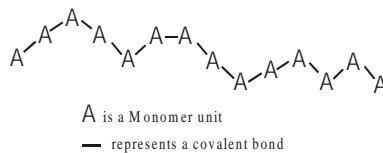


## Introduction to polymers

### 1. Polymeric materials – basic definitions, structure, classification

#### 1.1 Molecular structure

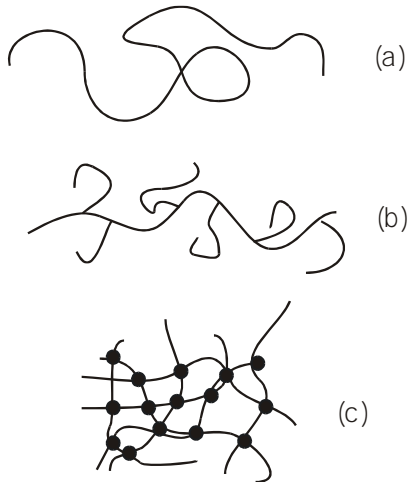
Polymers (or macromolecules) are very large molecules made up of smaller units, called monomers or repeating units, covalently bonded together (Fig 1). This specific molecular structure (chainlike structure) of polymeric materials is responsi-



**Figure 1:** A polymer chain.

ble for their intriguing mechanical properties. Polymer architecture can vary. In Fig 2 three possible molecule architectures are depicted.

A *linear polymer* consists of a long chain of monomers. A *branched polymer* has branches covalently attached to the main chain. *Cross-linked polymers* have monomers of one chain covalently bonded with monomers of another chain. Cross-linking results in a three-dimensional network; the whole polymer is a giant macromolecule. *Elastomers* are loosely cross-linked networks while *thermosets* are

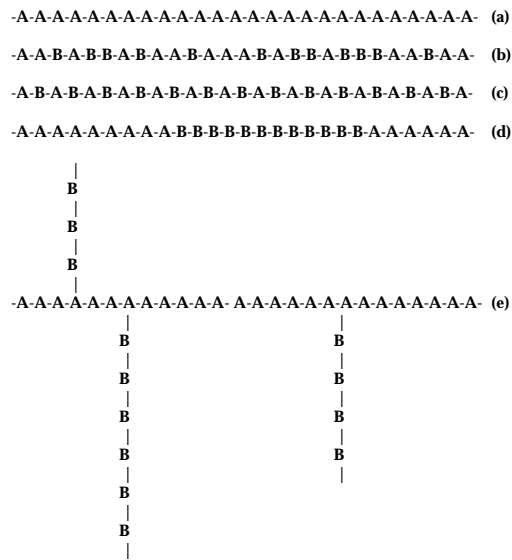


**Figure 2:** Types of molecular configuration: (a) Linear chain. (b) Branched molecule. (c) Cross-linked network: molecules are linked through covalent bonds; the network extends over the whole sample which is a giant macromolecule.

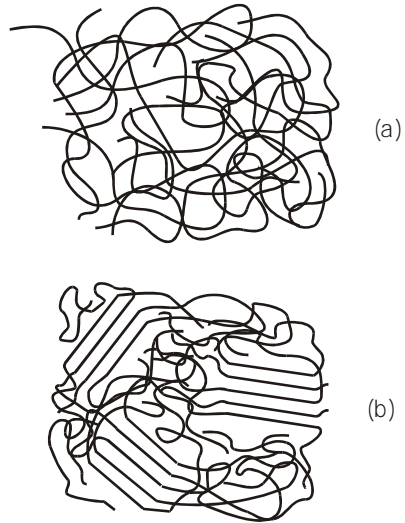
densely cross-linked networks.

Another classification of polymers is based on the chemical type of the monomers (Fig 3): *Homopolymers* consist of monomers of the same type; *copolymers* have different repeating units. Furthermore, depending on the arrangement of the types of monomers in the polymer chain, we have the following classification:

- In *random* copolymers two or more different repeating units are distributed randomly
- *Alternating* copolymers are made of alternating sequences of the different monomers
- In *block* copolymers long sequences of a monomer are followed by long sequences of another monomer
- *Graft* copolymers consist of a chain made from one type of monomers with branches of another type.



**Figure 3:** (a) Homopolymer. (b) Random copolymer. (c) Alternating copolymer. (d) Block copolymer. (e) Graft copolymer.



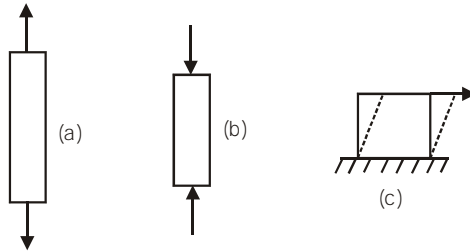
**Figure 4:** (a) Amorphous polymer (observe the entanglements among the polymer chains) and (b) semicrystalline polymer.

### ***1.2 Microstructure***

Many properties of polymeric materials depend on the microscopic arrangement of their molecules. Polymers can have an *amorphous* or *semicrystalline* (partially crystalline) structure (Fig 4). Amorphous polymers lack order and are arranged in a random manner, while semicrystalline polymers are partially organised in orderly crystalline structures.

### ***1.3 Thermal Behaviour***

Thermosets, which are densely cross-linked in the form of a network, degrade upon heating, while thermoplastics, which do not contain cross-links, melt upon heating.



**Figure 5:** Examples of types of forces: (a) Tensile force. (b) Compressive force. (c) Shear force.

### ***1.4 Composite materials***

Polymers are often mixed with inorganic particles (usually in the form of fibers, such as fiberglass) in order to modify and improve their mechanical properties. Such materials are called *composites*.

## ***2. Mechanical behaviour of polymeric materials***

Whenever a force is exerted on a solid material, the material will *deform* in response to the force. Depending on the particular orientation of the force with respect to the material surface different types of forces can be identified. In Fig 5, some common types of forces are depicted. For our subsequent analysis, *tensile* (pulling) forces will be used. A mechanical test using tensile forces is called a tensile test. Generally speaking, the basic concepts remain the same for all types of forces.

### ***2.1 Elastic behaviour***

A material is *elastic*, if upon an applied force, its deformation is instantaneous and constant, and upon the removal of the force, its recovery is instantaneous and

complete (i.e. the material will return to its original shape).

In order to make the analysis of a mechanical test independent of the materials size, it is useful to define a quantity called *stress*  $\sigma$ ; it is defined as the force  $F$  divided by the cross-sectional area  $A$  of the material [units  $\text{N/m}^2 = \text{Pa}$ ]. The deformation is quantified by the *strain*  $\varepsilon$  which is defined as the length change  $\Delta l$  divided by the initial length  $l_0$  and it is dimensionless. In case of a tensile test the strain is often called *elongation* and is usually expressed as a percentage increase in length compared to the initial length.

The stress-strain relationship is given by the following equation

$$\sigma = E\varepsilon \quad (1)$$

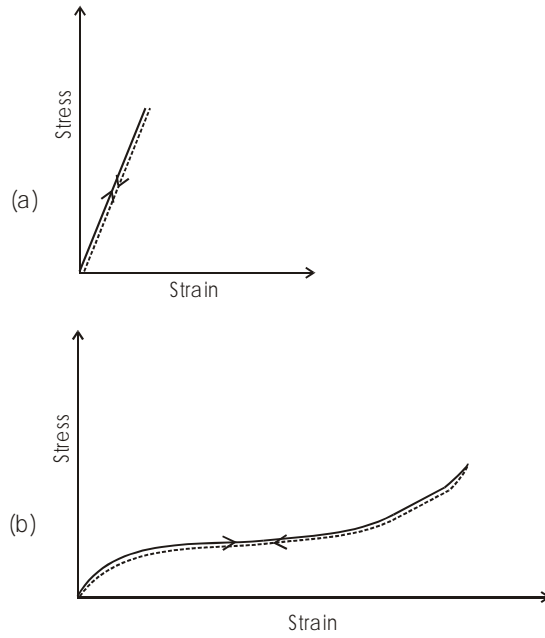
where  $\sigma = F/A$ ,  $\varepsilon = \Delta l/l_0$  and  $E$  is the Young's modulus [units  $\text{N/m}^2 = \text{Pa}$ ].

In Fig 6 two stress-strain(elongation) curves are shown. The first one is linear and reminds us of Hooke's law of mechanical springs ( $F = kx$ ). In this case, Young's modulus is constant and mathematically it is the slope of the stress-strain curve. The solid materials that exhibit such behaviour are called linear or *hookean*. Practically, this behaviour is encountered in almost all materials (metals, ceramics and polymeric materials) only at sufficiently low stresses and deformations (e.g. 1 per cent). The second stress-strain(elongation) curve corresponds to the elastic behaviour of a *non-linear* or *non-hookean* solid and it is characteristic of elastomers. In elastomers the elastic behaviour holds for very large deformations (several times the original sample length, e.g. 400 per cent) which can be attained by relatively low stresses. *It is clear that elastic behaviour is not always linear.*

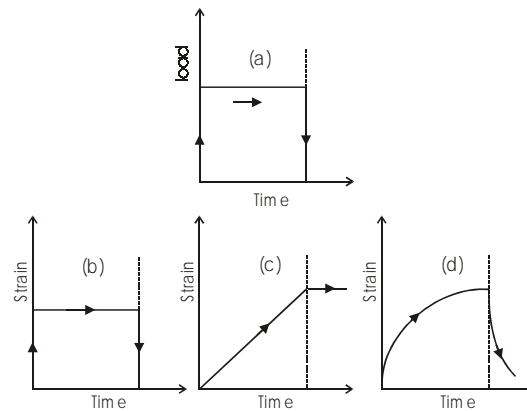
A material with high Young's modulus is called stiff, while a material with low Young's modulus is called compliant.

## 2.2 Viscous behaviour and viscoelasticity

Fluids show a characteristic resistance to movement (flow), which is called *viscosity*. Viscosity results in a frictional energy loss, which dissipates in the fluid as heat. Polymeric materials behave both as viscous fluids and elastic solids. They



**Figure 6:** Elastic behaviour: (a) at low strains for all materials; (b) at low stresses (but large elongations) for elastomers (e.g. rubber elasticity).



**Figure 7:** Mechanical response (deformation) of a material subjected to a constant load for a finite time interval (up to the dotted line). (a) Load application; (b) solid – elastic behaviour (c) liquid – viscous flow behaviour (d) polymer – viscoelastic behaviour.

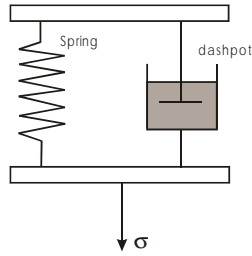
are *viscoelastic* materials. The most important characteristic of viscoelastic materials is that their mechanical properties depend on time.

### 2.3 Creep

The deformation of a material over time due to the application of a constant load is called *creep* (Fig 7).

A purely elastic material responds instantaneously to the load and the deformation remains the same, in addition, it will recover its initial shape upon the removal of the load. On the contrary, a viscous liquid will deform as long as the load continues to be applied. Upon the removal of the load, the fluid does not return to its initial position. The response of a viscoelastic material is intermediate between the solid and the liquid (see Fig 7d). Creep depends on the applied load, molecular characteristics, microstructure and temperature.

We can use combinations of springs (linear elastic behaviour) and dashpots (linear



**Figure 8:** Voigt element: Combination of a spring and a dashpot in parallel.

viscous behaviour) in order to quantify the mechanical behaviour of polymeric materials. In Fig 8 the *Voigt element* is shown. This is a parallel combination of a spring and a dashpot. The total stress  $\sigma$  is distributed between the spring  $\sigma_1$  and the dashpot  $\sigma_2$ , so that

$$\sigma = \sigma_1 + \sigma_2 \quad (2)$$

However the strains of the spring and dashpot are the same, that is

$$\varepsilon = \varepsilon_1 + \varepsilon_2. \quad (3)$$

We know that

$$\sigma_1 = E\varepsilon_1. \quad (4)$$

For a viscous liquid

$$\sigma_2 = \eta \frac{d\varepsilon_2}{dt} \quad (5)$$

where  $\eta$  is the viscosity. Thus,

$$\sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt} \quad (6)$$

Solving the differential equation for constant stress (as in a creep test), we obtain

$$\varepsilon(t) = \frac{\sigma}{\eta} [1 - \exp(-Et/\eta)]. \quad (7)$$

For the recovery (relaxation,  $\sigma = 0$ ), we obtain

$$\varepsilon(t) = \varepsilon_0 \exp(-Et/\eta). \quad (8)$$

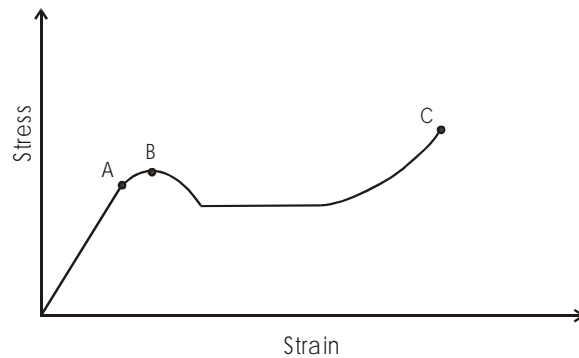
Eqns 7 and 8 agree qualitatively with the viscoelastic behaviour shown in Fig 7d. Although the Voigt element and other more complicated combinations of springs and dashpots provide some useful insight into the viscoelastic properties of polymers, they are inadequate in describing the creep behaviour of a real polymeric material. Many empirical equations have been proposed. One which applies to some of the common engineering plastics, has the form

$$\varepsilon(t) = K\sigma^n \quad (9)$$

where  $n$ ,  $K$  are constants for a given polymer and  $0 \leq n \leq 1$ . In cases where  $n = 0$ , the material behaves in a purely elastic manner. Alternatively, at  $n = 1$  the material behaves as viscous fluid. The value of  $n$  obtained from creep data is therefore a measure of the relative contributions of elastic and viscous deformation to the creep process.

#### ***2.4 High-strain behaviour and failure***

If a material is subjected to high-strain deformation, it deforms permanently (plastic deformation) and ultimately fails. In fig. 9, we show a graph of stress-strain behaviour over the entire strain range and the ultimate failure (rupture) for a typical polymeric material subjected to a tensile test. For sufficiently low stresses and strains, the polymeric material behaves as a linear elastic solid. The point where the behaviour starts to be non-linear is called the *proportional limit*. The local maximum in the stress-strain curve is called the *yield point* and indicates the onset of plastic (*i.e.* permanent) deformation. The corresponding stress and elongation are called *yield strength* and *elongation at yield*. Beyond the yield point the material stretches out considerably and a “neck” is formed; this region is called the *plastic* region. Further elongation leads to an abrupt increase in stress (strain hardening) and the ultimate *rupture* of the material. At the rupture point the corresponding stress and strain are called the *ultimate strength* and the *elongation at*



**Figure 9:** Typical stress-strain curve of a polymeric material. A is the proportional point, B the yield point and C the rupture (break) point.

*break*, respectively.

The stress-strain behaviour of a polymeric material depends on various parameters such as molecular characteristics, microstructure, strain-rate and temperature.

### 3. Brief molecular interpretation of the mechanical behaviour of polymeric materials

- The observed elastic behaviour of solids at low stress-strains is due to the stretching of their chemical bonds, which are inherently short-range. Particularly in polymers, although the above mechanism cannot be excluded, the elastic behaviour is more complicated due to the chain-like structure of the macromolecules. A polymer chain resists stretching because it reduces its entropy (we can also say that a polymer chain resists stretching due to its thermal movement which is significantly hindered if stretched). The associated restoring force is elastic and it is the underlying cause for the mechanical behaviour of elastomers (e.g. rubber elasticity).
- Viscosity is a measure of the friction and the associated energy dissipation between molecules of fluids. Polymeric materials due to their macromolecular (long-chain) structure are expected to have high viscosities.

- Creep, flow and plastic deformation in polymeric materials results from the irreversible slippage, decoupling and disentanglements of polymer chains (or groups of chains in semicrystalline polymers).
- Strain hardening results from the high orientation and alignment of polymer chains at high strains.

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