urban environments [UFF 08].

What is really the surface area developed by a city like Paris, or Shanghai, for example? Five seconds of reflection suffice to realize that the real surface area, exposed to the atmosphere, vertical or horizontal, has nothing in common with the ground's surface. This enormous surface area attributed to building envelopes, including roofs, in the current state of architectural design, is not used to its full functional purpose. Its first role – and this is, clearly essential – is structuring space and manipulating light. But this is a passive role. Moreover, whatever the material concerned, the surface gets dirty, ages, and is the main source for maintenance costs.

This situation is in the process of evolving. With growing attention paid to surface qualities, the materiality of envelopes is disappearing in place of the image that it transports, and the functions that it has. In this evolution, natural or synthetic polymer materials, are not alone in the running, but in terms of multi-functionality, these are the materials with the most positive attributes to be valorized. Let us put some of the functions back into order which have recently been integrated into the building envelope.

28.1. A structured, decorated and communicating skin

The massive arrival of curtain walls in the construction industry, especially tertiary, has doubled by a minimalist tradition with regard to decoration. Recent developments, in particular with the use of a “double skin”, represent a trend reversal. Practically all surfaces, from aluminum to concrete, and passing by steel, wood and polymers, have become structurable and printable.

Concrete is particularly spectacular. Using ultra-high performance concrete fiber, whose implementation would be impossible without last generation superplasticizer admixtures, allows lattice envelopes whose smoothness not so long ago would have been considered incompatible with material.

The project for the Museum of European and Mediterranean Civilizations in Marseille, (architect Rudy Ricciotti) is a good example. Even monolithic concrete surfaces are decorated with photographic type decorations, not by printing inks or pigments, but by micro-structuration using set-retarding admixtures, according to a technique developed by photographer Thomas Ruff [WIL 06]. This is the case for

the library at the Eberswalde technical school, about 50 km to the east of Berlin, whose architects are Jacques Herzog and Pierre de Meuron.

However polymeric materials offer the most possibilities for decoration and, especially, communicating. The envelope for the Allianz Arena, the Munich football stadium, in a very large sized example. The envelope, made from ETFE/EPDM, can light up the colors of the lining up teams. Apart from the decorative effects accessible to other materials, polymers authorize without too much difficulty the introduction of photochromic or electrochromic properties, by including photo or electro-active molecules into the mass; or still including light emitting diodes (LED), possibly implemented using semiconductor-polymer junction (OLED), for example Novaled® from the *Fraunhofer Institute of Applied Polymer Research* in Germany; or the introduction of liquid crystals into polymeric matrix pores [RIT 07].

28.2. An energy collecting surface

Cities are currently an extremely energivorous environment, unable to guarantee its own subsistence, including food, and unable to internally manage the waste it generates. These are not just a few micro wind farms, or a few tens of m² of photovoltaic panels per building which will restore the balance. Even with optimized equipment, roof surfaces are manifestly insufficient.

A notable progress could be accomplished by using the envelope's whole surface area to collect ambient, solar or different kinds of energy. The most spectacular recent progress in this domain is probably the introduction of transparent photovoltaic glazing. A particularly impressive achievement is the Sharp factory, in Kameyama, Japan. Equipped with a total photovoltaic power of 5.41 MW, including 5.21 for glazing and 0.20 for the roof, this factory of 330,000 m² accumulates an impressive number of innovations, such as electrical energy storage in superconductive loops, or electric production by high power fuel cells at high temperature.

The transparency of photovoltaic glazing can be only be acquired at the price of a notable output loss, but this is more than compensated by increased usable surface area. The key to this success resides in abandoning traditional photovoltaic cells made from mono or polycrystalline silicon or amorphous silicium, and moving onto thin layers of semi-conductive alloys on glass substrates. Nothing prevents us from extrapolating this technology to the totality of building envelopes, provided that an adequate substrate is identified. With glazing being regulated, the polymer skin could be a good choice for other envelope surfaces.

28.3. A self-cleaning and depolluting envelope

Energy supply is not the only problem which must be faced by urban environments. Air quality and, quite simply, the environment's visual quality is another. Photocatalysis offers a means of transforming the building's frame into active space, capable of self-cleaning, self-sterilizing and, especially, purifying the urban atmosphere (ozone, nitrogen oxides, organic volatile components) under light, even in poor insolation and intense traffic conditions [CAS 04]. Titanium dioxide used as anatase is the most robust photocatalyst identified up till now, but its absorption spectrum is limited to near UV. The narrowness of this spectral window, and its position at the most energetic end of the solar spectrum reaching the earth's surface could be considered as potential handicaps. Actually, it is an asset because this situation means that the photocatalytic function will not interfere with photovoltaic coat absorption, which reach their maximum efficiency at larger wavelengths.

The relevance of the self-cleaning, depolluting photocatalytic surface, also on the level of traffic lanes, is currently being demonstrated. The substrates which have known the first commercial developments are glass, concrete and ceramic materials, the latter primarily being for internal use (cleaning and disinfection kitchens). Polymeric materials are still significant, but they need to have been protected. Indeed, the photo-oxidant effect of a thin anatase deposit on a polymeric membrane is such as it is likely to oxidize the polymeric material itself until the CO₂ stage. It therefore needs protection, firstly by an inactive, photocatalytic layer made of silica, for example. This does not pose any major engineering problems. A construction made from tended membranes using this technique is the chapel at the Hyatt Regency in Osaka, achieved by the Obayashi Corporation [RIT 07]. A polymeric skin generating photovoltaic electricity while being self-cleaning and depolluting is therefore not a Utopia.

28.4. A self-repairing envelope

Resilience is one of the most sought after properties, either in the world of construction or civil engineering works; in a strict sense (shock resistance), but also in a broader in terms of remaining operational even in the presence damage. The first step for avoiding risks and reducing vulnerability is without doubt having a correct design, but the materials themselves can contribute. The development of "self-repairing" materials is part of this logic.

Reinforced concrete is the first material tolerant to damage, thanks to its reinforcements. But, however, it is not generally self-repairing. Concrete can be partly turned into a self-repairing material, if the cracks are not too wide and if we

leave it to time, by giving a “hydration reserve”. This is the case for ultra-high performance concrete, where the cement is only partially hydrated. In the event of weak crack growth, a simple rehydration allows for at least partial cicatrization [VER 04].

Polymeric materials have been the subject of a similar process. One of the possible methods consists of vascularizing the polymeric object, and to include polymerizable resin pockets through oxidation into the object. If rupturing begins, resin invades the crack and polymerizes when in contact with the air. An epoxy beam of this type was carried out in a laboratory [TOO 08].

Another procedure is that followed by the Ludwik Leibler team in the ESPCI-ParisTech [COR 08]. Thanks to a supramolecular design and the use of reversible hydrogen bonds, an elastomer material could be synthesized from fatty acid derivatives. After rupturing, the simple recontacting between the two ruptured surfaces lets us find all the initial mechanical properties. A great excess of open hydrogen bonds and a long life lifespan on fracture surfaces allows this cicatrization. The crack lips can be welded up to one week after the crack has opened, at room temperature. Beyond this, the hydrogen bonds balance on each face and more quickly when the temperature is raised.

The use of simple fatty acid derivatives as “molecular bricks” opens up the prospect of producing these elastomers by using plant oils – which would be by far preferable for energy assessments and preserving the plant – or algae. The prospects for using these materials in the road domain are extremely tempting.

28.5. An air-conditioning envelope

In the arsenal of materials and methods to be implemented for “high-quality environmental” buildings, and, possibly, “to positive energy” [MAU 04], [QUE 08], phase shifting materials make an original contribution by their aptitude to exceed simple insulating capacities, and to store then release thermal flows at the most convenient time.

During a rise in temperature above the inclusion melting point – typically during a midday peak – this melts by absorbing a quantity of heat relating to its latent melting heat, limiting heat transfer towards housing. During nocturnal cooling, the liquefied inclusion is solidified by restoring the latent heat, at a moment when this restitution is pleasant or at least not penalizing to comfort. The result is a smooth thermal cycle, similar to that which for material with strong thermal inertia, massive and with strong calorific capacity, like concrete for example. Paraffin and salts, in encapsulated form, are the most common phase shifting materials. Their use benefits

from the latent heat associated with melting-solidification. Incorporated into plasterboards or double glazing, we are already finding them on the market. Nothing prevents polymeric materials, in particular polycarbonate walls, from being used in the same way [RIT 07].

From a more remote point of view, we may wonder why such a small amount of attention has been paid to the liquid-vapor transition for the most common substance: water. The latent heat of water vaporization is, indeed, many ten times higher than the latent melting heat for paraffin. One major reason is probably due to the particular conditions which must be joined together so that the capillary evaporation-condensation phenomenon can be used as a thermal regulator and relative humidity at the same time. These conditions are bound, on the one hand, to the distribution of pore sizes, which must correspond to the hydrous boundaries of the material's operational system and, on the other hand, to the porous network's connectivity, which must ensure fast exchanges. Such connectivity conditions and pore size hierarchy seem to be joined together in natural macromolecular materials, such as hemp fibers. We may think that, thanks to a well conceived porosity engineering, similar properties may be introduced into polymeric panels.

An alternative would be to develop this porosity engineering in concretes or other inorganic materials but, still, using polymers proves to be necessary. The most powerful technique currently used to synthesize inorganic materials with controlled porosity – known as *templating* – calls on tensioactives (surfactants) or, more and more, on amphiphilic diblock polymers whose micellar edifice (spherical, cylindrical, cubic or more complex still) determine the shape, size and connectivity of the pores in the final material [OZI 05]. This technique, whose principle is remarkably simple, consists of synthesizing the inorganic material by using soluble precursors, in an aqueous solution of amphiphilic molecules. The inorganic framework is then rolled up in some sort around the molecular joins of the polymer or the tension-active. To generate porous material, it is sufficient to eliminate the organic part which was used as the structure's template.

28.6. Conclusion

The five functionalities which were briefly mentioned in this contribution illustrate the considerable potential of multi-functionality of polymeric materials in the construction domain. They are far from exhausting all the potential of polymers like functional materials in construction. The field of electroactive polymers [BAR 08] or shape memory polymers [LEN 09] for actuators or sensors, which were not dealt with here, open up vast prospects which, beside the already existing applications in the biomedical domain for example, will certainly find other prospects in domotics.

Whatever the application, the high added value which would result from using polymeric materials justifies the need to achieve it.

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Chapter 29

Thoughts on the Futurology in Research and Development of Innovative Materials

29.1. Difficulty of prediction

Prediction is a very difficult art. In 1935, Lord Rutherford (the father of modern atomic physics) said, in a conversation with N. Bohr and W. Heisenberg, reported by W. Heisenberg, [HEI 69] “speaking about the technical exploitation of atomic nuclear energy is pure nonsense”. This happened ten years before the achievement of the Manhattan project in Hiroshima!

This is not an isolated example: who, among the most optimistic, would have been able to envisage, a century ago, the development of energy consumption, the disappearance of animal haulage in industrialized countries, the multiplication of electricity uses, the capacity of bridges built in the 18th century to bear convoys of thirty-nine gross tons loaded to seventy? The last one hundred years have seen considerable progress. An example is provided by the rail journey lengths from Paris to Marseille (Table 29.1).

Year	1867	1895	1914	1938	1960	1983	1994	2001
Length (h/min)	16.15	13	12	9.14	7.33	4.50	4.10	3

Table 29.1. *Journey length times, Paris to Marseille by rail*

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The last result on this table was made possible by the existence, on the main part of the journey, by a high speed track where trains with more electronic equipment than an Airbus can circulate, costing 24 M€. Simultaneously, the French highway network has grown by 60% over the fifteen last years. In 2005, French electricity production, always growing, was at 86% nuclear origin and 4.2% hydraulic origin, where a good portion of this energy comes from nuclear plants used to make water rise from dam to dam. This does not prevent the growth of global coal and oil consumption (important since 1760 and 1859 respectively), which increase the content of carbonic gas in the atmosphere, the reason inducing climatic changes. Among the grades of steel produced in France, two thirds did not exist fifteen years previously [MUD 95] whereas it is an extremely old technique: cast iron was produced in China from the 4th century BC, and its steel transformation in the 2nd century BC.

The multiplication of radioelectric transmissions is an exponential time function; they are now usually used on distances of one meter for an office telephone, to a thousand kilometers for *Global Positioning Systems* (GPS) while the Earth's first artificial satellite has been operational for only 50 years (Sputnik I).

29.2. The current state of things

Currently, the most developed part of the world, except Japan, is operated by people of European origin. In these regions, population structure is very different from how it was a century ago: the life expectancy has gone from 45 to more than 75 years old. Professions have quickly changed: a considerable manpower growth in services, and declines in agriculture, industry and building and public works activities. Countrysides were depopulated, for the benefit of the cities. The preeminent roles of manual skill and physical force have been replaced by the aptitude for understanding processes, the attention and the capacity to react to degraded situations.

Consumption has greatly evolved: the proportion of French household income devoted to the subsistence went from 60 to 20%. One hundred years ago, only a few thousands products were sold to the public, now a supermarket currently has more than 50,000 references.

Part of this progress is the result of scientific and technical research. Large organizations dedicated to these activities were founded in the 20th century: for the basic research, the British Council (1934), *Centre national de la Recherche scientifique*/National Center for Scientific Research (1939), the National Science Foundation (1950) and, in France, for technical research since 1946, *Commissariat à l'Energie Atomique*/Atomic Energy Commission, *Bureau de Recherches*

géologiques et minières/ Geology and Mining Research Office, *Centre national d'Etudes des Telecommunications*/National Center for Telecommunication Studies, *Office national d'Études et de Recherches aéronautiques*/National Office for Aeronautical Studies and Research, etc.

Regional inequalities have increased. The data relative to extreme wealth, such as the number of millionaires (Table 29.2) is not convincing.

Country	Number
USA	2,960
UK	825
Germany	440
France	260
China	250

Table 29.2. *Number of millionaires (in US\$) in 2006*

Global information, such as night photographs taken by a satellite is more significant: the populated parts of Sub-Saharan Africa like Siberia are not very enlightening.

In front of us, large changes are happening: Asia and South America are waking up while the world-wide population is continuing to grow; each year it grows from the effective total population of the Roman Empire to its apogee.

29.3. Extrapolation attempts

From the current state of affairs, we can try extrapolation but it is necessary to bear in mind the considerable risks of blundering.¹

¹ “In any case, we will not go backwards. We will not see the good farmer slowly trailing behind his two white oxen, marked with red, fourteen hours a day, his wife Jeanneton, washing in the river in all weathers, she who he gave twelve children, ten of which died prematurely; never again will we see the beautiful laces from Le Puy and the lace makers blind at twelve years old; never again will we see beautiful meat from old times, without hormones or additives, that half of the population would eat once a year. This blessed time will never come back; the good wild is dead” [ABR 73].

29.3.1. *Primary resources*

Faced with increased consumption, anxiety appears with regard to the limitations imposed by the finite character of exploitable natural resources. This is the case, in particular, for oil, which is, nowadays, behind two fifths of the world's power consumption. We may, however, notice that for 50 years, the usage length of proven reserves has been constant. Admittedly, this situation will come to an end, but when? With the current knowledge, we cannot seriously answer this question. For coal, whose extraction is also rapidly increasing, the predicted time for using up the resources is much longer. Then the content of carbonic gas in the atmosphere become intolerable? Certain operators of these resources have become aware of the danger to their commercial future, and research has begun for its storage in deep saline aquifers. They are, currently, in the pilot stage.

These raw energy materials are essential for our cause. City gas works were in use in France from 1799 to 1970 (150 of them in 1946); along with coking plants, they were the source of tar used for road construction. Natural gas supplies made these factories disappear, and tar from coking plants is especially useful, now, with the manufacturing of carbon electrodes. For roads, tar is replaced by bitumens. Bitumen outcrops were exploited from the Neolithic era to caulk and build [CON 91, DES 01]: “they had brick for stone, and bitumen for mortar” [BIB]. Now, they come from (with energy-generating products, lubricants, paraffins and bitumens) from oil refineries which are also the source for petrochemistry products. Some of these are used for manufacturing organic polymers, whose production has been multiplied by four in 30 years, whereas steels have only increased by 30% [SIL 02]. One fifth of these products (6.8 Mt) are used by the building and public works activities [MOU 06]. Extrapolating these recent tendencies shows, on the one hand, that such materials substitute ceramic products or metals, for roofing and, on the other hand, for packaging (35% of the polymer market), that easily biodegradable materials are being used more and more. A development of the market' part for building and public works is foreseeable. Petrochemistry also develops treatments and adhesive bonding for wood (see *supra*, chapter 15), admixtures and macromolecules are also incorporated in concretes. The tonnage of these materials sold is the most important after water. The annual production of hydraulic cement is higher than 1.5 Gt. Building in only 1% of organic matter in 10% of consumed cement would lead to 1.5 Mt! The uses for these types of materials are being developed. This is going in the direction generalizing the use of heterogeneous artificial objects where, historically, the first examples are paper and tires made of organic polymers and mineral fillers.

29.3.2. *Some social tendencies*

Projecting some current trends may restrain these developments. Thus the presence of more than half the world's population in cities where socio-spatial segregations mean that part of urban inhabitants are lacking urbanity. This is a source for insecurities for people, equipment, goods and the environment. The solution is eminently political, but for technical aspects, these facts lead to the need for being attentive to the construction's vulnerability. Another evolution may be observed: risks refusal (zero accident tolerance)² and the will to point out a culprit in the event of harm, even limited to one victim. This leads to various phenomena. First of all, an increased power for judges whose scientific and technical knowledge in the domain of construction materials is not a priority in their training. This may generate a timid attitude in manufacturers using innovating methods. Another consequence is the prolixity of national, European (30,000 pages at a cost of 50 k€ for civil engineering) and international standards. An already achieved result is the elongation of the duration of studies which take into account a multitude of situations including the most degraded, and not only development phases and use, but also waste decomposition and processing. This leads journalists to say that the thing is "finally available". The procedure complexities for testing and transportation, and the needs for workers' qualifications means that a delivery to entirely conform to contractual engagements is increasingly rare. The need for operational safety gives a certain element of surprise when a complex system "is working".

The accelerated appearance of innovation is the reason behind two kinds of disadvantage. On the one hand, the short usage period prevents sufficient feedback and, on the other hand, a suspension in marketing leads to a stop in the supplies for consumable and pieces necessary for maintenance, on a global scale, a certain mess.

29.3.3. *The complexity of technical systems*

Networks are being fixed more and more. To illustrate this point, simply think of the costs of changing the traffic orientation of a city street, a direction initially set during Gallo-Roman times. It is remarkable that the extent of damage due to the vulnerability of large networks to natural or human aggressions is, now, obvious. For example, a cut in the electrical power supply affected 200 million people in India on January 2nd, 2001 [LAG 07]. In a developed economy, this leads to disturbances in transport of both people and goods, in information transmission, water

² The first motor vehicle test (Cugnot 1770) ended in an accident. Applying the precaution principle, had it been in trend at that time, could have ended up completely prohibiting this kind of transport.

and gasoline distribution, means of payment and disturbs safety and rescue organizations. The results of such phenomena can be uncontrolled panic with the means available, as well as violence. In these situations, the society's fragility is all the bigger because "zero stock" management means that a supermarket, for example, only has food for one day's consumption. This sensitivity of large networks to dysfunction and their social importance may block their development.

A less important remark is the growing attachment for preserving certain heritages. In certain areas of recent intense civilizations such as North America, this is not very abundant. On the other hand, in regions with rich and old culture, their importance is such that the community does not have sufficient means to maintain them. This is particularly the case for Italy³.

29.3.4. Research

The majority of scientists and technicians carried by the Earth are still alive; this explains the accelerated advance in knowledge and practices. The fast growth in knowledge makes their access to those who could use and develop them difficult. This phenomenon is particularly clear for mathematics. Another complication is popular within the discussions between specialists. Some think that we should wait for the result to be definite. They are likely to be waiting until they die! In fact, hindsight is frequently lacking to be able to appreciate discoveries and inventions. The spatial distribution of researchers is quickly changing, as can be seen by their relative productions, in physics for example (Table 29.3).

Regions	1981	1998
USA	33	25
European Union	29	38
Asia	10	28

Table 29.3. *Changes in percentage for the number of physics publications*

Thus in 2006, if there were 1.3 million people employed for research in the USA, there were 1 million in China, where spending, especially public, for research and development was 100 G€ (1.2% of the gross domestic product), i.e. higher than for

³ A humorist claims that, in order to visit an interesting area, you must use the following transport systems according to the country: airplanes for the USA, the super-highway in Germany (after the destruction of so many wars), bicycles in France, on foot in Italy, etc.

Japan and twice as high as for Germany. Therefore, new knowledge accumulates progressively quickly, and allows us to study scientific subjects which were inaccessible before. This is the case, in particular, for technically usable products like the mixtures of many chemical species, a phenomenon depending on a great number of parameters, or whose response is not proportional to action, or where one cause can have several effects, etc. New knowledge allows for inventing new equipment, innovating materials, some of which are used by entire society. Indeed, research has two functions: cognitive and productive. These two objectives are closely dependant because to understand it is, often, knowing how to produce it, even if this last aspect is greatly deferred.

Science is a body of rational doctrines, independent of religious dogmas, of political⁴ and legal powers and which would like to be independent of the legislative power. This concept appeared with Hellenic civilization. The oldest mathematician and physicist whose work is known, Thales (640 BC–564 BC) was independent of his city; he was a rich olive oil merchant. The need for independence was recognized from the time of Ptolemy I in Alexandria, 3rd century BC. The following organization began: the slaving fellah, the armed tax collector and the sovereign who provided, selectively, in theory, funds for the scientist responsible for understanding nature in order to control it. We should notice that nowadays, researchers are still organized like in the societies with orders into three categories: ploughman who work, noble with in principle a military function, and ecclesiastic who pray. We find, with varied denominations, these three kinds everywhere in the world.

There are many uninitiated who believe that the techniques come from applied science. If this is often exact, it is no less true than, for example, discovering the need for stimulated emissions in 1917 [EIN 17] which led to the invention of the LASER in 1958 which was, then, a solution which awaited a problem. The relationships are in fact more complex which makes prediction more difficult. A first example shows that scientific knowledge is, sometimes, induced by engineering problems. Newcomen built, for pumping water out mines, the first usable steam engine in 1712. This was to solve a practical problem, i.e. the bad yield of these machines, that S. Carnot [CAR 24] carried out his reflections on the power of fire and founded one of the most abstract disciplines of physicochemistry: thermodynamics. A second example shows that it is not a question of one single phenomenon. At the end of the 19th century this was a practical problem, measuring furnaces temperatures, which was behind the works of many German-speaking physicists in thermodynamics. They created the concept of quantifying action exchanges between radiation and matter [PLA 00].

⁴ These are scientific associations who decided to name the chemical elements, even when it was a question of honoring a person who in the past had a political role.

It also happens that an innovation in one technical field could overwhelm another industry. An abundant source of oil had been looked for so as to replace animal and plant oils powering lamps. The solution came from drilling wells. This abundant product provided stable lubricants at high temperatures. They allowed overheating in steam engines which improves the yield predicted by the Carnot's theorem.

A current trend is to bring together fundamental and applied research. The technical organizations responsible for recruiting young researchers trained in academic laboratories with a tendency more than ever before to be concerned with problems which can, possibly, have a practical interest⁵, provided that it lasts! It is necessary to keep in mind that, on average, the spending for applied research and development, although much lower than manufacturing costs, is considerably higher than expenses caused by basic research. In addition, the times, if they are fundamentally unpredictable for fundamental discoveries and inventions, are, in general, extremely long in technical domains. For example, studies for high speed railways lasted for thirty years, and we can count approximately forty years between their introduction (1981) and the generalization of their use on French territory. Another example, prospective for the moment, is that of *International Thermonuclear Experimental Reactor* (building a star on Earth). After very long diplomatic discussions, an agreement was concluded in 2006; building started in 2008; functioning is planned to start in 2018; an industrial demonstrator should exist in 2030 and the link with electrical network is considered for 2050. The period of decision making is sometimes an essential factor. Therefore, for the first underground line in Lille, the discussions lasted seven years and construction (with overtime on Sunday) three years.

A current feature, common to research whose expansion is foreseeable, is the use of digital computers to carry out calculations and simulations. These processes have already proved their effectiveness. However, qualitative elements should not be forgotten, and quantitative elements also have their limits⁶.

The fact that globally for each type of industrial business, a positive correlation between the variations in the number of employment and the variations in research and development spending exists [EUR 95] added to other economic arguments, shows that the social use of research is now generally accepted. A positive

⁵ We knew a time when a good dissertation subject consisted of dealing with a small question, a question for which everybody was sure the answer would never be of any practical use.

⁶ If we want to carry out an accelerated ageing test on an egg by raising the temperature, we do not get a rotten egg, but a chick or a hard egg, which is not predicted in the Arrhenius law [ARR 89].

consequence is that, with highs and lows, the general tendency is the progression of means granted to this activity. However negative consequences also appear: utilitarianism for example. Bureaucracy (which obtained to destroy the most historically expanded empire) wishes to increase the proportion of research on project, which comes back down to researchers having to announce what they have found before they have even started the research. Whereas, in fact, the means are not defined according to requirements which need to be fulfilled, but in proportion to the gross domestic product or turnover.

In this respect, the *European Institute of Technology's* project is very characteristic. The only objectives assigned are "to concentrate on important subjects offering commercial opportunities". It has planned "communities of knowledge and innovation" with lifespans from seven to fifteen years. The examples given are: climate change, renewable energies, information society, sciences and medical technologies and nanotechnologies, meaning, in short, subjects which are the fashion of the day. Will they still be so in fifteen years? The estimated costs are, for five years, of 2.4 G€. While reasoning by referencing to past experiments, financing research for practical goals have led, to improve lighting processes, to financing Chevreul's researches to improve tallow candles, whose result was the invention of the wax candle.

Actually, to lead onto the electric lamp, this was done by research on frogs by Galvani, in 1771, which would have needed subsidizing (they finally led to Edison's carbon filament lamp in 1879, then the tungsten filament in 1907). How difficult this is to predict! Another bureaucratic criterion of granting money is the number of patents, i.e. what became of an old legal invention (the first one was granted on February 22nd, 1584, by the General states of the Netherlands for a windmill meant for drainage). One of the consequences from this is an expansion of completely useless patents.

One tendency has recently appeared: the claim for control by the public over scientific and technical developments. It seems to us that, initially, it would be desirable for representatives of this public, elected officials and, why not, journalists whose responsibility is to inform, to make the efforts necessary to make themselves capable of doing so.

The observation of contemporary evolutions leads us to another remark. Risk taking is very different according to nation. There are two examples here: the proportions of power plants with nuclear boilers (Lithuania 89%, Netherlands 2%) on the one hand, and the proportion of grounds sown with willingly genetically modified seeds (more than 60% for corn in the USA and negligible in France) on the other hand.

Another recent evolution should also be stated, related to man-power. Not only the proportions, but also the number of graduates and students for science and technique are falling. Admittedly, there are one million unemployed people, but we can see on the television the *Fédération nationale des Travaux publics*/National Union of Public Works announcing advertisements to recruit personals in this sector. This is the same for an important corporation in this profession. The disaffection of young people for oil professions can create a serious problem in the future [APP 07]. If such situations are developing, they may become a bolt against future development.

29.4. Futurology

It is useful to not limit perspectives to hazardous extrapolations, and to try to imagine the future which, and this is obvious, is no longer what is was. It is better to speak about sustainable development. But still, development must continue to exist.

The theorem of existence has led us to the following interrogation: is civilization able to avoid a major war which could break the growth of the total human population, the economy, and consequently knowledge? Indeed, since the existence of abundance nuclear arms, until now, there has been no direct confrontation between well armed, large armies. The lessons of recent wars implementing different modern techniques – Serbia (regarding Kosovo), Iraq or Lebanon – are of little use for our cause: in these cases, the objective could not be the destruction of an army or an economy comparable to that belonging to the attackers which did not exist, but actually the destruction of the adversary's infrastructures (ports, airport speedways, bridges, electric plants, etc.) But, there is no lack of conflict: access to soft water resources, dispute over the existence of one theocratic state by another, the presence of military forces on foreign lands to control oil rich areas, etc. Moreover, the number of states having weapons of mass destruction is continuing to grow. Faced with these dangers, the common attitude is to ignore them, which does not constitute as a response to the question.

In assuming that, to be optimistic, the disaster is avoided, we must not forget the sources of tension are not lacking either. In addition to those already mentioned, the rapid development of Asia and the difficulties of Africa (who, on many different fronts, currently beat the records in terms of catastrophes) induce changes in power struggles which can be badly dealt with by some. More especially, traditions and politics are far from being uniform. It should also be feared that the abuse of many abundant and niggling regulations may result in reactions which are slow to formulate but which may also explode violently.

Subject to the hypothesis for the best world, research could have a good future. There is considerable knowledge already acquired, and to be exploited, here. For

example, the known organic molecules (around one million new ones each year), essentially synthesized for their potential therapeutic effects and, on average, at least around ten of them are kept for this use, are a treasure which is rarely used. New productions can produce new residues. It would be good to look for uses for them, as was the case for domestic gas or oil fuels (see *supra*). Uncountable phenomena already known are not exploited by techniques. Here, it is a question of engaging in processes similar to that of the Manhattan project (section 29.1) which consists of creating new technologies to benefit from available fundamental knowledge. It is therefore necessary to be attentive to discoveries and inventions which conceal new concepts, particularly those which can be adapted to complex situations which are met with organic materials used for construction. This complexity has a tendency to increase with the multiplication of treatments which are applied to them and with their combined use with other kinds of products. This may lead to the need for developing characterization methods and tests which are still more rational and have better performances.

In the same way as production and services, the demands for workers to have qualifications⁷ will increase in research jobs. The growing social implication of this will demand rigorous respect for their ethics, whatever the pressures of all sorts which could be imposed upon them.

29.5. Conclusion

Since the end of WWII, meaning more than sixty years ago, there have only been localized conflicts. Globally, this long peaceful period has seen considerable progress in the total population, in the economy, in life styles, and knowledge.

For the future, extrapolations may be used, which are often highly hazardous, with tendencies that are currently being noticed: “L’historisation du passé est une condition de la construction optimiste de l’avenir conçu comme la poursuite de l’histoire”⁸ [CHA 75]. Some are euphoric, others present dangers for the aftermath of the happy evolution of this last half a century. But no prolonging of the recent past can foresee the unforeseeable. It is, then, necessary to complete it by foreseeing the future. This is the job for fortune tellers and other charlatans. The scientist, armed with the causality principle proves to be powerless when faced with the multiplicity of causes, some of which can have many distinct effects. Even if an enlightened spirit were to instill a certain clarity in us, we could still oppose it by the

⁷ These are much more important for the development and maintenance of an automatic testing device than for an employee responsible for the same task.

⁸ “Historicizing the past is a condition of the optimistic construction of the future, conceived as a continuation of history”.

remark made by Planck for scientific discoveries, “a new scientific truth does not triumph by convincing its opponents and making them to see the light, but rather because its opponents eventually die, and a new generation grows up, that is familiar with it” [PLA 48].

Is this little exercise to be pessimistic or optimistic? The future will decide.

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Conclusion

The position of organic materials in relation to sustainable development has been observed in this book across each material's prism. The conclusion that we will be developing here, will approach this problem in a more global way.

The term "sustainable development" is used everywhere today, and by everyone. "Sustainability" is also used frequently, but it is especially understood and manipulated by material specialists. The term "resources" is, today, particularly mystified. Are they natural, or renewable? A serious question. These terms challenge all parts of society, from the citizen to the decision makers, contractors, passing through the technician and main contractors.

In this conclusion, we are going to try to pacify the debate by approaching it from a strictly technical angle, because behind every technological choice, there is always a reasonable and reasoned base foundation, using scientific truths, which can therefore be demonstrated and measured.

Let us start by analyzing the term sustainable development and its famous three pillars.

The economic pillar is limited by the fact that construction materials must be available in large quantities within reasonable vicinity. "Available in large quantities" inevitably induces the smallest cost possible. But, what is the cost of construction materials? It is firstly the cost of extracting the raw materials, followed by the cost of transformation and development, then costs for transport, and finally, the cost of implementation.

We know today that the intervention of these transport costs means that a construction material, as well as other costly materials, is economically viable if the

Conclusion written by François BUYLE-BODIN.

distance between the production site (extraction then transformation) and the place for implementation is as small as possible.

The environmental pillar has become, today, the most difficult to qualify and the easiest to be led astray. Where, really, can we find a respect for the environment, and the notion of *environmentally friendly*? There is a superimposition of criteria, all of which are acceptable, and which distinguish themselves by aggregation methods, multi-criteria analyzes, etc. Everybody is losing their way. We are speaking of parameters, systems, subsystems, charges. We will criticize the incomplete data bases. In sum, there is still some prospective work to do, even if a lot of it is already done, and the remarkable tools today in the biggest number available would have us believe that this chapter is closed.

The social pillar is no longer the simplest pillar to consider, above all when we are referring to organic materials and health matters – and the recent regulations, such as the European directive on chemical substances REACH have not helped matters. This may be paradoxical because everything is chemical in our modern world. Yet, everything is pushing the citizen to fear materials coming from organic chemistry. Psychoanalysis of our society, which has seen its apogee thanks to synthetic materials, and which rejects them today, would be particularly welcome.

The first question asked is: what is the difference between the sustainability of a material and the lifespan of a construction? In other words, how do we make sure that the life cycle analysis of a construction gives a better result by wisely choosing the best performing products, but not necessarily the most sustainable?

Material sustainability and the LCA of constructions

Without going into detail, we can define a material's sustainability as its capacity to endure time. To endure means to preserve its functional capacities, the reasons for which it was chosen. This book, as well as others, has shown that this notion is not simple.

The sustainability of a construction material depends, indeed, on the environment in which it is implemented and where it will be working, as well as the methods used to build it and its maintenance. This is not forgetting that, in a construction, each material considered is part of a bigger whole. It may, then, have some weaknesses, but another material will protect it from these weaknesses. It may also be more or less efficient, according to the vicinity where it is implemented (for example, the problem of compatibility between materials).

The lifespan of a construction is even simpler to analyze. Is it the highest common denominator or the smallest common multiple of the combination of the sustainability of implemented materials? Some materials can be replaced many times during the construction's life (tiles, for example, and the opposite, insulating sandwiches). Therefore, the notion of being modular, subtle, and replaceable when necessary is added to the notion of raw materials used in construction, once and for all.

Where is the LCA in all of this? Here, let us distinguish the absolute from the relative. The life cycle analysis is only fundamentally a tool which can evaluate the environmental impact induced by producing a material object, or the implementation of a service.

Let us specify this considered object. This is expressed by the analysis and the analyzed system's perimeter. Let us be clear, here, so easy as it is to apply various LCA techniques to technological objects which are more and more sophisticated but limited (from bottles made of PET to the electric car), and so complicated it remains for classic BTP objects, constructions, structures, infrastructures, etc.

Today, we are making progress for infrastructure type products, we are also starting to know how to distinguish for current construction materials, such as concrete, the positive effect of using industrial by-products.

Fundamentally, what is causing the problem, and why is the LCA still today an imperfect and faltering tool for the construction sector?

The limits of the LCA in the world of construction

The LCA first of all considers the object to be analyzed during its life cycle, in other words, "from cradle to grave".

But the cradle is only generally the ultimate stage in the gestation period, meaning, from the end of the assembly of a set of materials which are more or less developed, for which the life cycle had already started well before. We can also add to this the design phase, which for many objects, greatly exceeds a year and requires multidisciplinary, collaborative approaches, gathered under the term *lifetime engineering*.

The object's life corresponds to its use, its functionality. For a BTP object, it will last for many decades, or even many centuries, which distinguishes it from current technological objects. It will inevitably undergo maintenance, repair, be kept up to

date. Moreover, the object is a carrier for human activity which, through the importance of their impacts, will mask the object itself (road traffic, heating, etc.).

The end life is the moment when the object stops working. Here, also, the world of construction is complex. A magnificent suspended bridge at the beginning of the 19th century, classed as one of the world's historic monuments and today exclusively reserved for pedestrians, has it left the realm of analysis? In an old restored factory at the peak of high technology, what is *dead* and eliminated, what is re-used?

The analyzed system's perimeter is the first choice to be made when we perform a LCA. Here, we invite the reader to read the abundant amount of literature that the corpus of norms ISO 14 000 tries to bring together on the subject. This perimeter is, of course, largely dependent on the objectives that the decision makers assign to the analysis.

Let us focus on the quantitative stage of the LCA which consists of making an inventory of "incoming" and "outgoing" flows.

Incoming flows comprise energy, water, raw materials and more or less developed materials.

Energy is certainly the easiest to quantify since its price has rocketed since the 1970s. Its ever growing value means that its use today is measured by more and more "intelligent" counters, whatever its nature.

For water, this has been late in coming, but presently this resource is no longer considered as abundant and limitless, and serious accounts are starting to be developed.

The subtlety between raw materials and more developed materials is important in defining the analysis perimeters. On this point here, we can confirm that the construction sector is that which uses the most, along with the farming sector, materials with low levels of development. This notion of "level" is not indifferent. The more a material is developed, the more there is a need, theoretically, to go upstream in the definition of its perimeter.

We can, clearly, limit ourselves to only considering that which comes under the act of upgrading a material, but the current trend consists of making the operator or the downstream builder assume all or part of the environmental responsibilities for its providers upstream. This procedure has been initiated by many multinationals, and is not completely absurd in the globalized market, when we know that certain environmental impacts must inevitably be considered on a global scale (the global carbon market, for example).

The concept of renewable resources is becoming more and more acute. It is not easy to apprehend. In fact, few materials used in the construction domain are renewable (let us remember the notable exception of wood) but many of them are abundant on the earth's surface (crude mineral resources). For organic materials, asking the question comes back to thinking about "the post-oil" period, which will arrive eventually, but definitely in a more gradual way than is being predicted.

A good approach certainly lies within our capacity to recycle or re-use these materials that we are using in such large quantities, to ensure the biggest aspect of humanity's vital needs.

Outgoing flows include, as well as the product itself, everything which was generated during its production, then its use, and finally its elimination.

Amongst them, we find production rejects, but also that which is found rejected in water, in the air and in the ground. Respecting Lavoisier – "nothing is lost, nothing is created, everything is transformed" – the outgoing flows are made of products which are only the result of the transformation of products coming *into* the system. But this transformation is not necessarily innocent for man and his environment. Chemistry is therefore often the referee for the LCA, and for respecting the environment.

Next, it is appropriate to upgrade the incoming and outgoing flows into environmental impacts.

Their classification may be geographical, translated in local, regional, and global terms. This division may be considered as arbitrary, and is often dependent on the nature of the impact.

It can also be related to the type of support considered; air, water, soil, ecosystems, human systems, etc.

For these points, we advise the reader to consult the many works available online dealing with this subject. To give a simple example, when we transport a product in a truck, we consume fuel and this consumption may be brought back to the functional unit (FU) considered in the product's LCA, such as x liters of fuel per FU. Fuel combustion generates environmental impacts in the air, including the famous greenhouse effect, in water (acid rain), etc. But, must we only consider fuel consumption, or add the impacts generated by extracting crude oil, its transportation and refining, distribution and fuel storage to it?

Finally, knowing all the impacts linked to incoming and outgoing flows implemented in the LCA's considered perimeter, the major question is then related

to the considerable reduction in sizes, in one or many indicators, relevant to the person who ordered the LCA. Here, also, the scale on which we are located is prominent.

A first scale consists of positioning ourselves in relation to a national or international lawful context, while targeting conformity. Another consists of being in a better position than the competition, which we call the marketing argument. A third scale may reveal more noble aspirations, ethics, etc.

We could have a more integrating approach by using weighting, standardization, and aggregation techniques.

Without going into too much detail, this comes down to looking for a relevant indicator, allowing us to classify a solution, amongst others, in terms of efficiency; firstly environmental then indirectly social and economical. Thus, as is practiced in northern countries, we will give a great importance to the impacts which lay heavily on society in terms of costs; either economic, or human if they generate health effects.

Let us now ask a second question.

Why are organic materials struggling to enter in the virtuous circle of sustainable development?

The previous chapters have shown the variety of organic materials used in the construction sector. Some of them are structural; others contribute to improving characteristics of the most “robust” materials, often minerals, as is often the case for the construction sector.

Let us retain the traditional distinction between masonry, and fixing and finishing.

For masonry, with a long lifespan, whose basic function is structural and partially closed and covered, mineral and metallic materials are dominant (with the exception of structural wood). As for transport infrastructures, by masonry we mean base layers, which are always minerals. Organic materials are not, however, absent, like concrete admixtures, for example. It improves the performance of the base material it is added to, makes it more sustainable and less likely to influence the environment. It also contributes to improving working conditions on site, all by increasing its productivity. Upgrading has important effects on sustainable development, which can be dealt with by a system approach which is still underdeveloped today. Let us quote the approaches which have accompanied the

development of high performance concretes (BHP national project, 2000) and self-compacting concretes (national project BHP).

For fixings and finishing, with more varied lifespans, often replaced many times during the construction's lifespan and where there are multiple functions, organic materials are seen more. For infrastructures, for the sake of an analogy, we can consider surface courses, most often made from "black" organic products, containing bitumen.

As the materials are more often implemented in components, the LCA will be the best adapted tool for evaluating the environmental impacts of products. Beyond this, the capacity for being disassembled, recycled and re-used will be fundamental for leading complete life cycle analyzes on the scale of constructions or structures.

The advantages of organic materials will certainly be found more on this scale than that for base components, but the lifecycle assessment tools, which can quantify this, are still relatively under developed today.

What is the future for organic materials with regard to sustainable development?

The future is certainly in the continuation of the most reasoned use of materials.

Before sustainable development, choices were made on the basis of functional and economical analyzes. Functional analyzes consisted of putting the expected function of the object, including the material, in relation with the materials' properties. The economic function was based upon a unique factor – cost – at the same time as the material's availability, the distance that it had to travel, the complexity of transforming and implementing it.

Today, sustainable development has added to the problem of minimizing environmental impacts, including the rarefaction of resources and health matters. The choice has simply become more complex, and multi-criteria based. But the price, since it is gradually integrating more of these new limitations, is still the Justice of the Peace, the decider. Really, the choice of material which responds best to the function is still, in most cases, the material which will be the best, both in terms of sustainable development on the condition of knowing how to design it, and how to produce it. Organic materials are, in this context, those materials offering the best flexibility.

In conclusion, to position organic materials in relation to sustainable development, there is no need for particular tools. It is simply enough to adopt a

reasoned approach, similar to that followed for other construction materials, either mineral or metallic, and maybe being more vigilant on points such as impacts on health, the capacity for recycling or re-use, reasoned use which integrates the different lifespans of components, etc.

Above all, we must not forget the great flexibility offered by organic materials in adapting a material for its use, which constitutes its strength in engineering materials for its design, and in engineering processes for its production.

Acronyms and Initials

Polymers and chemical bases

ABS	Styrene, butadiene and acrylonitriles copolymer
APP	Poly(phosphoric) acid modified bitumens
VOC	Volatile organic compounds
EP	Epoxy resin
EPDM	Ethylene propylene diene monomer
PAH	Polycyclic aromatic hydrocarbon
HR (fibers)	High resistance
PA	Polyamide
PAN	Polyacetonitrile
PEEK	Polyether ether ketone
PES	Polyester or Polyethersulfone (according to context)
PET	Polyethylene terephthalate
PMMA	Poly(methyl methacrylate)

PMS	Polymelamine sulfonate
PNS	poly naphthalene sulphonate
PPA	Polyphthalamide
FRP	Fiber reinforced fiber
PTFE	Poly tetra fluoro ethylene
PUR, PU	Poly urethane, polyurethane
PVC	Poly(vinyl chloride)
PVDF	Poly(vinylidene difluoride)
UP	Unsaturated polyester

Structures, types of construction products, characteristics, tests, tools

ACGIH	American Conference of Governmental Industrial Hygienist
LCA	Life cycle analysis
SCC	Self-compacting concrete
EC	Envinronmentally friendly concrete
HPC	High performance concrete
SEC	Steric exclusion chromatography
IARC	Internation agency for research on cancer
CNDB	Comité national pour le développement du bois (National commission for wood development)

DMA	Dynamical Mechanical Analysis
DPU	Use duration
DSC	Differential Scanning Calorimetry
GFC	Gel filtration chromatography
FTIS	Fourier transform infrared spectroscopy
LHA	Hydraulic binder based product
LHM	Polymer modified hydraulic binder based product
PAV	Pressure Ageing Vessel
PCC	Polymer cement concrete
RMN	Nuclear magnetic resonance
RTFOT	Rolling Thin Film Oven Test
TBA	Softening point “ring and ball”
TRP	Cross-linkage time
TWE	Time weighted average

Organizations, documents

ADEME	Agence de l’environnement et pour la maîtrise de l’énergie(French Environment and Energy Management Agency)
AFNOR	Association française de normalisation (French Standardization association)

ALTREX	ALTREX CHIMIE: analysis software for exposure results
<i>ATex</i>	Fast procedure for technical evaluation formulated by a group of experts, CSTB
ATR	Attenuated total reflection (infrared spectrometry)
Cnam	Conservatoire national des arts et métiers (National Conservatory of Arts and Crafts)
CEFRACOR	Centre français de l'anticorrosion (Anti-corrosion center)
CETU	Centre d'études techniques des tunnels (Center for tunnel studies)
CSTB	Centre scientifique et technique du bâtiment (Scientific and technical center for construction)
CTBA	Centre technique du bois et de l'ameublement (Technical center for wood and furnishings)
UTD	Unified technical document
EMPA	Eidg. Materialsprüfungs- und Forschungsanstalt/ <i>Swiss Federal Laboratories for Materials Testing and Research</i>
ENPC	Ecole nationale des ponts et chaussées (National school for bridges and roadways)
ESPCI	Ecole supérieure de physique et chimie industrielles (Industrial physics and chemistry institution)
FNTF	Fédération nationale des travaux publics (National federation for civic works)
GPB	Groupement professionnel des bitumes (Professional bitumen group)

LCPC	Laboratoire central des ponts et chaussées (Central laboratory for bridges and roadways)
LRPC	Laboratoire régional des ponts et chaussées (Regional laboratory for bridges and roadways)
<i>NTIC</i>	Nouvelles technologies de l'information et de la communication (New technologies for ICT)
SHRP	Strategic Highway Research Program

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