IV.1. Introduction ;

Les polymères sont des matériaux organiques constitués de macromolécules. Ils sont largement utilisés dans de nombreuses applications industrielles, notamment dans l'emballage, l'automobile, la construction, la médecine, etc. La structure moléculaire des polymères peut être amorphe, semi-cristalline ou cristalline. Le comportement thermique des polymères est principalement influencé par leur structure moléculaire. Dans ce cours, nous discuterons en détail des polymères amorphes, semi-cristallins et cristallins. Nous explorerons également les transitions de phase, la viscoélasticité et le comportement mécanique des polymères.

IV.2. Amorphous phase:

When the regular arrangement of macromolecular chains is not achieved, an amorphous structure is obtained. In other words, an amorphous phase is a phase where there is an absence of long-range order. It is often represented as a "plate of cooked spaghetti (Figure VI.1). The amorphous structure of polymers is directly related to the flexibility of the chains, which is defined by several factors: chain length, branching, and steric hindrance. It is particularly due to the possibility of rotation around the σ bonds, which are the main bonds in the skeleton of macromolecular chains.

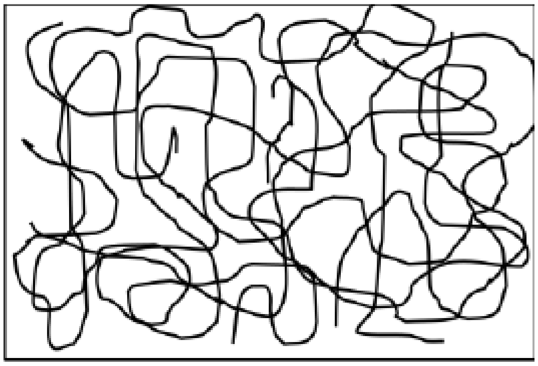


Figure IV.1: Diagram of an amorphous structure.

An amorphous polymer can be obtained by rapidly cooling the material from the molten (or liquid) state, due to branching, cross-linking, or large groups within the monomer preventing the periodic organization of the structure. At low temperatures, polymers are hard and brittle. However, at high temperatures, they are soft and viscous. An amorphous polymer is typically physically characterized by its glass transition temperature (Tg). The glass transition was first observed in elastomers (natural rubber), but quickly it was observed in all non-crosslinked polymers, consequently in thermoplastics. The glass transition is a phenomenon related to the possibility of movement of segments of macromolecular chains within the amorphous phase. Above this temperature, the amorphous polymer transitions from a glassy behavior to a rubbery behavior (Figure IV.2). In the rubbery state, the polymer is characterized by a low elastic modulus. It corresponds to a high capacity for reversible deformation related to greater mobility of the molecular chains. Below the Tg, in the glassy plateau, materials are much stiffer, not very ductile or even completely brittle.

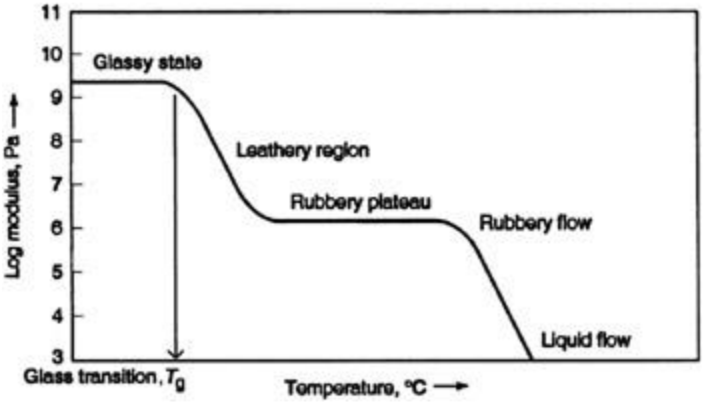


Figure IV.2 Variation of the elastic modulus of an amorphous polymer as a function of temperature.

The glass transition temperature of an amorphous polymer depends on several structural parameters: the rigidity of the main chain, the side groups, the effect of isomerism, the molecular weight, and cross-linking.

IV.2.1 Amorphous phase in the rubbery state:

For polymers with a glass transition temperature lower than room temperature, the amorphous phase exhibits a rubbery behavior at room temperature. This corresponds to non-linear elasticity, not obeying Hooke's law. This type of behavior corresponds to the long amorphous chains, each of which can take an infinite number of possible conformations. The amorphous phase in the rubbery state is characterized by the shear modulus beyond Tg , which is defined by the theory of rubber elasticity:

$$G_n^0 = \frac{\rho RT}{Me}$$

Where ρ is the density of the amorphous phase, R is the gas constant, and is the molar mass between entanglements.

IV.2.2 Amorphous phase in the glassy state:

For polymers with a glass transition temperature above room temperature, the amorphous phase exhibits a glassy behavior at room temperature, such as PET and PLA. At low stresses, the deformation varies linearly with stress. The behavior is therefore linearly elastic, and the behavior law obeys Hooke's law. Below the Tg, the movements of the main chains and the sliding of the segments are blocked. The elasticity module of the amorphous phase is significant.

IV.2.3 Techniques d'analyse des polymères amorphes :

There are several techniques for analyzing amorphous polymers, such as infrared spectroscopy (IR), X-ray diffraction (XRD), and differential scanning calorimetry (DSC).

X-ray diffraction (XRD) is used to determine the crystalline structure of semi-crystalline polymers. However, XRD can also be used to determine the amorphous structure of amorphous polymers. XRD can help understand the structure of amorphous polymers and differentiate between amorphous and semi-crystalline polymers.

Differential scanning calorimetry (DSC) is used to measure phase transitions in amorphous polymers. DSC measures the heat absorbed or released by the polymer when it undergoes a phase transition. DSC is used to determine the glass transition temperatures of amorphous polymers, which can help understand their properties.

IV.3. Phase cristalline

IV.3.1. Microstructure of the crystalline phase

The crystalline structure can be considered as the result of the periodic repetition in space of an elementary unit cell, which generates ordered regions. These ordered regions are composed of chains aligned parallel to each other. The organization of the ordered regions in a semi-crystalline polymer is observed differently depending on the different scales:

- The crystalline phase which consists of elementary unit cells whose lattice parameters are of the order of angstroms. An elementary unit cell is a set of chain segments that organize regularly.
- The crystalline lamellae, which are sets of folded chains with a thickness of the order of tens of nanometers.
- Spherulites are aggregates of lamellae in the form of spheres whose size is of the order of micrometers (from 10 to 100 microns).

IV.3.2 The crystalline network:

In the liquid state, polymer molecules are disordered in the form of coils. At the crystallization temperature, the molecular chains come closer to each other and align in parallel until they reach an equilibrium state where the molecular chains are arranged regularly. This arrangement forms an ordered zone that can be defined by a crystalline lattice. However, the order will be very different in the direction of the chains and in the plane perpendicular to them.

The most common polymer crystalline lattices are: monoclinic, triclinic, orthorhombic, quadratic, and rhombohedral (trigonal). Figure IV.3 shows the crystalline structure of polyethylene terephthalate (PET) given by Bunn et al. The parameters of the triclinic lattice are as follows: a = 0.457 nm, b = 0.595 nm, c = 1.075 nm.

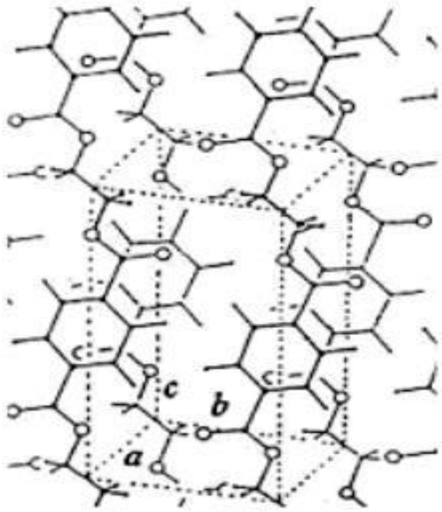


Figure IV.3: Triclinic unit cell of the crystalline phase of PET.

A polymer can exist in different crystalline structures such as poly(lactic acid) (PLA) : orthorhombic form α, β, and γ.

Due to the difference between intramolecular (van der Waals) and intermolecular (covalent) bonds, polymer crystals are highly anisotropic from a mechanical point of view. Cohesion in the axis c is greater than that in the axes a and b.

IV.3.3 The crystalline lamellae:

The structure of a semi-crystalline polymer is formed of the crystalline zone where the molecular chains are ordered and the amorphous zone where the chains are disordered. The crystallized zones are denser than the amorphous zones. The lamellae typically have a thickness of 10 to 20 nm , which is much smaller than the length of macromolecular chains, which are about 10 to 20 µm in length. figure IV.4

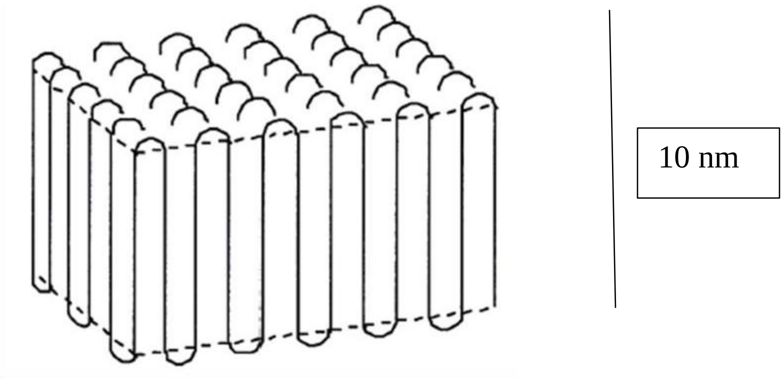


figure IV.4: Chain folding model in a single crystal

IV.3.4. Determination of crystallinity

IV.3.4.1. By densimetry

Densimetry is a method used to determine the crystallinity of a semi-crystalline polymer. This method is based on the difference in density between the crystalline phase (ρc) and the amorphous phase (ρa). It is often used when the values of ρc and ρa are sufficiently far apart to obtain sufficient precision. First, the density of a semi-crystalline polymer is measured by weighing a sample in air and then in a liquid. The liquid used in these measurements is distilled water. The density of the semi-crystalline polymer is calculated using the following formula:

$$\rho = (m_{air}\,\rho_{wather})/(m_{air} - m_{wather})$$

Where m_{air} is the mass of the sample in air.

m_{wather} is the mass of the sample in water.

ρ_{wather} is the density of water at the temperature of the test.

The degree of crystallinity (Xm) by mass is calculated using the formula below:

$$Xm = \rho_c(\rho-\rho_a) / \rho(\rho_c-\rho_a)$$

and in volume as:

$$X_v = (\rho-\rho_a) / \rho(\rho_c-\rho_a)$$

This technique is only used for PET as the densities of the crystalline and amorphous phases are sufficiently different, unlike PLA. The mass density of the crystalline and amorphous phases of PET are $\rho c = 1.445$ g/cm^3 and $\rho a = 1.335$ g/cm^3, respectively, which is a density difference of 0.11 g/cm^3. For PLA, the values are $\rho c = 1.29$ g/cm^3 for the mass density of the crystalline phase and $\rho a = 1.24$ g/cm^3 for the amorphous phase, which is a density difference of 0.05 g/cm^3.

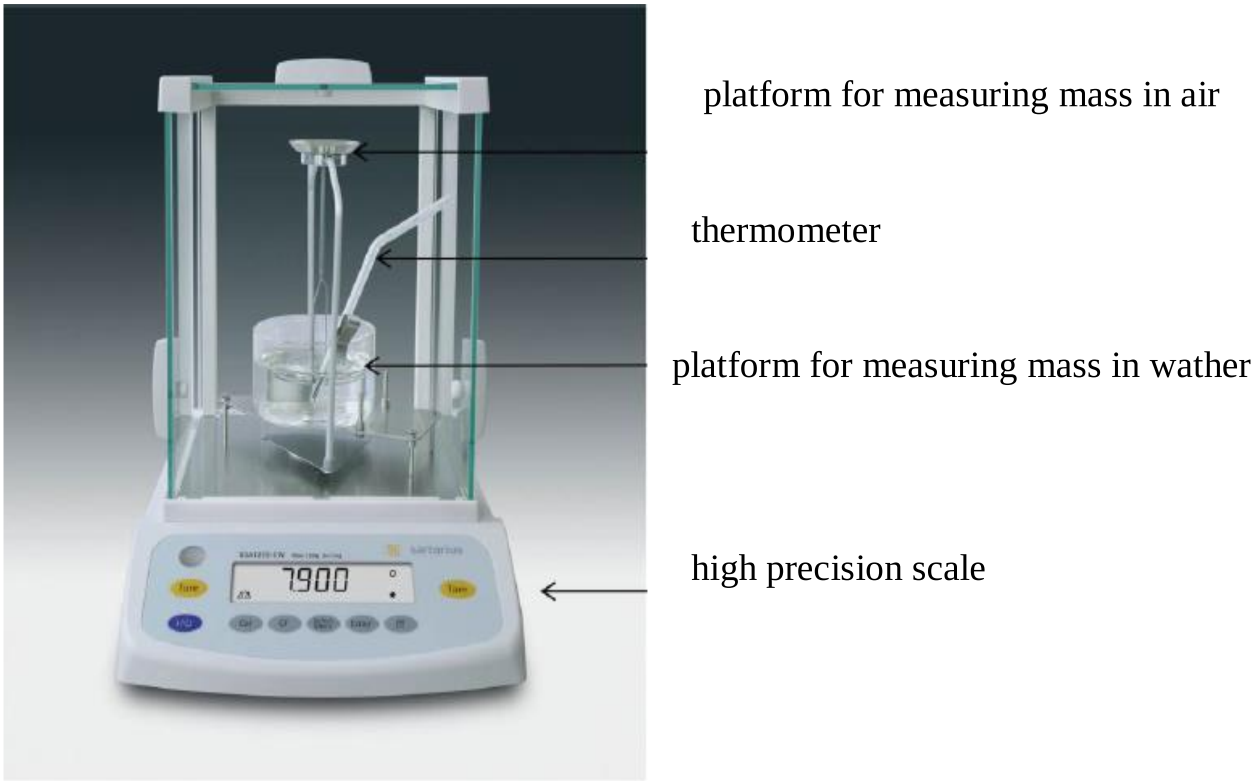


figure. IV.5 Sartorius YDK01 Density Device

IV.4. Semi-crystalline Polymers:

Semi-crystalline polymers have a molecular structure that includes both crystalline and amorphous regions. The crystalline regions have a regular and ordered structure, while the amorphous regions have a disordered structure. Semi-crystalline polymers are common and are used in many applications, including food packaging films, pipes, and wires.

IV.4.1. Crystalline Structure of Semi-Crystalline Polymers:

The crystalline structure of semi-crystalline polymers is formed by the regular stacking of polymer chains. The chains are arranged in a regular and ordered manner, creating a crystalline structure. The size and shape of the crystals depend on many factors such as temperature, pressure, and cooling rate. Crystals can be small and irregular or large and regular.

IV.4.2. Properties of Semi-Crystalline Polymers:

Semi-crystalline polymers have unique properties that distinguish them from amorphous polymers. The crystalline regions are more rigid and stronger than the amorphous regions. The mechanical properties of semi-crystalline polymers depend on the amount and size of crystals present in the material. Semi-crystalline polymers also have better heat resistance than amorphous polymers.

IV.4.3. Applications of Semi-Crystalline Polymers:

Semi-crystalline polymers are used in many applications due to their mechanical and thermal properties. They are commonly used in food packaging films, pipes, wires, toys, and sports equipment. Semi-crystalline polymers are also used in the automotive industry to manufacture interior and exterior parts.

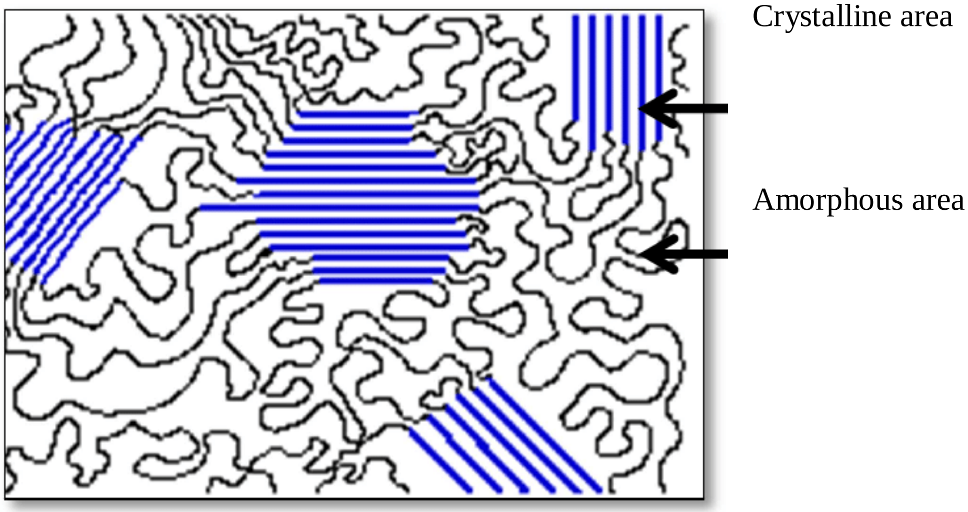


figure IV.6 Schematic of a semi-crystalline polymer

IV.5. Thermal behavior: (glass transition)

IV.5.1. Glassy state:

In the glassy state (at low temperatures or high speeds), the molecular movements accessible to the polymer cannot initiate cooperative movements along the chain skeleton. The accessible deformations are therefore weak and the modulus is high. Elastic deformation is controlled by the enthalpic term of its internal energy, as in metals. Despite being in a glassy state, the polymer is not frozen. There are always temporal and spatial fluctuations of conformation, controlled by temperature: they are more rapid and numerous as temperature increases. Therefore, it becomes "easier" to deform the material as its temperature increases. The modulus is thus thermodependent and decreasing. Similarly, the material remains viscoelastic. Under high stress, plastic deformation processes can be activated at medium temperature and speed, but are inoperative at low temperatures or high speeds. This results in the existence of a temperature (and/or speed) of ductile/fragile transition, lower than the glass transition temperature. Let us say that the apparent behavior of the polymer when it is in a glassy state is viscoelastic, viscoplastic, with more or less developed macroscopic ductility depending on temperature and speed.

IV.5.2 Transition zone:

The D transition zone, associated with glass relaxation, or the viscoelastic zone, marks the moment when global conformational changes, i.e. cooperative movements along the chain skeleton, become possible. The modulus therefore decreases rapidly and the behavior is highly evolving.

IV.5.3 Rubber zone:

In the rubber zone, the temperature is sufficient for the chain to spontaneously sweep all its possible conformations in a time much shorter than the representative time of the solicitation. However, the temperature is too low to allow the unraveling of the chains on a large scale. Macroscopically, the chains therefore appear flexible, but flow is prohibited. The material gradually becomes hyperelastic, in fact viscohyperelastic, if it is not cross-linked. Plastic processes give way to entropic elasticity at large deformations.

The existence of crystals partly compensates for the loss of modulus and cohesion of the amorphous polymer. Thus, the rubber plateau of a semicrystalline material is not only higher but also longer than that of an amorphous material. These two points explain why a semicrystalline material, such as PP or PE, can be used above its a transition, while an amorphous material, such as PS, will be limited to its glassy plateau. To use an amorphous material beyond its glass transition, it must be cross-linked, which are elastomers. In parallel, the crystal always has enthalpic elasticity and plasticity processes. A semicrystalline polymer thus remains viscoplastic, with structural hardening and/or damage, on its rubber plateau (Figure IV.7).

It is also important to note in Figure 3 that PC and PP have very similar macroscopic behaviors, although they are the sites of very different processes: amorphous and glassy for one, and semicrystalline and rubbery for the other.

IV.5.4 Fluid zone:

The fluid zone appears when chain disentanglements become probable. The chains appear statistically independent of each other. The solicitation can therefore easily move them relative to each other. The behavior becomes mostly viscous, but remains viscoelastic.

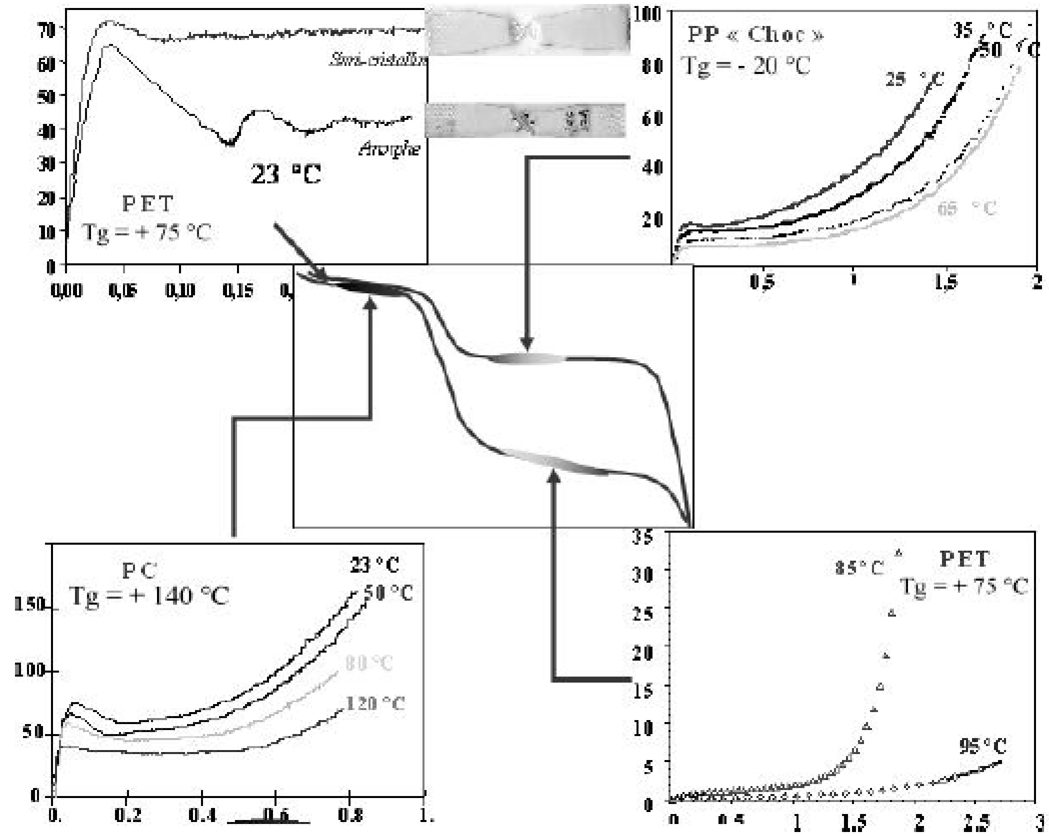


Figure IV.7 : Example of tensile behaviors of polymers at 0.001 s^{-1} as a function of temperature (given with respect to their respective Tg).

IV.6. Viscoelasticity:

Viscoelasticity is a phenomenon that characterizes the mechanical behavior of materials, especially polymers. It refers to the ability of a material to exhibit both viscous and elastic responses to an external force. In other words, viscoelasticity combines the characteristics of both a liquid and a solid material. Understanding viscoelasticity is crucial in the development of many everyday products that we use, such as rubber bands, tires, and plastics. In this paper, we will discuss the viscoelastic behavior of polymers, its importance, and its applications.

IV.6.1 Viscoelastic Behavior of Polymers:

Polymers are long chains of molecules that have a complex internal structure. They are made up of repeating units called monomers, which are joined together to form a chain. Polymers can be classified as either amorphous or semi-crystalline, depending on their structure. Amorphous polymers have a disordered structure, while semi-crystalline polymers have regions of ordered structure, called crystallites, within a disordered matrix.

When a stress is applied to a polymer, it deforms elastically up to a certain point, after which it deforms plastically. At low deformation rates and high temperatures, the polymer exhibits a viscoelastic behavior. This means that the polymer exhibits both viscous and elastic behavior, depending on the rate of deformation and the temperature. The viscous response is characterized by a time-dependent flow, while the elastic response is characterized by a time-independent deformation.

The viscoelastic behavior of polymers can be understood by considering the motion of the polymer chains. At low deformation rates, the polymer chains have enough time to move and align themselves along the direction of the applied stress. This alignment results in a viscous response, which causes the polymer to flow. At high deformation rates, the polymer chains do not have enough time to align themselves and instead deform elastically.

IV.6.2 Mechanical Models:

The linear viscoelastic response of polymeric solids can be described for many years by a number of mechanical models that can provide a useful picture of time dependent deformation processes. It is possible to analyze the deformation of viscoelastic materials with appropriate combinations of elastic springs, which obey Hook's law and viscous dashpots that obey Newton's law of viscosity; the dashpot is imagined as a piston moving in a cylinder of viscous fluid.

IV.6.3 Maxwell model:

the Maxwell model consists of spring and dashpot in series as shown in Fig. (IV.8).

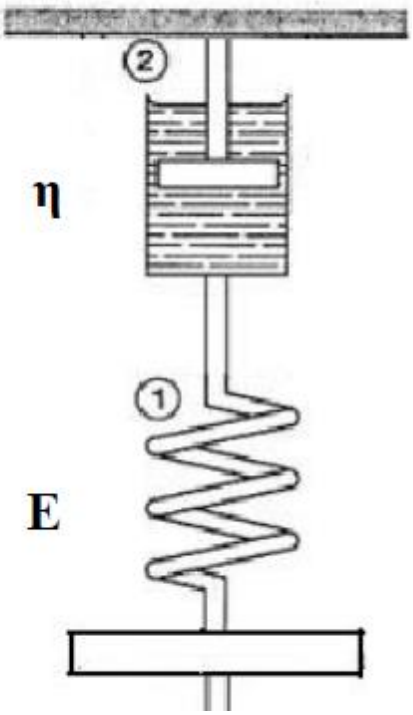
For creep, stress is constant ($\sigma = \sigma_o$),

strain will change with time;

so $d\sigma/dt = 0$. ($\sigma = \sigma 1 = \sigma 2$, $\varepsilon = \varepsilon 1 + \varepsilon 2$)

The final equation of Maxwell model is :

$$\varepsilon = \sigma_o t / \eta \qquad \text{(IV.1)}$$



Eq.IV.1 corresponds to the response of only viscous element, which is not very realistic form of behavior because in this equation strain increases linearly with time (viscous behavior). This is not generally true for viscoelastic materials where the creep behavior is more complex.

IV.7. Mechanical characterizations:

IV.7.1 Tensile test:

This is a basic test for homogeneous plastics. It allows determining the stress at break, the elongation at break, and the modulus of elasticity.

A specimen with a well-defined geometry (see figure IV.9) is clamped at both ends using jaws or grips. One of these fixed jaws is connected to a dynamometric system for measuring forces via a ball joint so that the axis of forces is aligned with that of the specimen. The other mobile jaw is connected to a driving system that operates at a constant speed or a constant load, but less commonly (see figure IV.10).

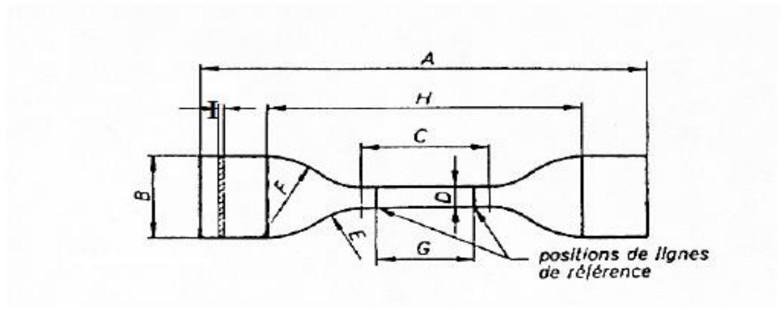


Figure IV.9: Altered specimen for tensile testing.

Dimensions:

A : Longueur totale minimale.	75.00 mm
B Width of the ends	12.5 ± 1.0 mm
C Length of the calibrated part	25.0 ± 2.0 mm
D Width of the calibrated part	4.00 ± 0.4 mm
E Small radius	8.00 ± 1.0 mm
F Large radius	12.5 ± 2.0 mm
G Distance between reference lines	20.0 ± 1.0 mm
H Initial distance between jaws	62.5 ± 5.0 mm
I Thickness.	2.00 mm

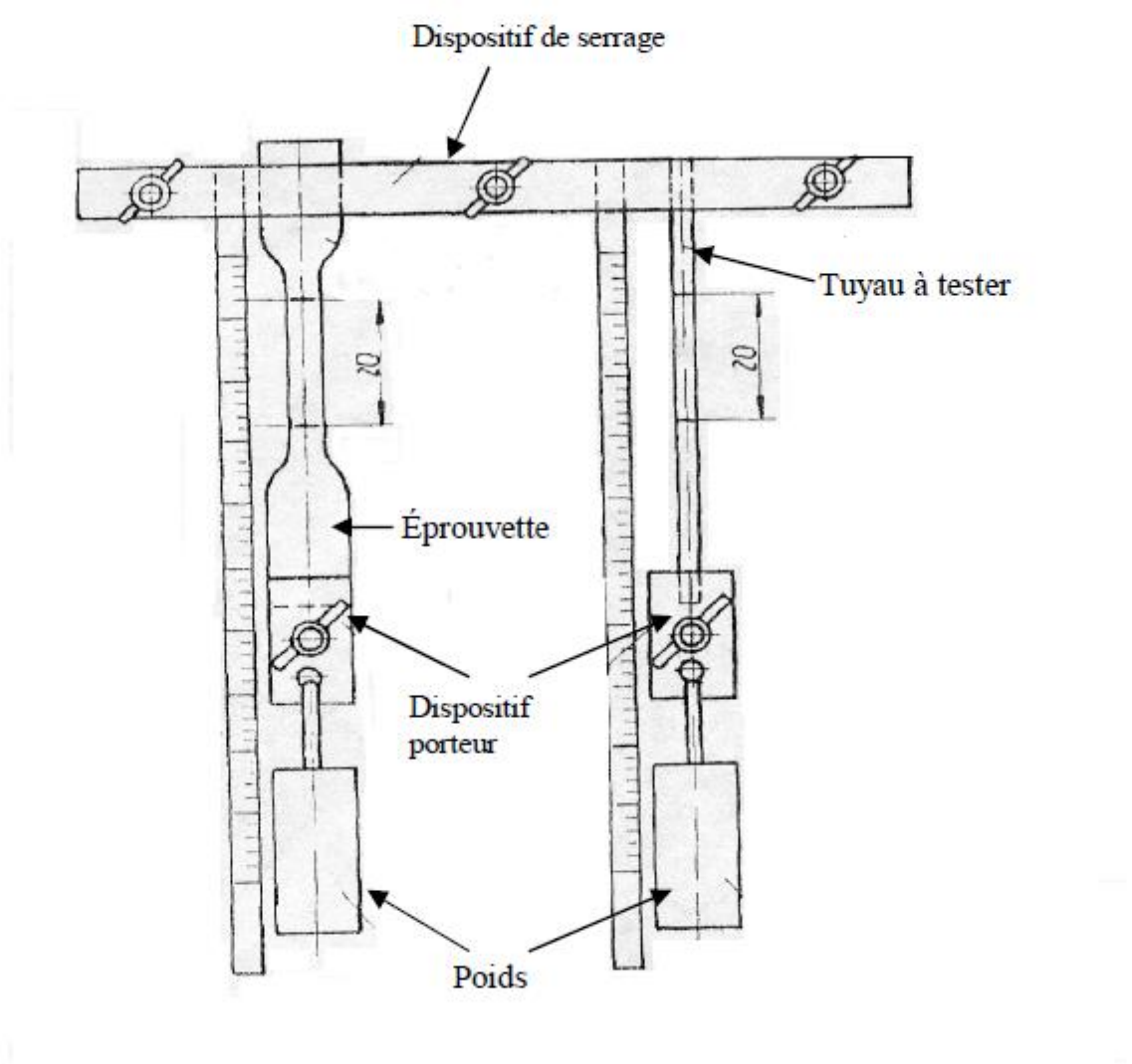


Figure IV.10 depicts a diagram of a tensile testing machine at break.

The stress at failure was calculated using the following equation:

$$R (\sigma) = F/ S$$

F: The applied force (N)

S: section of the specimen (mm)

The elongation at break was calculated using the following equation:

$$\text{All }\% = [(l - l_0) / l_0] \times 100$$

All: elongation at break in %

l : final elongation measured in mm, l_0 : initial test elongation measured in mm.

IV.7.2 Hardness test:

The hardness of a material is its resistance to penetration by a given shaped and sized indenter (a steel ball or a diamond cone).

The Shore hardness penetration index, commonly referred to as Shore A or Shore D hardness, is the result of a measurement carried out according to a specific procedure using a Shore A or a Shore D durometer.

The specimen can have any shape (square, rectangular or disc) provided that the dimensions allow for at least five measurements at different locations at least 6 mm apart from each other and at least 12 mm away from the edges of the specimen. The surface of the specimen to be measured should be as flat as possible. It is preferable to use specimens with two parallel faces to have a flat and horizontal testing face.

The test is performed after checking the marked mass of 1 kg for the Shore A durometer or 5 kg for the Shore D durometer and ensuring proper positioning of the specimen on the mobile plate, as shown in Figure IV.11

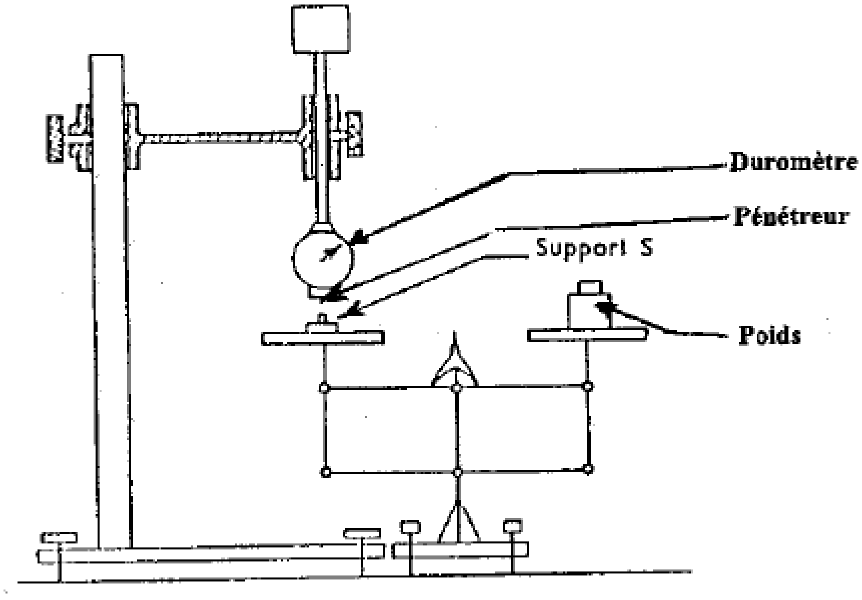


Figure IV.11 Schematic of a hardness tester

One quickly raises the platform to apply the presser foot on the specimen without impact, as soon as stable contact is established, the durometer is triggered, and the reading is taken after (15 ± 1) seconds.

Shore hardness is expressed as follows:

$$\text{Dur. Shore } X = M$$

X: represents the letter corresponding to the type of Shore durometer used: A or D.
M: represents the calculated average value.

IV.7.3 A loss of mass

All the tests mentioned above are instantaneous tests, that is to say, they make it possible to determine the characteristics of the material in the short term. It is certain that depending on the conditions of use, these characteristics will evolve over time. It is therefore necessary to consider long-term tests that take into account mechanical stresses.

The mass loss is based on weighing the sample before and after the heat treatment.

The mass loss was calculated using the following formula:

$$P = \Delta P / S$$

P: loss of mass in g/cm2

ΔP: difference in weight in g.

S: surface area of the specimen in mm2.

where this surface area is calculated using the following formula:

$$S = (180\,E + 1256)/100$$

E : thickness of the specimen in mm.