

## Chapter 1

# Organic Polymers

Organic polymers belong to a family of materials whose industrial development is very recent. It is believed that the first synthetic “plastic material” was developed in 1862 by the English chemist Parkes by mixing sulfuric acid and nitric acid with cotton wool. The nitrocellulose thus obtained was stabilized with castor oil and camphor, and dyes were added and various objects were produced using this mixture. However, for production on an industrial scale, this formula had to be modified slightly and “Parkesine” was forgotten, to be replaced by “celluloid”, developed by the American Hyatt brothers. It is believed that they developed this product in 1869 for a competition organized by New York City to discover a substitute material for ivory in the manufacture of billiard balls. The same scenario repeated with the other pioneers of plastics: “Bakelite”, patented in 1909, was in fact a laboratory discovery of the 1870s; “Plexiglass”, the first organic glass, was synthesized in 1877 but it would be developed only in the 20<sup>th</sup> century.

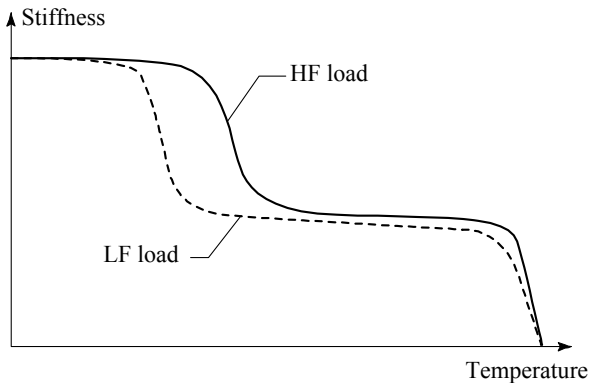
Concurrent to this flowering of discoveries, which was occasionally fortuitous but always the achievement of brilliant chemists, there was a need for a comprehensive reflection on the structure of these materials. Thus was born macromolecular chemistry.

Among the pioneers who marked the development of scientific studies on organic polymers, we must mention Staudinger, whose research dates back to the 1920s. He was one of the first to introduce the concept of macromolecule and his team’s research won the Nobel Prize for chemistry in 1953. In France, we can cite G. Champetier, who marked several generations of physicists and chemists with his passion for macromolecular chemistry [CHA 69, CHA 72, AUB 74].

The main polymers were discovered before 1940 (“nylon” was commercialized in the United States in the beginning of the year 1940) but during this period their economic potential was not yet understood. It was only in 1945 that the annual production crossed the million ton mark. Since then, the development of polymers has literally exploded with a growth rate of 10 to 15% per year, in other words, practically doubling production every 5 years. Currently, it exceeds 130 Mt/year and there is a good correlation between a country’s GNP and its consumption of polymers. And in terms of volumes, the production of organic polymers currently surpasses the production of metals.

A number of fields have gradually infiltrated into the construction of organic polymers, both as construction materials strictly speaking as well as substances incorporated into the cement matrices, such as products for repairing or reinforcing structures or materials for protecting and finishing structures. A recent European colloquium [ORG 02] has confirmed that organic materials, i.e. essentially polymers and bitumens, have a promising future in the field of civil engineering. This conclusion holds all the more true for the entire building industry, in which the applications of these products are even more numerous than in civil engineering.

It is therefore interesting to examine the specific character of organic polymers, and why they are regarded as a distinct group of materials, just as metals form a specific class. The answer to these questions calls for a rather complex study – and this is the subject of this first chapter – but can be illustrated, to begin with, using a diagram on the behavior of organic polymers when subjected to an external load that is on the whole viscoelastic (Figure 1.1).



**Figure 1.1.** *General behavior of organic polymers*

Organic polymer-based materials react differently to a mechanical load depending on load time (or frequency) and temperature. Thus, for a static load, the material already exhibits two types of behavior in the solid state, depending on whether they are above or below the temperature at which the above curve undergoes a rapid decrease. This temperature is called glass transition ( $T_g$ ).

This change in behavior in the solid state is specific to viscoelastic bodies to which organic polymers belong (and assimilated like silicones, which are strictly organometallic polymers). It forms the originality of these materials, which we will now present from a physico-chemical perspective [DOR 86, GFP 80, KUR 87, MER 93, OFT 95].

### 1.1. Definitions

A polymer is a substance composed of macromolecules whose structure is characterized by a large number of repetitions of groups of atoms, called structural units, repeat units, monomeric units or constitutional units.

These macromolecules are molecules with very high molecular weight. The macromolecular chains are composed of an array of a very large number of constitutional units linked together by covalent (and therefore very strong) bonds. They are bound by secondary bonds of lower energy but whose overall importance accounts for the originality of these materials.

Macromolecular compounds generally have heterogeneous molecular weight. This property results from the random nature of most synthesis reactions.

The average molecular weight and the distribution of molecular weights have a significant influence on the technical characteristics (elasticity modulus, breaking strength, impact strength, etc.) and the forming conditions of polymers. It is therefore important to specify this distribution. One way to do so is to consider the average molecular weights in number and in weight, the comparison of which helps determine the degree of heterogeneity in the molecular weight of the polymer.

We can thus define:

– the *numerical average molecular weight*  $\overline{M}_n$  by the expression:

$$\overline{M}_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

where  $n_i$  is the number of molecules with degree of polymerization  $i$  and  $M_i$  is the molecular weight of the molecule with degree of polymerization  $i$ ;

– the *weight-average molecular weight*  $\overline{M}_p$  by the expression:

$$\overline{M}_p = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

– the *polymolecularity or polydispersity index*  $I$  by the expression:

$$I = \frac{\overline{M}_p}{\overline{M}_n}$$

This index, which is equal to 1 for a strictly isomolecular polymer, is always greater for real compounds and can vary up to 30 or 50.

The most common methods to determine  $\overline{M}_n$  are osmometry, cryometry and ebulliometry. The best technique to determine  $\overline{M}_p$  is by light diffusion.

The technological properties of polymers depend highly on the distribution of molecular weights but also on the macromolecular structure, which we will discuss now.

To use an organic polymer-based material correctly, the user needs some data on the macromolecular structure as well as on the synthesis of polymers.

## 1.2. Macromolecular structure

Macromolecular structure refers to the sequence of repeat units. We can distinguish linear macromolecules and cross-linked macromolecules.

*Linear* macromolecules are made up of individual chains. They are often likened to cooked spaghetti. The cohesion of the corresponding material is primarily due to the cohesion of the chains, to their entanglement of the macromolecules and the presence of secondary bonds between chains. We can already note that an increase in temperature or the addition of a solvent will break these bonds and result in the individualization of the macromolecules. This means that the material is soluble in some solvents and generally fusible by an increase in temperature. Inversely, cooling or the evaporation of the solvent will return the product to its initial state. We will see further below that this material exhibits a thermoplastic behavior.

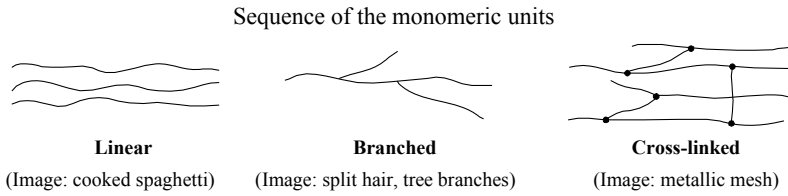
Branched macromolecules, i.e. with generally long chains connected to the main chain, also belong to this family.

*Cross-linked* macromolecules form a three-dimensional network. They can be compared to a wire mesh (high voltage tower, for instance). Their cohesion results from the entanglement, but essentially from the high energy covalent bonds existing in the various branches of the network: these bonds cannot be broken by an increase in temperature (at least within certain limits beyond which the compound decomposes), or by the action of solvents. Such a material is infusible and insoluble. It is therefore not recyclable. In the presence of an appropriate solvent, it can, however, expand significantly (partial solubilization of the remaining oligomers).

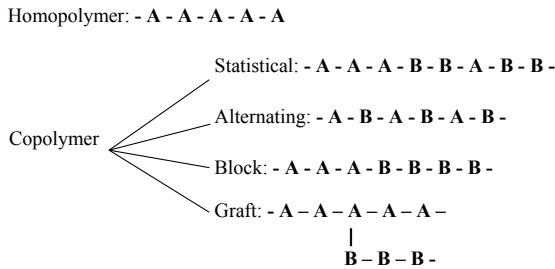
Besides, we can also consider *the nature of constitutional units* or repeat units and their sequence. We can then distinguish:

- *homopolymers* where the constitutional units are all identical to each other;
- *copolymers* where the macromolecule is formed from several monomeric units with different chemical characteristics (in general, less than four different units). They are arranged in a wide range of ways. Thus, we can distinguish, depending on the manner in which the synthesis has been done: *statistical copolymers* where the monomeric units are distributed randomly on the macromolecular chain; *alternating copolymers* where two different units alternate regularly; *block copolymers* which are made up of sequences of homopolymers connected to each other (in general 2 or 3); and *graft copolymers* where a linear polymer carries grafts of another type. *Star copolymers* can be assimilated to this last category.

All this is summarized in Figure 1.2.



**Homopolymer and copolymer**



**Figure 1.2.** *Macromolecular structure*

**1.3. Synthesis of polymers**

Polymerization is generally described as the process of chemical transformation during which the monomers react with each other to give rise to a polymer. In reality, we must distinguish two chemical mechanisms for this reaction: polycondensation and chain polymerization. These reactions differ in terms of the energies that come into play, the process in which the macromolecules grow and the associated kinematics. They finally result in polymers whose molecular weights are very different.

**1.3.1. Step polymerization or polycondensation**

Here, the growth of the macromolecules is the result of chemical reactions between reactive functional groups of monomers (“steps”).

**1.3.1.1. Mechanism of polycondensation: polycondensation and polyaddition**

The mechanism of polycondensation is that of a classic chemical reaction: two chemical entities A and B meet and give rise to a third entity, with possibly (but not necessarily) elimination of a volatile compound (or a compound with low molecular

weight). The rate of the reaction is proportional to the probability of the meeting of the two initial reactants according to the expression:

$$v = k(T) \cdot [A]^p \cdot [B]^q$$

where [A] and [B] are the concentrations of the reactants A and B, p and q are the coefficients depending on the complexity of the reaction mechanism and k(T) is a function of the temperature.

### 1.3.1.2. Practical applications

The creation of a polymer by the polycondensation process implies that every monomer molecule has at least *two* reactive chemical functions. Two scenarios can then arise:

- when all the monomers have a functionality  $f = 2$ , the polymer obtained is linear;
- when one of the monomers, at least, has a functionality  $f > 2$ , the reaction produces a cross-linked polymer.

During the entire duration of the reaction, i.e. approximately several hours, all the reactional groups remain active. The size of the macromolecules obtained is relatively modest: about 200 to 300 constitutive units per molecule, i.e., molecular weights in the order of 20,000 to 50,000 g.mol<sup>-1</sup>. The kinetics of the reaction obeys the classic laws of probability. When the medium becomes too viscous, the exchanges can no longer occur and the reaction stops.

A particular characteristic of polycondensation reactions that result in the formation of a three-dimensional network is the occurrence of the phenomenon of *gelation*: the first reactions between the monomers give rise to polymers of low molecular weight called *oligomers* (these are polymers containing less than 30 constitutional units, in terms of size). At this level, the material remains soluble in solvents adapted to its structure. But when the degree of progress of the reaction reaches a certain value, known as the critical value, the system suddenly gains weight, a process which is called gelation.

From the gelation point onwards, the system can be separated into two fractions: the gel that is insoluble in all solvents that do not degrade it, and the sol that remains soluble.

When the reaction continues, the sol fraction decreases progressively as the gel increases, and from a certain degree of progress onwards, we get a totally insoluble macromolecular compound. This is at the most a giant molecule or rather a relatively limited number of highly entangled giant molecules.

To complete this description, we must however add that these processes can be disrupted at low temperatures by the phenomenon of *vitrification*, i.e. the transformation of the reactive phase into glass where molecular movements are frozen. We then use Gillham's TTT diagrams (transformation, time, temperature) to describe the various types of phenomena observed [FEV 86].

Lastly, *from a practical viewpoint*, the fact that the kinetics of polycondensation obey laws of probability implies in particular that the proportions of the mixture to be made to obtain the desired polymer are not indiscriminate. Thus, for example, if we want to make a mixture between two components called "base" and "hardener" (as is the case for epoxy resins), it would be a gross error to add the hardener in excess in order to obtain a "harder" or faster cross-linked product. Only the contrary would be achieved. In this type of materials, we must compulsorily comply with the proportions indicated by the manufacturer. This is why these products are generally available in predosed packages ("kits"). In general, we must never forget to read the product's technical data sheet.

As examples of polymers formed by polycondensation, we can mention *epoxy resins and polyurethanes* (see sections 3.1.3.1 and 3.1.3.2).

### **1.3.2. Chain polymerization or polymerization strictly speaking**

This type of reaction obeys a mechanism that is very different from polycondensation. It involves unsaturated monomer molecules (i.e., in this case, containing carbon-carbon double bonds that open when they are reactivated, giving rise to a carbon-carbon single bond and to two new bonds with other atomic groups). We give them an unsaturation index  $i$  equal to 1 per reactive double bond. The chain reaction mechanism comprises three steps: initiation, propagation and termination.

The initiation of the reaction requires the presence of a polymerization initiator (commonly though incorrectly called "catalyst") which creates active centers in very low concentration ( $10^{-7}$  to  $10^{-8}$  mol.L<sup>-1</sup> in the case of radical polymerization). These active centers make a large number of reactive double bonds of monomer molecules ( $10^3$  to  $10^5$  molecules per second) react in a very short period of time (generally less than a second). The reaction continues until the depletion of the monomers present or deactivation of the active centers following termination reactions if any.

In a chain polymerization, a macromolecule containing 1,000 to 10,000 constitutional units is built in an extremely short period of time (0.1 to 10 seconds). The macromolecules obtained are linear or cross-linked depending on the degree of unsaturation of the monomers. As this involves the opening of double bonds, it is



enough to transpose the logic followed for polycondensation by considering that a C=C double bond shows a functionality equal to 2 when it can be made reactive.

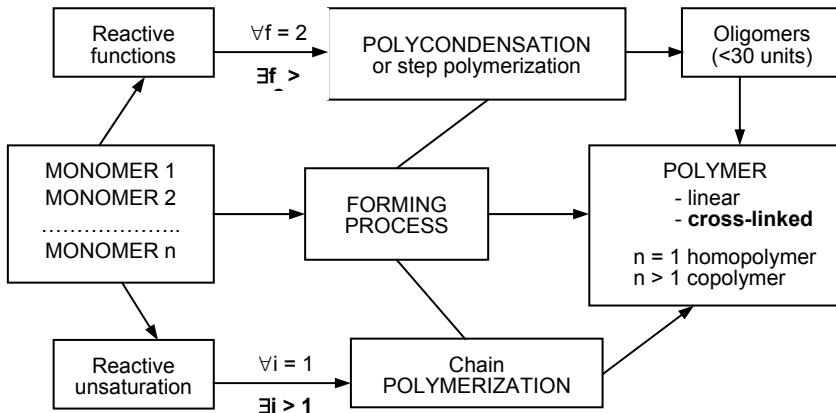
As examples of polymers formed by chain polymerization, we can mention *unsaturated polyester resins* and *methacrylic resins* (see sections 3.1.3.3 and 3.1.3.4).

The case of unsaturated polyesters as glass fiber reinforced composite matrices (see section 5.2) are sufficient to illustrate all the above notions:

- preparation in the workshop of *polymers* by *polycondensation* (with *elimination* of water) of a mixture of saturated and unsaturated diacids with diol; this unsaturated polyester is then brought into solution in styrene (unsaturated solvent, so potential monomer);

- *in situ* processing of the composite by *chain polymerization*, or more precisely *copolymerization* of that mixture (the unsaturated polymer, strictly speaking and the styrene itself) by the opening of the double bonds, reaction initiated using a “catalyst”, in reality a polymerization initiator, and an accelerator.

Based on the above data, summarized in Figure 1.3, we can envisage the various ways of processing polymers.



**Figure 1.3.** Formation of polymers (*f*: number of reactive functions; *i*: number of reactive unsaturations of the monomers; when these terms appear in light face, the mechanism results in linear polymers but if they appear in bold, cross-linked polymers are obtained)

## 1.4. Processing: thermoplastics and thermosets

Whether we want to form, mix or spread a material, the first thing to do is to make it deformable, even fluid. As regards organic polymers, we can distinguish two families of materials: thermoplastics and thermosets. The latter, once processed and correctly cross-linked, have a thermorigid behavior. They are also called thermohard materials. We will see further below that this distinction into two families does not cover all types of organic materials.

### 1.4.1. *Thermoplastics and thermosets, thermorigid or thermohard*

A polymer with a linear structure has the property of softening when it is heated, reversibly, as the essential characteristics of this class of polymers is the individuality of the macromolecules, which allows them to go to a liquid state (if their heat stability is sufficient) and to dissolve in certain solvents.

Linear polymers therefore yield thermoplastics.

As regards cross-linked three-dimensional polymers, we generally speak of thermosets, because these polymers owe their cohesion to the network that is constituted during the exothermic reaction that gave rise to them. There is no individuality of macromolecules. At the most, when the cross-linking has been completed, we could consider that the network forms a single macromolecule at the macroscopic level. They are in fact very large in number, highly entangled and held together by topological obstacles, i.e. by significant threshold energies.

These notions are summarized in Figure 1.4.

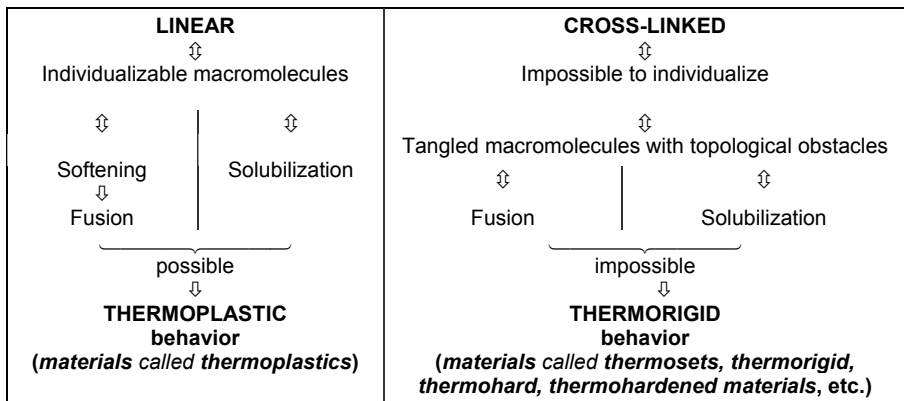


Figure 1.4. *Thermoplastics and thermosets*

### 1.4.2. *Monocomponent and bicomponent*

The processing of thermoplastics follows directly from their characteristics described in the above section. Thus:

– we can soften them by heating them *before their forming* using one of the following processes:

- simple compression molding, transfer compression molding or injection molding,

- extrusion,

- calendaring,

- cast, rotational or dip molding,

- forming, forging, etc.,

or *before their processing*, by cold casting and a cooling system freezes the thermoplastic material in the desired form;

– we can dissolve them in suitable solvents (essentially organic in nature) and process them in the form of solutions for applications in relatively thin coats;

– we can disperse them in the form of water emulsions or stable dispersions for polymers that are not water-soluble, which presents the advantage of processing a vehicle (water in this case) that is not expensive and not polluting in itself. From this technique follow all the other types of dispersions that tend to replace organic solutions and use surface active agents to maintain a certain stability in the system (see section 2.4.3.1); we can mention in particular glues, flooring, paints, etc.;

– lastly, the synthesis can be done *in situ*.

This last technique is the only one that can be applied to thermosets. This implies that, for manufactured objects, we must transpose any one of the methods described above for hot forming, and for construction materials, glues and structural adhesives, we must make the right mixture just before the processing.

Therefore, for cross-linked polymers, we are compelled to use products that are in the form of two components (and sometimes three) that must be mixed at the time of usage.

We can note in this context that this processing mode is exactly the same as that of classic hydraulic mortars in which we mix the cement (and the sand) and water at the last moment. We will see further below that this analogy can be observed with respect to the mechanical properties of the finished product.

To illustrate all this, we can take the example of paints where the active element to be processed is the binder. We can see:

- hot processing; this is the case of some road marking products spread using a heating device;
- solutions in an organic solvent, which can be diluted with white spirit, for instance;
- water emulsions or dispersions, which are increasingly developed currently (vinyl, acrylic paints, etc.);
- for certain uses like the anticorrosion protection of metallic structures, epoxy paint or polyurethane systems that are applied just after the preparation of the mixture between two reactive components called “base” and “hardener”.

Through these various examples, we can see two modes in which the material is presented:

- when it is enough to fluidify it, to soften it by heating or apply it in the form of emulsion or solution, we directly use the product supplied by the manufacturer, without any chemical modification, and this is called a *monocomponent* product;
- on the other hand, when it is necessary to mix two reactive constituents at the time of use to synthesize the polymer, we call this *bicomponent*. This term encompasses at times more complex mixtures, for instance when the product is filled and the filler is supplied separately or when the reactional system contains a base, a catalyst and an accelerator that must be mixed at the last moment and in the correct order. This is called *tricomponent*.

Having said this, we must not conclude that all monocomponents result in thermoplastic materials and bicomponents in thermosetting materials. Thus, the chemistry of polyurethanes (see section 3.1.3.2) helps in the formulation of *monocomponents reacting with the humidity in the air*, which are in fact bicomponents insofar as atmospheric water plays the role of a second monomer, or *monocomponents based on “blocked isocyanates”* which use the thermoreversibility of the reaction by which polyurethanes are formed to free one of the reactants of the polycondensation. These two types of “monocomponents” can also yield both thermoplastic and thermosetting materials.

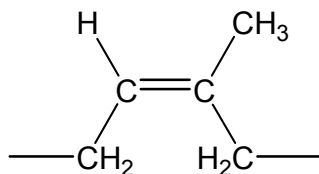
As we can see, things are not as simple as they might appear. The user must never play the role of an “amateur chemist”, i.e. take initiatives in the preparation of the mixture to be applied. That is why formulators have developed mixing spray guns, screw systems, etc. that help obtain the desired product directly.

## 1.5. Elastomers

The distinction between linear and cross-linked polymers, if it takes into account a very important difference between the two families of polymers, is not always very clear-cut in practice. In fact, there are linear polymers, including those with a thermoplastic behavior, whose reactivity has not been fully exploited, for instance unsaturated compounds with a large number of free double bonds after the formation of the macromolecule. If we perform a slight bridging between the chains by reaction with a third body or by limited polymerization, we will create a partially cross-linked structure, consequently with characteristics somewhere between the two families described above. If moreover the entropic properties of the chains are such that the glass transition temperature of the product is markedly lower than its usage temperature, an elastomer is formed.

This bridging reaction is normally called vulcanization. It is the reason for the development of a particular material: rubber. Natural rubber has been known to mankind for a very long time. Used for several centuries by the Indians for ball games or for making rainwear, it was discovered almost by chance in the middle of the 18<sup>th</sup> century by two French scholars, La Condamine, sent by the Paris Science Academy to Quito to measure an arc of the meridian near the equator and Fresneau, engineer and botanist based in Guyana, who studied in particular a rubber tree, *hevea guianensis*. The French term “caoutchouc” (i.e. rubber) means in the Mayan language “caa (tree) o-chu (that cries)”, thus illustrating the way in which latex was harvested. It was soon discovered that there are several kinds of trees or plant species capable of producing rubber, of which the most suitable for intensive cultivation was the *hevea brasiliensis* of the banks of the Amazon [CUR 84].

Latex is an ultrafine emulsion in a plant serum of natural polyisoprene, with the following constitutional unit:



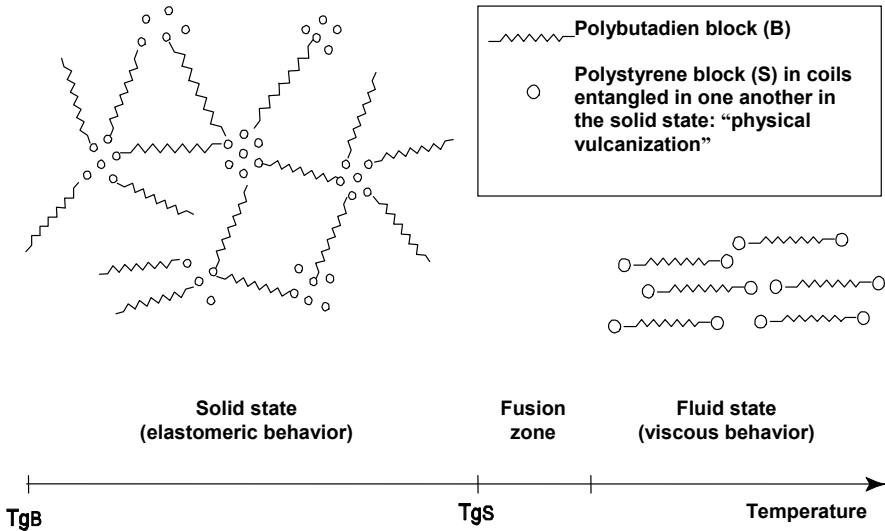
After coagulation of this latex, the material obtained exhibits rubber-like characteristics with elastic recovery under low strains. Unfortunately, it is not stable and oxidizes rapidly in the presence of oxygen in the atmosphere. A whole century was to pass before mastication and more particularly vulcanization processes, the latter discovered fortuitously by the American industrialist Goodyear, could give rubber its true importance.

Rubber elasticity strictly speaking, i.e. the elasticity observed in natural rubber, brings into play an energy variation of entropic origin (see section 1.8.3) particularly because of the existence of a double bond in the constitutional unit. The conformation of the macromolecule at rest corresponds to the formation of compact coils. When the material is subjected to a tensile force, the coils are undone reversibly until a certain stress level. Beyond this value, the material creeps.

Vulcanization reaction is the creation of a bridging, by sulfur, of polyisoprene chains with small chains  $-(S-S)_n-$ . The vital characteristic of rubbers is their great deformability, which can exceed 600%. This property results from the cross-linking density, which is lower than in the case of thermosetting polymers. Vulcanization is most often done by heating rubber to 130-150°C with 7 to 10% sulfur. If we gradually increase that rate, we observe that the elastic properties diminish progressively. When the fixation of sulfur reaches about 32%, we obtain a very rigid hard matter, ebonite. Rubber then behaves like a thermosetting material and has been used as an electrical insulator.

The shortage of rubber experienced by the main adversaries of the Second World War promoted the creation and development of other types of elastomer, new macromolecules (neoprene, chloroprene) with other modes of vulcanization. Thus was developed what some have called reversible *physical vulcanization*: some block copolymers like SBR (styrene-butadiene rubber) or SBS (styrene-butadiene-styrene) containing in themselves a physical incompatibility between the block types. At rest, the polybutadiene blocks of the various macromolecules tend to place themselves outside the polystyrene coils created simultaneously. The bonds between the chains are physical here whereas in the case of the vulcanization of rubber, we have chemical bonds by polysulfur chains. SBR and SBS have at normal temperatures elastic characteristics comparable to those of vulcanized rubbers. Under stress, these bonds loosen and the coils are undone, reversibly. Likewise, when the temperature

increases, the freedom of the chains sliding over one another increases and the agglomerates loosen. These materials therefore behave at high temperature (above  $T_{gS}$ ) like thermoplastics. They are therefore called *thermoplastic elastomers* (see Figure 1.5).



**Figure 1.5.** Thermoplastic elastomers. Case of SBS copolymer

The thermodynamic interpretation of this behavior first requires the knowledge of the phenomenon of glass transition, which we will discuss further below.

## 1.6. Preliminary conclusions

All the above information already explains certain properties of polymers. These are summarized in Table 1.1. We will see further below that the precise definition of the materials presented in this table requires the knowledge of an internal transformation of macromolecules, marked by a specific temperature, viz. glass transition.

<b>Classification according to:</b>	<b>The polymer is:</b>			
macromolecular structure	<b>Linear</b>		<b>Cross-linked</b>	
	semi-crystalline or amorphous with $T_{use} \ll T_g$	amorphous with $T_{use} \gg T_g$	slightly	highly
mechanical behavior	<b>Thermoplastic</b>	<b>Elastomer</b>		<b>Thermoset</b>
commercial presentation	<b>Monocomponent</b>			<b>Bicomponent</b> (tricomponent)
Technique of processing or use of the product	Manufactured product as such Binder, 3 possibilities: - heating - solution (organic solvent) - emulsion or aqueous dispersion	As such (manufactured product)		Mixing of the constituents at the time of use
<b>Polymer families in question</b>	<b>Thermoplastics and elastomers</b>  Polyvinyl chloride (PVC) Polyethylene and polypropylenes (LDPE, HDPE, PP) Polystyrenes (PS) Polyamides (PA) Linear polymethyl methacrylate (PMMA) Acrylic and vinyl derivatives (EVA, EVA-PIB, etc.)	<b>Synthetic rubber and thermoplastic elastomers</b>  Butyl rubber Polychloroprene Neoprene SBR, SBS, SIS EPDM	<b>Vulcanized rubbers</b>  Polyisoprenes Silicones	<b>Thermosets (resins)</b>  Epoxy resins (EP) Methacrylic resins (PMMA derivatives) Unsaturated polyester (UPE) and vinylester resins
	Polyurethanes			

**Table 1.1.** Classification of the polymers used in civil engineering



Table 1.1 gives a preliminary overall picture of the organic polymers used in construction, the notions that have been introduced provide avenues for explaining the usage properties of these materials, but all this still does not help us understand the behavior constitutive laws that govern them: their cohesion in the solid state, their reactions to various strains depending on time and temperature, their capacity to associate with other materials and their durability.

To try to answer these questions, we must get back to the study of the physical properties of polymers. This calls for the introduction of the notions of crystalline polymers and amorphous polymers.

### **1.7. Crystalline polymers and amorphous polymers: glass transition**

Whereas small organic molecules are generally, in the solid state, in a crystalline or microcrystalline form, this state is exceptional in the case of polymers. Thus, at normal temperatures, natural rubber is a flexible elastic solid, polymethyl methacrylate (PMMA) is vitreous, hard and rigid, whereas polyethylene is hard but flexible. Further, the same material can exhibit a wide range of behaviors in the solid state depending on the temperature at which it is subjected to a load. Thus, natural rubber becomes hard and brittle when it is immersed in liquid nitrogen.

The interpretation of these observations urges us to distinguish, firstly, two types of polymers in the solid state: crystalline polymers and amorphous polymers.

#### **1.7.1. *Notion of crystalline polymer***

Chemical species of low molecular weight between which interactions (Van der Waals forces, hydrogen bonds), such as paraffin or water, are capable of organizing themselves in space according to a three-dimensional network made up of the repetition of an elementary unit called crystalline mesh. The edifice obtained, known as crystal, has a very high regularity and its free energy is minimal.

As regards polymers, such an organization is not easy to achieve. It requires structural characteristics (in particular, the molecules must be identical) and particular preparation conditions (very slow decrease of the temperature from the molten state so that the system can reach its equilibrium conformation).

We can then understand that the existence of totally crystalline polymers is exceptional. We can however observe semi-crystalline polymers characterized by a

partial organization, juxtaposition of crystalline polymers, called crystallites, where the chains turn in on themselves to give rise to crystals whose outer geometric forms can reflect the crystalline arrangement and amorphous zones where the macromolecules are entangled and arranged in disorder.

We can lastly note that it is in the crystalline zones that the compactness of the molecular edifice is the greatest, the number of secondary bonds the largest, and therefore the cohesion of the material (and consequently its strength) the greatest.

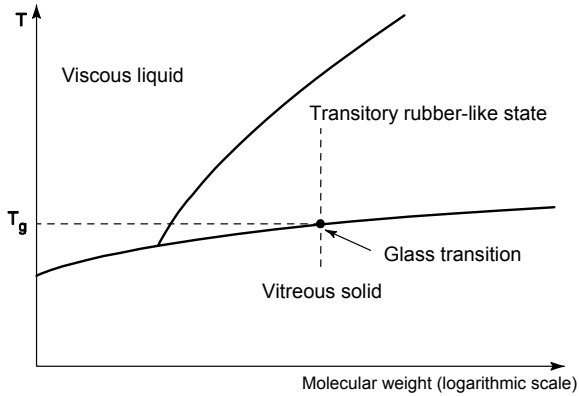
### **1.7.2. Amorphous polymers: glass transition**

The cohesion of materials made up of amorphous polymers or polymers comprising a significant proportion of amorphous zones (crystalline polymers with low crystallinity rate) brings into play the essential role of the entanglement of macromolecular chains when the temperature exceeds a certain value, known as glass transition.

Low molecular weight organic materials exhibit, when the temperature is raised, a direct solid–liquid transformation, called fusion. Things get complicated for amorphous polymers with high molecular weight: the entanglements of the chains maintain the cohesion between one another, which prevents this direct transformation and gives rise to a transitory state called rubber-like state where the molecular movements are restrained only by topological constraints such as the impossibility for a chain segment to move by sectioning a neighboring chain [MON 86].

The glass transition temperature ( $T_g$ ) thus marks the transition between the vitreous, rigid state and the rubber-like state. It marks the appearance of movements of long chain segments. The viscous liquid state is reached only at even higher temperatures, during another transition, as can be seen in Figure. 1.6.

We must however point out that the rubber-like state defined above does not imply that the material exhibits elastomeric properties. All amorphous polymers are capable of passing to the rubber-like state but only those that have a structure conforming to the definitions given above (see section 1.5) are elastomers. This point will be taken up again when we discuss the mechanical properties of polymers (section 1.8).



**Figure 1.6.** Phenomenon of glass transition (based on [MON 86])

The disordered structure of amorphous polymers gives them a low strength and a relative flexibility. The term “plastic” is directly associated with this type of material. On the other hand, semi-crystalline polymers are by nature very resistant. They manifest both a glass transition temperature for the amorphous regions and a fusion temperature for crystallites.

Glass transition manifests itself through a large number of physical properties: specific volume, dilatation coefficient, specific heat, dynamic modulus, dielectric loss angle, etc. It also manifests itself at the mechanical level as we will see now.

### 1.8. Mechanical behaviors of polymers: time-temperature equivalence

The mechanical properties of a solid material are generally studied under simple traction as this mode of stress is the easiest to apply and to interpret. The test consists of subjecting a material sample to a unidirectional deformation of constant rate; we then record the load depending on the deformation. We can thus measure the elasticity modulus, the breaking strength and the elongation at break.

With the same device, we can characterize the rheologic behavior of the material by subjecting it to a creep test, as shown in Figure 1.7. This test also helps describe the various behaviors that are manifested through the creep test.

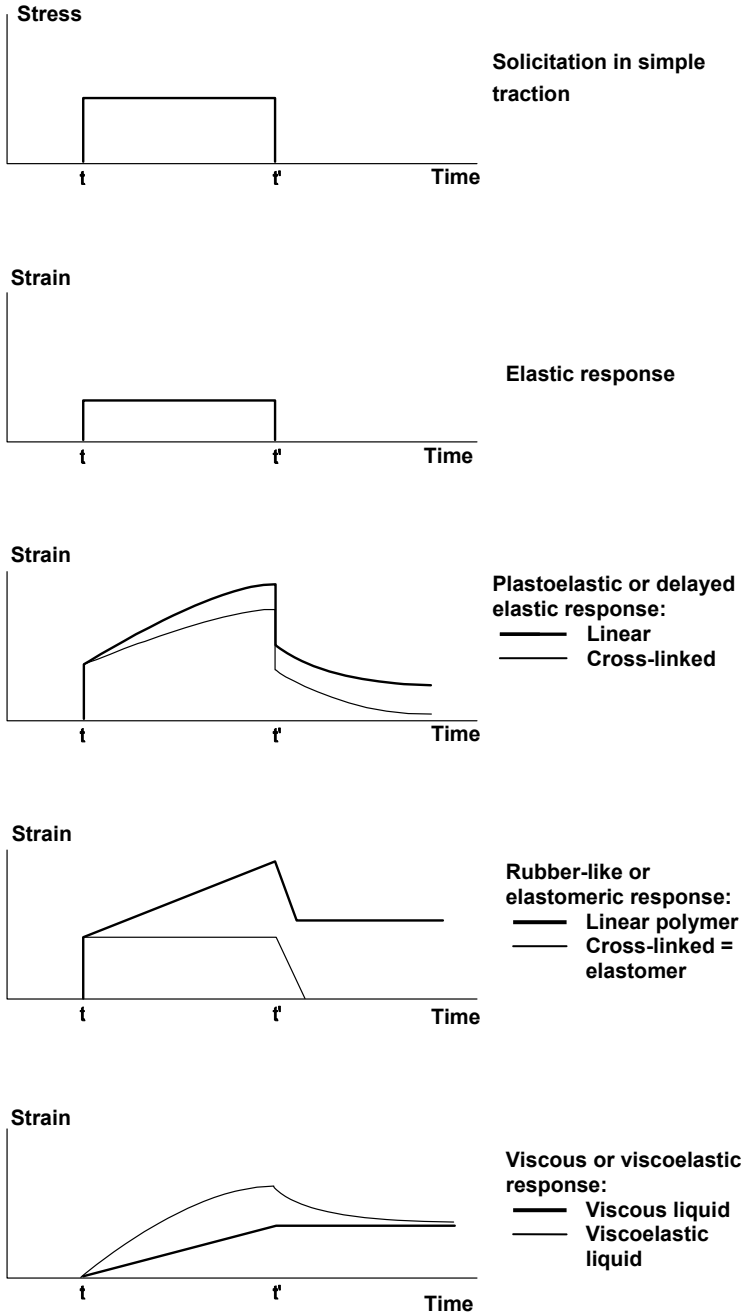


Figure 1.7. Reactions of a polymer to a mechanical creep strain

### 1.8.1. Elastic behavior

This behavior is common to all polymers at low temperatures (Figure 1.8). Its traction curve shows a linear section corresponding to a reversible elastic deformation. Its modulus of elasticity is high (in the order of  $10^3$  to  $10^4$  MPa) but its elongation at break is low (in the order of 5%).

When the break of the sample occurs after a low elastic deformation, but at high load, the material is described as fragile.

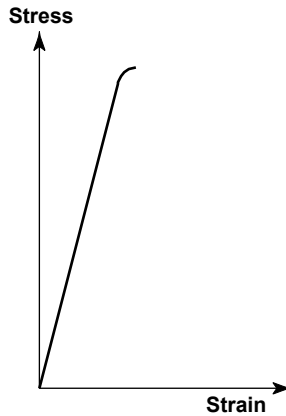


Figure 1.8. Elastic behavior

The elasticity brought into play is essentially of enthalpic origin, as the configurational organization of the polymer has not been affected.

It may be recalled in this context that the free enthalpy  $\Gamma$  of a body is the algebraic sum of two terms, enthalpic  $H$  and entropic  $TS$  where the temperature figures ( $\Gamma = H - TS$ ).

The behaviors described in the following two cases concern linear polymers. We will thereafter see (section 1.8.4) how cross-linked polymers behave.

### 1.8.2. Elasto-plastic behavior

A crystalline or semi-crystalline polymer with high crystallinity rate does not practically exhibit any glass transition when heated. However, before melting, it can go through a state where the chains tend to slide over one another under the effect of traction load.

Its traction curve (Figure 1.9) starts with a linear portion corresponding to an elasticity (which ends at a point called plasticity threshold or yield point). Beyond this threshold, two phenomena are superposed: a delayed elastic deformation involving the conformational state of the molecules, therefore reversible, and an irreversible plastic deformation, often accompanied by a hardening of the material (a phenomenon that makes the behavior of polymers resemble that of steels). This is a plastic, or rather elasto-plastic, behavior, as the creep occurs only above the plastic threshold.

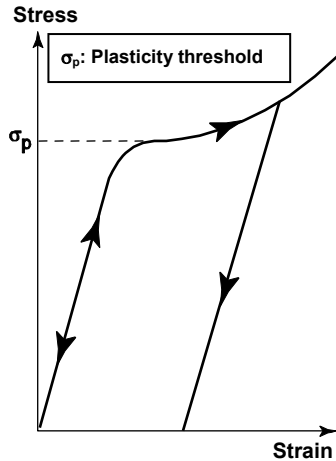


Figure 1.9. *Elasto-plastic behavior*

When the failure of the material occurs above this threshold, the material is called ductile. But when the strain is removed before failure, the material only retrieves the elastic part of its elongation, and evidently not its plastic deformation. Polymers that exhibit this behavior are also called *plastomers*.

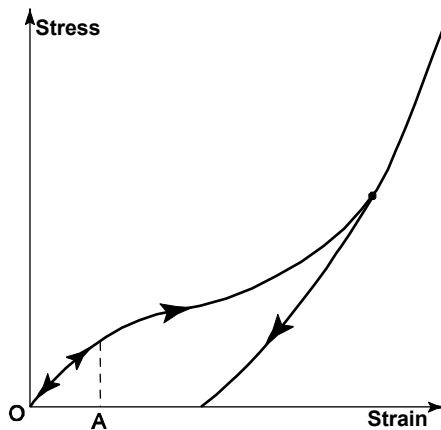
### 1.8.3. *Rubber-like behavior*

When an amorphous polymer is brought above its glass transition temperature, it exhibits a particular elastic behavior characterized by a low modulus of elasticity and a very significant deformation.

This behavior is essentially of entropic origin as it brings into play the conformational equilibrium of the macromolecules. This is confirmed experimentally by the fact that the stretching of rubber results in a heating.

During small deformations, i.e. for low stress levels, there is no difference between a vulcanized polymer and a non-vulcanized polymer. This reflects the first portion of the curve in Figure 1.10 (OA for example). But in order to completely deploy the chains without making them slide over one another, the polymer must be vulcanized.

We then observe that elastic return does not occur according to the stretch curve but with some delay and dissipation of heat. The phenomenon of hysteresis thus observed shows the entropic nature of rubber-like elasticity. Polymers that exhibit this behavior are called *elastomers*.



**Figure 1.10.** *Rubber-like behavior*

Here a new element comes into play: rubber-like behavior explicitly refers to a cross-linking (vulcanization). But the above behaviors were related to linear polymers. We must therefore go back to all the concepts we had discussed earlier about cross-linked polymers.

#### **1.8.4. Case of cross-linked polymers**

The behaviors described in sections 1.8.1, 1.8.2 and 1.8.3 presuppose linear polymers. The existence of segments linking chains with one another creates restoring forces that give cross-linked polymers significantly different behaviors.

At low temperatures, we do not observe any difference: the system is frozen and obeys Hooke's law, whether the polymer is cross-linked or not (Figure 1.7). When the temperature rises, we observe a glass transition that corresponds to the liberation of segment movements between the cross-link nodes in amorphous zones.

If the system has a relatively marked crystallinity or if the mesh due to cross-linking is particularly tight, this phenomenon can be attenuated. Above the glass transition temperature, the polymer exhibits a delayed elastic behavior (see Figure 1.7), i.e., the return to equilibrium requires both the retrieval of the instantaneous elasticity (as for linear polymers) but also the return to conformational equilibrium. This brings into play the entropy of the system, hence the delay observed for this operation. The existence of bond forces prevents the phenomenon of sliding and plastic return is practically complete.

For amorphous polymers, we saw that linear polymers react to a large extent as in the vitreous state for small deformations even though the phenomena brought into play (and the magnitudes of the stress and strain) are very different: after a brief elastic response (OA branch of the curve in Figure 1.10), the material creeps under the stress and returns to equilibrium with a delay due to the conformational equilibrium of the macromolecules.

Weakly cross-linked polymers behave like elastomers ("rubbers" as they are called commonly, which does not simplify our understanding of the phenomena ...), i.e. they describe the entire Figure 1.10 reversibly and return to equilibrium with the usual delay caused by entropic phenomena.

Lastly, strongly cross-linked polymers are practically not used above their glass transition temperature: otherwise, they decompose before reaching it, or quite simply, cross-linking is accompanied by an increase in this temperature such that the product is used in its vitreous state [MON 86].

To make things clearer, we can compare two elastic behaviors that are seen with amorphous polymers: enthalpic behavior, corresponding to the vitreous state (identical to that of a metal as it brings into play the distances between atoms) and entropic behavior, corresponding to the rubber-like state of an elastomer as we have just described.

The diagram in Figure 1.11 helps us understand the differences between these two behaviors and the energies brought into play by comparing the case of a schematic crystal (left) with that of a rubber-like medium (right).



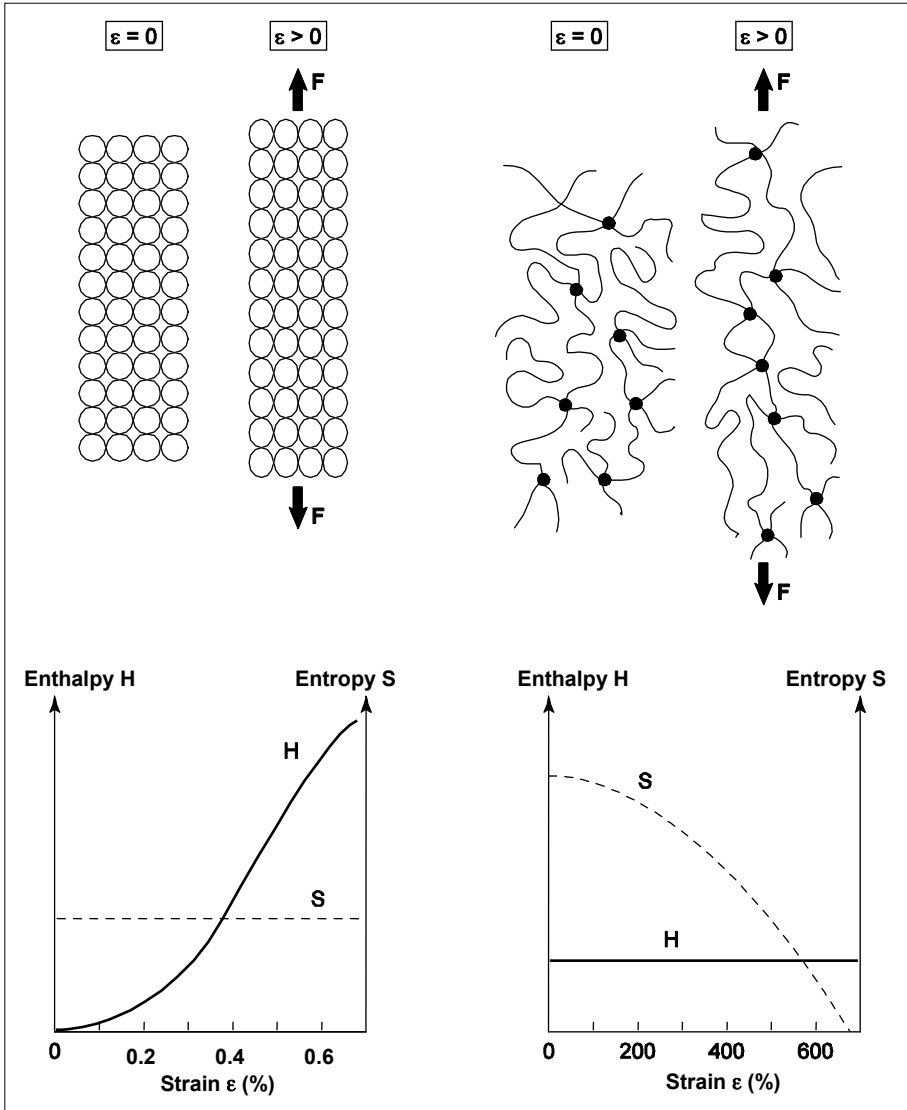
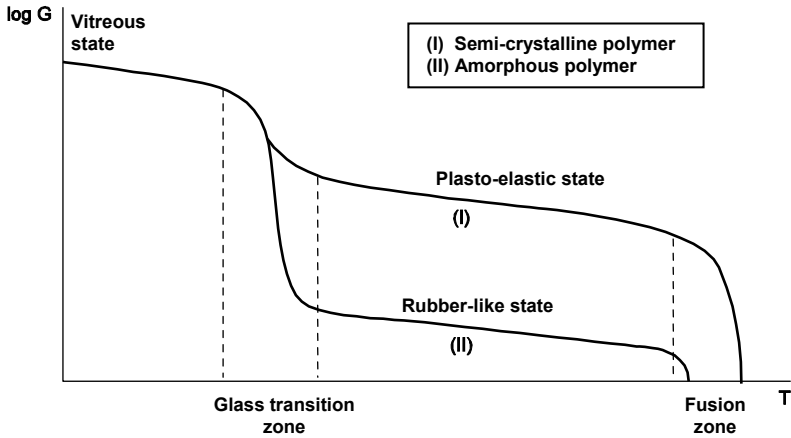


Figure 1.11. *Enthalpic elasticity and entropic elasticity (based on [KUR 87])*

All the above data can be summarized in a general diagram given in Figure 1.12.

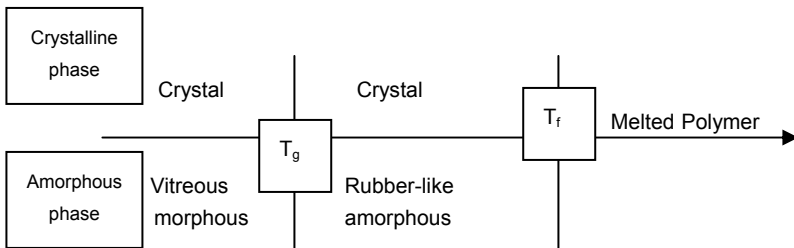


**Figure 1.12.** Mechanical behavior of linear polymers depending on the temperature

This diagram requires the following notes:

- the height of the rubber-like plateau informs us about the crystallinity of the polymer system studied, i.e. the polymer and its additives, because a finished product is always a mixture;
- for an *amorphous polymer*, we can distinguish two categories of materials depending on the value of their glass transition temperature:
  - when  $T_g \gg T_{ambient}$ , it is a *plastomer*,
  - when  $T_g \ll T_{ambient}$ , it is an *elastomer*.

We can also reason by studying the two types of phases and by bringing into play the glass transition and fusion temperatures (Figure 1.13).



**Figure 1.13.** Evolution of the phases of a semi-crystalline polymer with temperature

We can interpret the behavior of *thermoplastic elastomers* discussed in section 1.5 regarding SBS: the lateral blocks (polystyrene) have a glass transition

temperature  $T_{gS}$  in the order of  $100^{\circ}\text{C}$ , much higher than the ambient temperature where they are therefore in a vitreous state. The central block (polybutadiene), with a glass transition temperature  $T_{gB}$  of about  $-90^{\circ}\text{C}$ , much lower than the ambient temperature, is in the rubber-like state. The material behaves like a biphasic system at normal usage temperatures, exhibiting at high temperatures the classic behavior of a thermoplastic material (fusion when it is a plastomer like polystyrene) and an elastic behavior at low temperatures.

### 1.8.5. *Pure products and formulated products: plasticization*

The phenomenon of glass transition is characteristic of materials in the solid state, i.e. it takes into account the conformational system defined in section 1.2.2. Thus, the intimate mixture of a rigid polymer, at a high glass transition temperature, with a small quantity of smaller molecules inserted between the macromolecular chains can result in a material that exhibits a glass transition at a markedly lower temperature. This is the principle of plasticization, illustrated particularly in the family of polyvinylchloride where we can distinguish rigid PVCs from plasticized PVCs.

Plasticizers associate with polymers according to the same rules of miscibility as solvents. The difference between the two cases lies in the proportions of the partners involved. We call these bodies – chemically they are generally mono or diesters with short cycles (butyl to octyl) – *external plasticizers* as they are not chemically linked to the macromolecular system. As a result, they can migrate during the life of the object in which they are inserted and even escape. That is why some flexible materials become brittle due to aging.

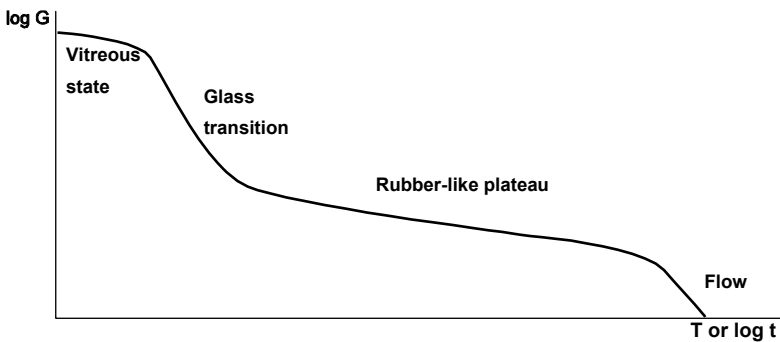
This drawback has led to the use of another family of products: *internal plasticizers* that occur essentially in so-called reactive products, i.e., products whose macromolecular network is formed just after the processing. The plasticizer is then part of the formation of the final macromolecule and plays a role of spacer between the chains allowing these movements that are prohibited to them when they are alone. Chemically, these are generally mono or bifunctional compounds of the same family as one of the constituents of the reactive mixture.

This principle applies to the entire manufacture of PVC products and to the formulation of various epoxy resin based products, for instance (see section 3.1.3.1). We can imagine the variety of possibilities offered to the polymerist or to the formulator, but this freedom is accompanied by corresponding constraints when it comes to guaranteeing stability over time and under the service conditions of the finished products made up of increasingly complex mixtures.

### 1.8.6. Time-temperature equivalence

The description of the various behaviors of polymers subjected to a tensile test refers to tests performed at a given traction speed and at various temperatures. In general, we could have carried out the same analysis at a given temperature and with different strain rates.

This twofold dependence of the mechanical properties of polymers depending on time and on temperature can be represented by a single figure where the relaxation modulus of the sample is seen depending on the time during which a stress is applied or depending on the temperature (Figure 1.14).



**Figure 1.14.** Schematic curve of the variations of the relaxation modulus with time and temperature

At low temperatures and for short load times, we observe a high modulus – this is the vitreous domain. We then observe a region in which the modulus varies with the temperature or time – this is the glass transition zone. We finally arrive at a temperature or time domain where the modulus hardly varies – this is the rubber-like domain. The latter is generally long depending on the molecular weight. The plateau corresponding to this domain is characterized by a very low modulus for a truly amorphous polymer whereas for a semi-crystalline polymer, it is influenced by its crystallinity rate. Finally, at high temperatures, for long load times, we observe a behavior identical to that of a viscous liquid, i.e. flow.

It is in the glass transition zone that the viscoelastic characteristics of the polymers are exhibited primarily. However, as we just pointed out, this character largely exceeds the zone in question and remains underlying in the other manifestations of the behavior of these materials.

In most cases, it is not possible to directly establish the curve in Figure 1.14. We then use the principle of equivalence, or the reduced variable method, which can be summarized as follows: we start with the observation that based on the measurement of any viscoelastic value of a polymeric material, a modulus  $G(T, t)$  for instance, at a given temperature and frequency (or response time), we can arrive at the same value  $G'$ , either by increasing the temperature, or by increasing the response time (or decreasing the frequency if it is a dynamic phenomenon).

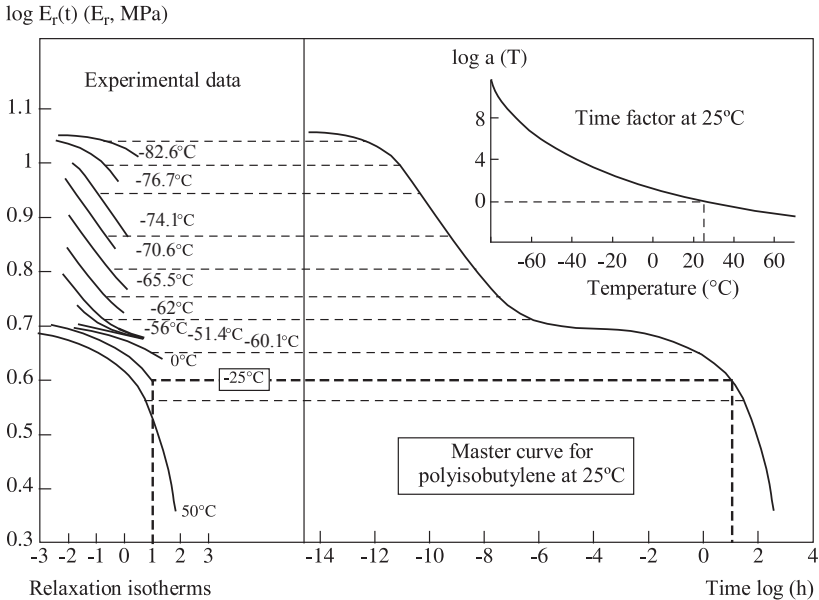
This logic is expressed schematically by:

$$G' = G(T, t) = G(T', t')$$

The theoretical explanation of this expression brings into play the spectrum of the representative delay or relaxation times of the behavior of a polymer (and more generally, a viscoelastic body) by superimposing, in parallel or in series, simple models. Thus, we assume that, when the temperature changes from  $T$  to  $T'$ , all the characteristic response times of the elementary mechanisms are multiplied by the same factor  $a_{T'/T}$ , noted more simply as  $a_T$ , less than 1 if  $T' > T$ .

The time factor  $a_T$  is better known by its logarithmic expression  $\log_{10} a_T$ , where the calculations are performed with respect to a reference temperature  $T_s$ , which is chosen for this purpose. It is then called the *shift factor*.

Thus, by measuring the variations of  $G$  with the response time (or the frequency of dynamic tests) in a reduced range of this parameter, at various temperatures, i.e., by carrying out measurement isotherms, we can plot the entire curve  $G(t)$  at this reference temperature  $T_s$  by simple shift (Figure 1.15). Inversely, from this curve, we can determine the behavior of the material at other temperatures. That is why it is called the pilot curve or more commonly the *master curve*.



**Figure 1.15.** Construction of a master curve (based on Mercier [MER 67])

This function, whose use supposes that the function  $\log a(T)$  is known, could be determined experimentally graphically, but efforts have been made to formalize it. Thus, Williams, Landel and Ferry have observed that it can be assimilated to the expression:

$$\log a(T) = \frac{-C_1(T - T_s)}{C_2 + (T - T_s)}$$

where  $C_1$  and  $C_2$  are constants dependent on the reference temperature  $T_s$ .

This expression is called the *WLF relation*. It applies relatively well to all the polymers around or above their glass transition temperature. At low temperatures, they rather obey the Arrhenius law whose expression is not, in the last analysis, very different from the above relation (linear in  $1/T$ , whereas WLF is homographic in  $1/T$ ).

Further, Williams, Landel and Ferry have observed that when  $T_s$  is close to the glass transition temperature of the studied material,  $C_1$  and  $C_2$  have practically the same values for all polymers, respectively 17.44 and 51.6 K. This rule is quite true in most cases, but shows deviations that we cannot ignore. We can then address the problem inversely by choosing the temperature  $T_s$  in such a manner that the values of the constants for the studied material are as close as possible to these quasi-universal values.

The WLF relation finds its theoretical justification through the concept of free volume developed in the glass transition theory, which is reassuring for a result derived from experience.

Lastly, we must add that the “reduced variables method” owes its name to the fact that it introduces not only a horizontal shift where the temperatures are brought to a reference temperature, but that it also takes into account the dimensional variations of the material and this introduces a slight vertical shift, which brings into play static complaisances and densities at both the temperatures.

### **1.9. Miscibility of polymers: concept of alloy**

By virtue of their high molecular weights, polymers exhibit a behavior that is highly different from that of small molecules when we try to dissolve them in a solvent. The adaptation of the mixture theory to organic macromolecules is not simple but it is nevertheless possible to describe a few of its aspects, in the perspective of the study on modified bituminous binders, for instance.

The notion of solubility can be defined as the possibility for a solvent to associate with the solute in such a manner that the association forms only one phase in the conditions of the experiment (temperature, proportions of the mixture). More precisely, the association is like the formation, around the solute molecules, of a set of several molecules of the solvent which “sheath” as it were the solute molecule. If we try to apply this definition to organic polymers playing the role of solute, we come up against a problem with quantity. What could be the meaning of “several” associated molecules encircling “one” solute molecule when the latter is a giant?

Firstly, we can already eliminate three-dimensional cross-linked polymers which, as we have seen earlier, tend to form a single macromolecule (or a set of macromolecules definitively tangled) at the level of a solid. There cannot be solubility, but we can observe in some cases the absorption of the solvent, which “swells” the polymer.

This swelling can be interpreted as a partial solubilization of the macromolecular medium, i.e. the dissolution of the oligomers that have not reached the critical molecular weight beyond which the network is formed.

As regards linear or branched polymers, the mixture theory has highlighted a value that is called solubility parameter. We will discuss it briefly.

### 1.9.1. Notion of solubility parameter

The miscibility of relatively non-polar compounds (which therefore exhibit weak and relatively non-directional interaction forces) supposes the existence of a low mixture enthalpy and can be translated by the expression:

$$\Delta H_m = k (\delta_1 - \delta_2)$$

where  $\Delta H_m$  represents the surplus enthalpy during the mixing,  $k$  a factor that takes into account the proportions of the mixture, and  $\delta_i$  is defined as the solubility parameter relative to the constituent  $i$ .

We can demonstrate that, for the solubility to be complete, this expression must be less than a certain critical value, i.e. that the difference  $\delta_1 - \delta_2$  must be low or zero. Hence the rule: *two compounds are miscible in any proportions if their solubility parameters are close to one another.*

These parameters can be determined in two ways:

– by calculation, for low molecular weight solvents, by means of the following formula:

$$\delta = \sqrt{\frac{L - RT}{V}}$$

where  $L$  is the latent vaporization heat, and  $V$  the molar volume of the solvent in question;

– experimentally in the other cases.

### 1.9.2. Estimation of the solubility

The knowledge of the parameters  $\delta$  must, in principle, help resolve all the solubility problems of polymers in a given solvent. We can even envisage the case where we use a binary mixture with a parameter  $\delta_{\text{mixture}}$  defined linearly from those of the constituents of the mixture:

$$\delta_{\text{mixture}} = x_1 \delta_1 + x_2 \delta_2$$

if  $x_1$  and  $x_2$  are the proportions of the mixture of solvents with solubility parameters  $\delta_1$  and  $\delta_2$  respectively.

This helps us find out how to dissolve a polymer using solvents which are both apparently non-compatible with the polymer, whether they are miscible with each other and whether their parameters  $\delta_1$  and  $\delta_2$  include that of the polymer.

There is, however, a limitation in this method. We have said that it supposes that the molecules are relatively non-polar. It is certain that if non-negligible directional



interaction or intensity forces develop between the solvent and the polymer, the theoretical bases that we used to define  $\delta$  are no longer valid and the method can only be considered as a preliminary approximation, which is at times misleading.

The solubility law based on the analogy of parameters  $\delta$  is not rigorous. It is preferable to see in it only a statistical result: the probability of dissolving a polymer in a given solvent is greater if their solubility parameters are close to each other. For information purpose only, Table 1.2 gives the solubility parameters of some solvents as well as their polarities.

The above considerations apply to pure products only. We can then ask ourselves whether they are applicable to complex mixtures like bitumens. The method has been used for studying the compatibility of bitumen-polymer couples and it has been observed that the solubility parameters of compatible polymers range between 16.6 and 17.6, which suggests that the average parameter of bitumen is in the order of 17 (see section 2.10).

Solvent	Electric moment	$\delta$ ( $J^{0.5} \cdot cm^{-1.5}$ )	Solvent	Electric moment	$\delta$ ( $J^{0.5} \cdot cm^{-1.5}$ )
Neopentane	0	6.3	Nitrobenzene	4.19	9.58
n-butane	0	6.64	Ethyl formiate	1.92	9.65
Isopentane	0	6.75	Chlorobenzene	1.70	9.70
Isobutene	0	6.78	Acetonitrile	3.98	9.75
Butadiene	0	6.83	Acetaldehyde	2.72	9.84
n-pentane	0	7.02	Acetone	2.95	9.81
n-hexane	0	7.25	Cyclohexanone	2.75	9.92
n-heptane	0	7.43	Hexyl alcohol	1.64	9.97
Diethyl ether	1.13	7.70	Dichloromethane	1.63	10.04
n-octane	0	7.80	Carbon sulfide		
Cyclohexane	0	8.25	Methyl chloride	0	10.1
Tetrachloromethane	0	8.62	Dioxanne		
Ethyl chloride	2.0	8.67	n-pentanol	1.86	10.2
Ethylbenzene	0	8.75	Pyridine	0.43	10.15
p-xylene	0	8.81	Butanol	1.65	10.55
Methylpropylcetone	2.8	8.92	n-propanol	2.22	10.87
Toluene	0	8.94	Nitromethane	1.59	11.25
Ethyl acetate	1.74	9.08	Ethanol	1.64	11.92
Styrene	0	9.20	Cresol	3.17	12.70
Benzene	0	9.21	Phenol	1.70	12.80
Acetic acid	0.65	9.24	Methanol	1.57	13.3
Dichlorethylene	0	9.27	Water	1.50	14.5
Chloroform	1.0	9.4		1.69	14.48
Tetrachlorethane	1.36	9.4		1.83	23.41

**Table 1.2.** Solubility parameters of a few solvents

### 1.9.3. Polymer-polymer mixtures: notion of alloy

The quest for new materials in the general field of organic polymers [OFT 95] can take different roads:

- develop new monomers;
- enhance polymerization and copolymerization methods to develop polymers or copolymers with an increasingly controlled structure (configuration in particular);
- search for stable polymer mixtures capable of cumulating their advantages and minimizing their weaknesses.

The first path is narrow: we have seen earlier that most polymers were discovered before 1950 and developed before 1980. This does not mean that all the possible monomers are currently known, but rather that there is little scope in this field.

The second regularly yields interesting results, whether for linear polymers with very low branching rate (which offers interesting mechanical and optical properties, for instance) or copolymers where we are increasingly in better control of the branching technology and which thus enables us to manufacture particularly pure polymers “à la carte” that can be produced at the industrial scale at affordable costs.

The third path concerns polymers mixtures frequently called *alloys* [PAS 95]. This term, which refers to metallic structures (by insertion or by substitution), has been criticized by a number of polymerists who prefer the term *mixture*. We must admit that the analogy with steels is not always evident, but it is convenient to describe the phenomenon and the term is now commonly used, particularly by producers who often consider this path the most promising.

We can say that two polymers are *miscible* when they are capable of giving a *homogenous mixture*. For two given polymers, this property can depend on the respective proportions of the partners and the temperature.

When the two polymers are not miscible and therefore it is impossible to obtain a homogenous mixture in the strict meaning of the term, we speak about *compatibilization* to denote the action of stabilizing the dispersion of one of the phases in the other by chemical (sequencing, grafting), physical (introduction of surface active agents called interface or compatibilizing agents) or mechanical (interpenetration of the networks) action or by the combination of these three modes of action. It is more precisely in this latter case that we speak about alloys.

Lastly, the mixture of a semi-crystalline polymer and an amorphous polymer can result in a heterogeneous product where the amorphous phase is enriched with a part of the crystalline polymer (the parts that have low molecular weight or are hardly crystallizable).

The study of the miscibility of polymers shows that it can exist only in relatively rare cases, for example when one of the partners is an oligomer. Another case is the preparation of a mixture between a copolymer and one of its homopolymers. Another uses the existence of specific interactions between the two partners.

To make these mixtures, which can be macroscopically homogeneous or heterogeneous, we generally use *mechanical means*.

Macroscopically homogeneous mixtures are made by high shear rate mixing of molten polymers. They have the drawback of exhibiting a bad thermal stability.

Heterogeneous mixtures in particular call for the technique of emulsion, in this case, the manufacture of microemulsions specially formulated so that the dispersion obtained is sufficiently stable. To this end, we play on the fact that diffusion in the macromolecules is very slow and we create metastable systems by techniques of co-reticulation, co-crystallization, in situ polymerization, etc.

As a general rule, we can say that polymer mixtures or alloys help us develop very interesting materials that can be varied infinitely, but whose stability is exactly equivalent to that of polymers or simple copolymers. This restriction is however not a drawback for their development when the usage parameters of the targeted finished product (temperature range, exposure to water, to solvents, etc.) are known and the mixture can be stabilized under these conditions (see section 1.10.1, regarding the notion of shelf-life associated with manufactured products). As a result, opinions are divided as regards the future of this method of manufacturing innovative materials, but we cannot ignore their importance.

On the one hand, the advances made in the process of synthesizing macromolecules have yielded materials with better performances and the new technologies developed in the field of grafting and the specific initiation of polymerization reactions are very promising.

All this shows that we have not yet fully explored the secrets of organic and organo-metallic polymers and that it is certainly in their field or with their help that tomorrow's materials will be developed. It may be noted in passing that organosilica polymers such as organosilanes and silicones can be considered in many respects as

very close derivatives of strictly organic polymers. That is why they will be assimilated to organic polymers in the rest of the study.

Lastly, it is remarkable to observe that the above discussion on polymer mixtures and alloys concerns molecules whose size is absolutely in the field of nanomaterials, i.e. systems of organized material ranging from a few nanometers to a few hundred nanometers. This is a recent approach in the knowledge of materials, which allows very interesting developments towards new achievements [OFT 01].

## **1.10. Durability and aging of polymers: life cycles**

“Plastics” are still often considered as second choice materials, not very durable, and which we must not hesitate to replace at the slightest defect. This image is not entirely wrong insofar as the habits of users have changed since the arrival of these materials on the market: rather than repairing, we dispose of the defective part or object and we buy a new one. But what is true for toys or small equipment must not be generalized without nuance to important civil engineering works. Organic polymers like all materials have a service life that the user must know before any use. We must not systematically believe that it is weaker than other materials, for instance, stone: everyone knows that we must destroy plastic packages that pollute public places and protect certain friable stones used in construction or decoration. In this field where reactions are often too subjective, even passionate, we must adopt a scientific outlook.

### **1.10.1. *Notion of aging***

We call aging any slow and irreversible evolution (under usage conditions) of one or more properties of the material in question. This evolution can result from modifications in the structure of the molecules that provide its mechanical cohesion, its composition or its morphology.

The influence parameters to be taken into account to study the aging of polymers include:

- data related to material: constitutive polymers, additives and loads, the chemical history of the polymer and additives during the processing, the morphology of the object, its thickness, etc.;
- data related to the environment and their variation over time: light, temperature, presence of oxygen, water, solvents, pollutants, application of mechanical stresses, etc.

The first set of data concerns the object that undergoes the aging and the second set concerns the factors involved in the deterioration of the object.

Among the material's characteristics that evolve during aging, we can mention in particular:

- the structure of the macromolecules present such as defined in section 1.2 with the influence of the various types of bonds ensuring the cohesion of the material (Figure 1.1);

- the composition of the formulated product, which includes, besides the main polymer, various additives and loads; if certain constituents disappear or just deteriorate, the product itself will suffer the consequences thereof;

- finally, the morphology of the object. This term primarily includes three terms: the *crystallinity* when we have a semi-crystalline polymer: (PE, PP, PA, PET, PBT, PVDF, PTFE), the *presence* if any of *microvoids* capable of acting as pockets of concentration of stress, therefore sites sensitive to aging, and *the gelation state* of the polymer which, when it is significant, has a protective role for the object against mechanical aggressions.

In general, we can note that crystalline zones are relatively not reactive and therefore resist chemical attacks, that impurities and structural irregularities are concentrated in the amorphous zones, which makes these vulnerable, but it is also here that the stabilizers added to the formulations are concentrated ... Besides, in the use of “plastics”, we often look for a material capable of resisting deformations, therefore with a partially amorphous structure. Formulation is the art of compromise.

Aging mechanisms are of various types:

- physical aging, with or without transfer of weight (action of solvents, diffusion, deplasticization by the departure of the plasticizer, for instance);

- chemical aging by the breaking of the chains, depolymerization, branching, reactions with additives or impurities.

In this last case, aging can be initiated or accelerated by light, heat or the presence of aggressive water. This is called thermochemical aging, oxydative or not, photo-oxydation, photodegradation, hydrolytic aging, etc.

To study and more importantly to try to foresee these mechanisms, we use accelerated or artificial aging methods, in which we must always specify the objectives and test conditions before arriving at conclusions.

In general, we define the useful life of an object as the time between the commissioning of this object (or manufacture, as the case may be) and the moment it becomes unfit for service. This property is not intrinsic to the material but depends on a well defined property and use. Further, a given material, characterized by its structure and its composition has a limited commercial shelf life, at the end of which it is replaced by a new material whose long term behavior is different.

Except in special cases, the commercial shelf life is no more than a few years. It is in the same order as the useful life and often shorter. Manufacturers are therefore confronted with the following problem: if they wait for the verdict of usage, they will effectively obtain indisputable information on the durability of the material, but will not be able to use it as this material will be obsolete (in the commercial meaning of the term) when they have this information. This means that it is vital to have methods to quickly evaluate their long term strength. Hence the importance of “accelerated” tests and the alertness that we must show in their interpretation.

We can finally note that it is dangerous to make a judgment on the durability of the material as such based on the behavior of a particular object manufactured from this material for a given usage. Often, it is possible that the formulation of the object is made with the ulterior motive that its durability must not exceed a certain value in order to supply the market correctly. This practice is common but never clearly admitted. The role of the various additives in the formulation is very important, just like the quality of the base material, but a good formulator knows how to use it one way or the other depending on the needs of the market.

### ***1.10.2. Principles of the methods for appreciating the life of materials***

The prediction of a material’s long term behavior is a difficult task [VER 88]. To understand it, we can adopt several types of approaches:

- the empirical approach, which proceeds by comparison and supposes that the kinetics of the evolution of the compared materials are the same; it is the simplest method, but is not always suitable;
- a mathematical approach, which consists of finding by successive approximations the mathematical relation that comes the closest to experimental data, without worrying about the observed phenomena; this method is generally acceptable for the interpretation of data at play within the model (interpolation), but dangerous when it comes to extrapolation;
- a physical or physico-chemical approach, i.e. trying to take into account the phenomena and to fit the model into the experimental data; this is evidently the best method as we can have a few assumptions at the start.

Based on these principles, we can discuss the study methodologies that always call for a judicious manipulation of the classic parameters: temperature (we know that the rates of physical evolution or chemical reaction increase with temperature), pressure in some cases, exposure to aggressive agents (solar or other radiation, oxygen, water, saline mist, etc.), mechanical fatigue, as the case may be, and the combination of all these processes within the “aging cycle” duly defined as such.

We can also add an important comment of general import: temperature generally has only a kinetic effect. It also acts, in a significant manner, on the thermodynamic equilibriums that can differ significantly from one temperature to another. We must therefore be careful while manipulating this parameter and always reason as a physico-chemist before adopting a new test protocol.

Every family of material has its battery of artificial aging tests. We will simply recall a few principles that have led to their use.

A good methodology for the study of aging relies on three main requirements [VER 84]:

- a scientific requirement first, which consists of defining precisely the parameters taken into account, separating as best as possible their specific actions by avoiding the formation of artifacts in the implementation of the chosen tests, and finally carrying out a rigorous analysis of the result using tested methods (statistical, in particular);
- a technological requirement, which recalls that we are essentially interested in a usage property of the material, for what it is used, and not what might happen to it in other contexts;
- and finally, an economic requirement: the study must be proportionate to the demand to justify the cost that it represents; in other words, we must use to the maximum existing data banks, available facilities and launch new studies only if we consider that the results will significantly increase the general level of knowledge.

A recent analysis of the studies on the aging of materials [OFT 03] has shown, regarding polymers, that there is a long way to go before the difficult transition from the microscopic, physico-chemical vision (structural modifications, for instance) to the macroscopic, mechanical vision (modifications of the usage properties) enhances the relevance of predictive models.

Lastly, we must never forget to resort to feedbacks.

### 1.10.3. *Fire behavior of polymers*

Organic materials have the reputation of being relatively incapable of resisting the effects of high temperatures and all the more of fire. It is a fact that the first generation polymers have demonstrated, excluding very rare exceptions and which we must relativize now. We know at present how to prepare thermoresistive polymers, precursors of new generations of products that will sooner or later impose their importance in the field of civil engineering materials.

The fire behavior of a part made from an organic polymer depends in reality on several factors [COL 99]. The polymer itself exhibits properties that we must consider only at the level of the order of magnitude as it is never used alone, but always formulated with various additives some of which are present just to increase its performances vis-à-vis fire, and particularly with a load rate that can be significant and which can considerably modify the behavior of the system. We must therefore consider the problem at the level of the part, the finished product.

We must then consider that this part is inserted in a system and that it is this system that can be exposed to fire. If judicious constructive provisions have been made to both protect the part (fireproofing cover, firewall, etc.) and to drain the thermal flows in case of fire, the part is no longer a sufficient threat for the use of the material in question to be prohibited.

Fire resistance brings into play notions that we need to recall briefly.

We call the *calorific value of a material* the quantity of heat released by the complete combustion of a kilogram of this material (expressed in MJ/kg).

But, as has been pointed out above, the material as such is not sufficient to define the risk being run. It is an integral part of an object or of a more complex set of pieces. We therefore use the notion of the *calorific potential of a system of materials* defined as the quantity of heat that this system would release by burning (expressed in MJ/kg).

Besides, we define the *reaction to fire* as all the phenomena that are exhibited from a rise in temperature and which result in the disintegration and then the inflammation of the gases released by the decomposition of the material. These phenomena are softening, carbonization, pyrolysis, combustion, emission of smokes, gases and soot, production of lighted drops or debris. This gives the classification of materials presented succinctly in Table 1.3.



Samples studied		Classification
Incombustible materials		M0
Combustible materials	Non-flammable	M1
	Not easily flammable	M2
	Moderately flammable	M3
	Easily flammable	M4
	Not classified	NC

**Table 1.3.** *Classification of codes of the fire resistance of materials*

We can note here that the effects of a fire also include the emanation of gases and smokes whose composition depends on the type of material attacked by fire. Thus, polyethylene burns like candle, phenolic resins char and rigid PVC dies out by itself.

For this particular aspect, we must therefore take into account the general behavior of the polymer when it is used in mass (Table 1.5) but without forgetting that it is incorporated into a system and that the probability of its catching fire or being consumed depends primarily on the heat flow that it receives.

Lastly, *fire resistance* is characterized by the time during which a structural element continues to perform its function despite the fire. It is translated by the definition of the qualities summarized in Table 1.4.

Samples studied	Classification
Stable in fire	SF
Fire break	PF
Fire stop	CF

**Table 1.4.** *Classification code of the fire resistance of materials*

These qualities are associated with a resistance rating that extends between a quarter of an hour and 6 hours.

A set of standardized tests are associated with these two classifications.

Thus, the fire behavior of a material is determined by its fire resistance classification whereas for a structural element, we must generally add the fire resistances of each of the materials composing it.

Polymer family	Monomer unit	Type of smoke released	Content of the smoke
Polyethylene (PE)	$-\text{CH}_2-\text{CH}_2-$	Light white smoke	CO, CO <sub>2</sub> , H <sub>2</sub> O, a few hydrocarbons
Polypropylene (PP)	$-\text{CH}(\text{CH}_3)-$	White smoke	CO, CO <sub>2</sub> , H <sub>2</sub> O, a few hydrocarbons
Polystyrene (PS)	$-\text{CH}(\text{C}_6\text{H}_5)-$	Heavy black smoke	CO, CO <sub>2</sub> , H <sub>2</sub> O, a few hydrocarbons
Polyvinylchloride (PVC)	$-\text{CH}_2-\text{CHCl}-$	Black smoke	CO, CO <sub>2</sub> , H <sub>2</sub> O and HCl
Polyamides (PA)	$-\text{R}_1-\text{CO}-\text{NH}-\text{R}_2-$	Light white smoke	CO, CO <sub>2</sub> , H <sub>2</sub> O, variable quantities of HCN
Polyesters, saturated (thermoplastics) or unsaturated (UPE), Vinylesters	$-\text{COO}-$ (common unit of the copolymers)	Black smoke	CO, CO <sub>2</sub> , H <sub>2</sub> O, a few hydrocarbons
Polyurethanes (PUR) (foam)	$-\text{R}_1-\text{COO}-\text{NH}-\text{R}_2-$	Light white smoke	CO, CO <sub>2</sub> , H <sub>2</sub> O, variable quantities of HCN
Phenolics	Copolymers complexes	No smoke, charring	CO, CO <sub>2</sub> , H <sub>2</sub> O

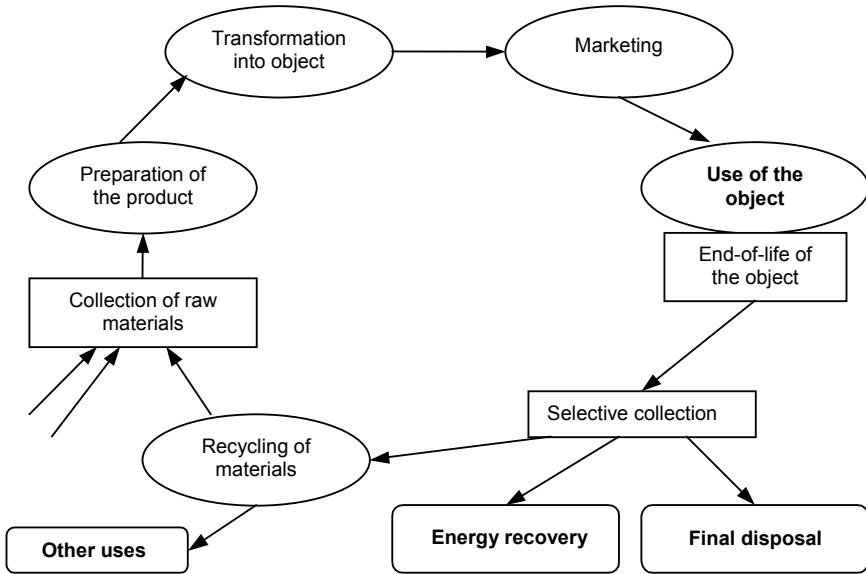
**Table 1.5.** *Smokes released by the main organic polymers used in bulk*

All these data are incorporated into the construction project.

To conclude, the fire behavior of a structural element comprising an organic polymer obviously depends on the nature of this polymer, but above all on its formulation and the architectural project of which it is a part, particularly construction dispositions that can increase the safety level of the project and make it comply with the specifications.

#### **1.10.4. General information on the life cycle of polymers**

Any finished product can be examined as a being which, after its manufacture, has been subject to a choice and to various movements to bring it to its place of use, performs a service for a certain time and ends its existence in various ways: recovery, recycling or disposal (Figure 1.16).



**Figure 1.16.** *Life cycle of an object*

This summary diagram immediately highlights the importance of selective collection. The current state of Western industrial fabric shows that this step is not idealistic as several projects are already operational and are operating well. But considerable advances are yet to be made.

Besides, we must not underestimate energy recovery: beyond the term that has a positive connotation, it is true that the recourse to incineration helps recover energy even while preventing the environmental impacts arising from the production of the same quantities of energy by a conventional process. In the case of chloride polymers, PVC for instance, as the incineration is done with the release of hydrogen chloride, this gas is recovered in smoke washing systems made compulsory in Europe by a 1990 Directive. We can also add that more than half of the HCl gas thus recovered comes from other constituents of household wastes, with the result that water washing treatment has become the rule for smoke treatment. It is fast becoming widespread.

It is clear that when we arrive at the stage when the object has completed its useful existence, and is therefore disposed of, it is the material that appears in the forefront and it is quite normal to come back to the life cycle of the material itself. We therefore define ecological balance sheets using life cycle analysis methods (ACV) [ROU 93], which are expressed, particularly on the technical datasheets of the materials, by indices such as those given in Table 1.6.

Indices	Standard units
Depletion of non-replenishable natural resources	kg.year <sup>-1</sup> .kg <sup>-1</sup> .10 <sup>-15</sup>
Increase in the greenhouse effect	t eq. CO <sub>2</sub>
Atmospheric acidification (acid rains)	g eq. H <sup>+</sup>
Eutrophization of rivers	g eq. PO <sub>4</sub> <sup>3-</sup>
Total production of solid wastes	g

**Table 1.6.** *Indices used for an ecological balance sheet*

The standard units given in this table are drawn from documents that have not yet received any recognized official approval but which have received a sufficient consensus for us to take them into account.

We must first make the sum of the resources extracted to manufacture a kilogram of the product and weight them by a coefficient that reflect their relative scarcity. The coefficient chosen is equal to the number of reserve years multiplied by the reserve.

The unit chosen for the contribution of a substance to the greenhouse effect is the CO<sub>2</sub> equivalent in weight.

For the contribution of a substance to acid rains, we have chosen the potential to release H<sup>+</sup> ions (whose cologarithm is pH) and for the contribution of a substance to the eutrophization of rivers, we have chosen the phosphate equivalent (eq. PO<sub>4</sub><sup>3-</sup>).

Every material can thus be evaluated, with the margin of uncertainty that this exercise implies, in the perspective of a general improvement of the living environment, but also that of the competitiveness of the various construction solutions available to designers. In this context, we can also point out there are too many preconceived ideas about the pollution caused by plastics. If these materials produce spectacular pollution, they are not the only ones, but our eyes, accustomed to other types of pollution, see only these. We must learn to relativize things.

### **1.11. Organic materials, the environment and health: evolution of the market**

The notions developed about the life cycle of polymers are related to the effects of the consumption of the planet's natural resources, their potential for consecutive replenishment and the effects of energy expenditures on the general functioning of the system. This is basically what we call the protection of the environment. All these problems have only recently become political concerns and have given rise in the dawn of the new millennium to new technical and economic constraints some of which have started to overturn the market of materials. We can mention in this

context the directives of the European Community, which regularly publishes the lists of products requiring more or less restrictive, even outright prohibitive, usage precautions.

In these considerations, man is only a part of the reasoning, even though the concern behind the entire issue is his long term survival. But his physical presence is clearly manifested in another recent awareness of the actors of the industrial society: occupational safety, workers' health and more generally public health about the use of materials whose toxicological effects, if any, are known.

We are witnessing a profound change in habits and mindsets. Some products are disappearing, taking away with them processes and industries used "forever" according to practitioners or leaving their place to substitute compounds, if possible, called "bio-", whose efficiency and usefulness are yet to be proved.

When we study the aggressiveness or the potential harmfulness of the products found on the market, we generally bring to the forefront organic products, both by the fact that molecules recognized as carcinogenic belong to organic chemistry and that these are "new products", and are therefore dubious. However, history associates the decline of the Roman Empire with the absorption by its leaders of tin salts from the goblets that they used to drink wine. Lead poisoning is the result of lead salts formed slowly in old pipes or old wall paints peeled by small children and not to mention arsenic so dear to all our legal columnists or asbestos ... Whether we admit it or not, at the start of the third millennium, organic products are still sources of fear.

In the field of construction, we will note in particular:

- the gradual disappearance, at least in consumer goods, of the use of solutions, i.e. the use of organic solvents to dissolve and make viscous mixtures, in favor of processes using water emulsions or dispersions;
- the more sudden disappearance of certain families of products used for synthesis, *in situ*, or even in workshops, because they are considered as seriously carcinogenic;
- the calling into question of manufacturing processes likely to harm the environment or produce wastes that are difficult to store.

The first series of constraints concerns firstly organic binders: disappearance of cutback and fluxed bitumens, solvent paints (to the great displeasure of amateur painters who see with nostalgia wholesale distributors selling off their good old paints with such pleasant odors ...) and certain glues. But there is no cause for concern: chemists have already developed alternative solutions; they must simply perfect them and convince the public to change their habits a little.

The second series is a challenge to manufacturers and formulators. The prohibition to use partially volatile aromatic amines for instance results in the obligation of either fixing them within non-volatile precursors or completely changing the manufacturing process. Besides, the obligation related to the marking of packages can exert a significant pressure to eliminate constituents whose use requires precautions rather ill-perceived by technicians.

Lastly, the complete upheaval comes with the third series of constraints whose consequences are indirect and are reflected in the price of the material itself.

It is therefore up to the chemists to take up these challenges and offer manufacturers “clean and healthy” but also “efficient” products – and it is certainly through a dynamic dialogue between the two professions that tomorrow’s technology can develop where organic materials will occupy an increasingly important place.

From all these data, we can now present a panorama of the main polymers used in civil engineering.

### 1.12. Main organic and organo-metallic polymers used in civil engineering

The use of organic polymers in civil engineering is considered in the collective conscious as marginal. The reality is different [MOU 02]. Table 1.7 shows the various fields in which they are used extensively.

For information purposes only, the statistics of the plastic manufacturing profession shows that the entire building and public works field used 23% of plastics consumed in France in 1998, i.e. a little over a million tons. We will see in the panorama presented by M. de Longcamp in Chapter 7 how things have changed and what trends can be seen in the coming years.

The polymers in question are primarily:

– polyvinylchloride, often called PVC: . . . . .	38%
– manufactured thermosetting materials (phenoplasts, aminoplasts, unsaturated polyesters): . . . . .	25%
– polyolefins (polyethylene and polypropylene) (HDPE, LDPE, PP,...): . . . . .	12%
– polystyrenes (PS and PSE): . . . . .	8%
– polymethacrylates (PMMA and derivatives): . . . . .	4%
– polyurethanes (PUR): . . . . .	4%
– poly(ethylene terephtalate) (PET): . . . . .	1%

In the remaining 8%, we find in particular products used for the interfaces, epoxy resins and glues, silicones, elastomers of the EVA family, fluorinated polymers, etc., materials technically important but used in small quantities.

The above statistics describe the entire building and public works industry, i.e. both construction and civil engineering, the latter representing only about 15% of the whole. In other words, they cover rather faithfully the field of construction. But for civil engineering, the materials used are the same.

<b>Field of use</b>	<b>Applications</b>	<b>Main polymers used</b>
Geotechnology, protection of the environment, below grade structures	Sealing: geomembranes and waterproofing system	PVC, HDPE, LDPE, chlorinated PE PmB = Modified bitumens with polymers: SBS, SIS, EVA, etc. Elastomers EPDM, etc.
	Reinforcement, separation, filtration, drainage: geotextiles and related fields	Polyesters, polypropylenes (PP) Polyamides (PA)
	Ultra-light alveolar structures for backfills or rainwater discharge	PP, PVC PS-E
	Energy or fluid transport networks (liquids or gas, water vapor)	PVC, HDPE (gas)
Routes	Surfacing: special mixes, surface coating, etc.	Modified bitumens with polymers (SBS, EVA, cross-linked polymer in place)
	Road equipments: noise abatement walls, panels, posts, etc.	Polycarbonates Methacrylic resins (PMMA) Glass fiber reinforced unsaturated polyester composite (UPE-GF)
Aerial structures	Reinforcement, repairing of structures, structural gluing, damp-proof membrane	Epoxy resins (EP), carbon fiber reinforced EP composites (EP-FC) Polyurethanes (PUR) Waterproofing systems
	Protection of structures by paint or plastic coating	Chlorinated rubber Acrylic or vinyl copolymers Epoxy, polyurethanes, polyvinylidene fluoride (PVDF), polyamides (PA)
	Sheaths for bracing cables or preload	High density polyethylene (HDPE)
	Support devices	Other elastomers
	Cornices, other equipment	PVC, PP

**Table 1.7.** Main fields of use of polymers in civil engineering

Another approach can be to classify polymers into large chemical families and to examine for each of them whether there are applications in the construction field in general and in civil engineering in particular (Table 1.8).

<b>Chemical families</b>	<b>Polymers in question</b>	<b>Applications (manufactured products, binders, additives)</b>
Polyolefins (or macromolecular paraffin)	HDPE LDPE PP	Gas pipes, bracing and preload sheaths Network pipes, tank sealing Large diameter pipes, geotextiles
Polyvinyl, polyvinylidene	PS, PVC P.vinyl acetate and derivatives (EVA) P.vinylidene fluoride (PVDF)	Lighting accessories Geomembranes, pipes, various equipments, PmB, additives for hydraulic mortars Anti-fouling protection
Acrylic derivatives	PMMA and derivatives  P.acrylamides	Noise abatement walls, lighting accessories, coating of industrial floors, epoxy mortar Geotextiles, hydroswellling mortars, superplasticizers for hydraulic concretes
Diene polymers (special rubbers)	P.isoprene P.butadiene and deriv. (SBR, SBS, EPDM)	PmB (polymer modified polymer; see section 2.10) PmB, geomembranes, road joints, structure bearing systems
Polyesters – saturated – unsaturated	  Copolymers (UPE), vinylesters	Geotextiles,  Chemical anchorage, cladding of structures, composites (glass fiber reinforced), industrial floors
Polycarbonates	PC	Noise abatement walls, lighting accessories, siding
Polyamides	PA	Geotextiles
Polyurethanes	PUR	Protection, insulation, paints
Polyether	Epoxy resins (EP)	Repair, protection (paints), coating, gluing, composites (carbon fiber reinforced)
Polysulfide	Ethylene, propylene polysulfide	Sealing of tanks, pipes
Phenolic and related derivatives	Phenoplasts, formophenolics or urea-form oligomers	Glues for wood (glue-laminated)  Superplasticizers for hydraulic concretes
Polyorganosiloxanes	Silicones	Sealing, anti-fouling protection

**Table 1.8.** *Polymers and their applications in civil engineering*



### 1.13. General conclusion

What must we remember from this presentation?

There is no doubt that organic polymers are chemical products but also that the user does not need to be physico-chemist to make use of them. The knowledge of this science is necessary only when he wants to really understand how these materials function. He can however keep a few important ideas in mind.

Organic polymers are the constituents of *materials which*, when subjected to a mechanical load, *react different depending on the time (or frequency) of the load and the temperature*. They exhibit in general a viscoelastic behavior. The influences of working temperature and the load time are closely interrelated (time-temperature equivalence).

This change in behavior in the solid state is called *glass transition* ( $T_g$ ). It is specific to amorphous polymers and to the amorphous part of semi-crystalline polymers. It is therefore all the more marked as the structure of the polymer is less crystalline.

Below the glass transition temperature, the polymer is hard, rigid and brittle. It is in a vitreous, frozen state.

Above this transition, it becomes soft, ductile and flexible, in a state described as rubber-like. Its cohesion is then essentially due to the entanglement of macromolecular chains. It is therefore important to know the position of the material's  $T_g$  with respect to the usage temperature range to be able to use it correctly.

However, commercial products are always mixtures. The art of plastic manufacturers and formulators of binder-based products consists of elaborating sufficiently stable mixtures for the expected effect – “softening”, plasticization, in this case, the decrease in the product's glass transition temperature compared to that of the pure polymer – is durable.

As regards semi-crystalline polymers, the cohesion of the crystallites (crystalline zones) is due to the interactions between macromolecular chains. These species can be compared to the crystals of mineral species and effectively exhibit a fusion temperature  $T_f$  if the polymer is still stable at this temperature.

We can distinguish two categories of polymers, thermoplastics and thermosets.

*Thermoplastics* are capable of relaxing when heated, according to the modalities shown above. When they are used as binders, they are in the form of monocomponents. Their behavior directly depends on their *linear* macromolecular structure.

*Thermosets* owe their specific resistance properties, their infusibility and their insolubility in all solvent to their *cross-linked* polymer structure. Their applications as binders in the field of construction deserve our special attention:

- Thermosetting resin based organic binders polymerize at the time of processing.

- *This reaction*, which is related to taking of hydraulic binders, is markedly more rapid than classic cements with water but is not done in the same manner for all products as it depends on the *polymerization mode*.

- Progressive and sensitive to temperature for epoxy resins and polyurethanes (*polycondensation*), it requires that the proportions of constituents must be meticulously complied with.

- Much faster for unsaturated polyesters and methacrylic resins (*chain polymerization*), it is less sensitive to temperature and requires less rigor in the dosage of constituents.

In all cases, the user must compulsorily refer to the products' datasheet supplied by the manufacturer.