The University of Edinburgh
School of Engineering and Electronics

3rd year materials laboratory

Deformation of Polymeric Materials
Theoretical Background
Vasileios Koutsos

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 responsible for their intriguing mechanical properties.

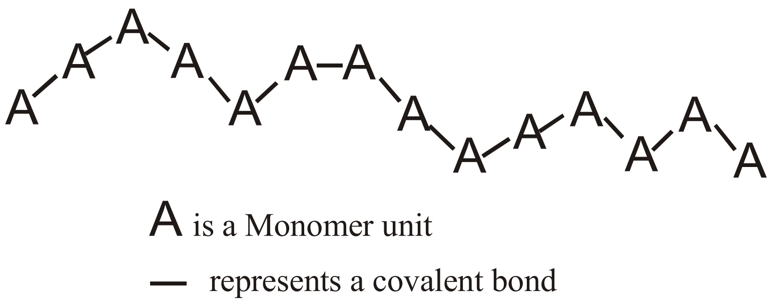


Fig. 1 A polymer chain

Polymer architecture can vary. In fig. 2 three possible molecule architectures are depicted.

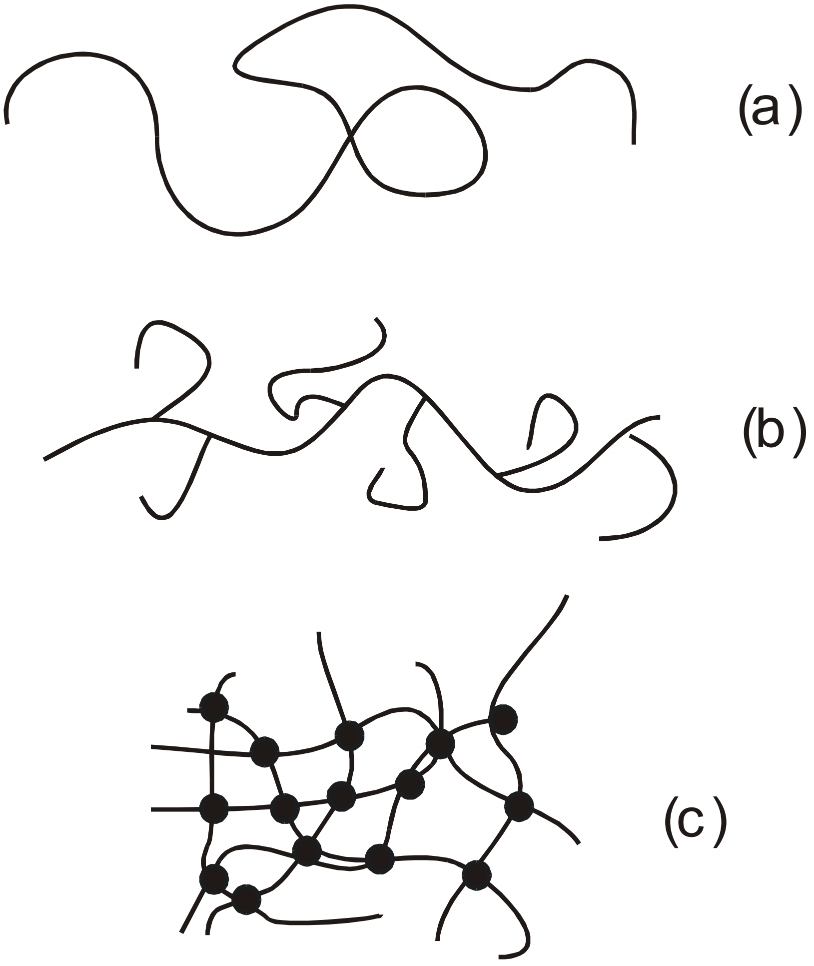


Fig. 2 Types of molecular configuration: (a) Linear chain (b) Branched molecule (c) Cross-linked network: Molecules are linked through covalent bonds; the network extends over the whole sample which is a giant macromolecule

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 densely cross-linked networks.

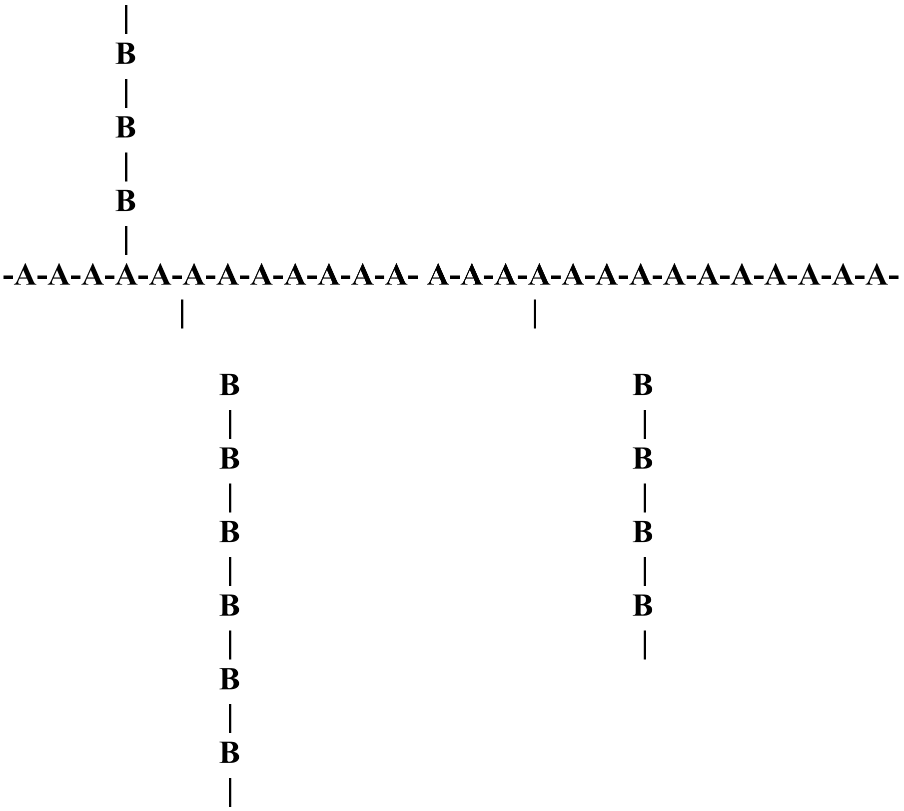
Another classification of polymers is based on the chemical type of the monomers (fig. 3): **Homopolymers** consist of monomers of the same type; **Copolymers** have different repeating units. Furthermore, depending on the arrangement of the types of monomers in the polymer chain, we have the following classification: In **random copolymers** the 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 the another monomer; **Graft copolymers** consist of a chain made from one type of monomers with branches of another type.

-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A- **(a)**

-A-A-B-A-B-B-A-B-A-A-B-A-A-A-B-A-B-B-A-B-B-B-A-A-B-A-A- **(b)**

-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A- **(c)**

-A-A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B-B-B-B-A-A-A-A-A-A- **(d)**



-A-A-A-A-A-A-A-A-A-A-A-A- A-A-A-A-A-A-A-A-A-A-A-A-A-A- **(e)**

Fig. 3(a) homopolymer (b) random copolymer (c) alternating copolymer (d) block copolymer (e) graft copolymer

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.

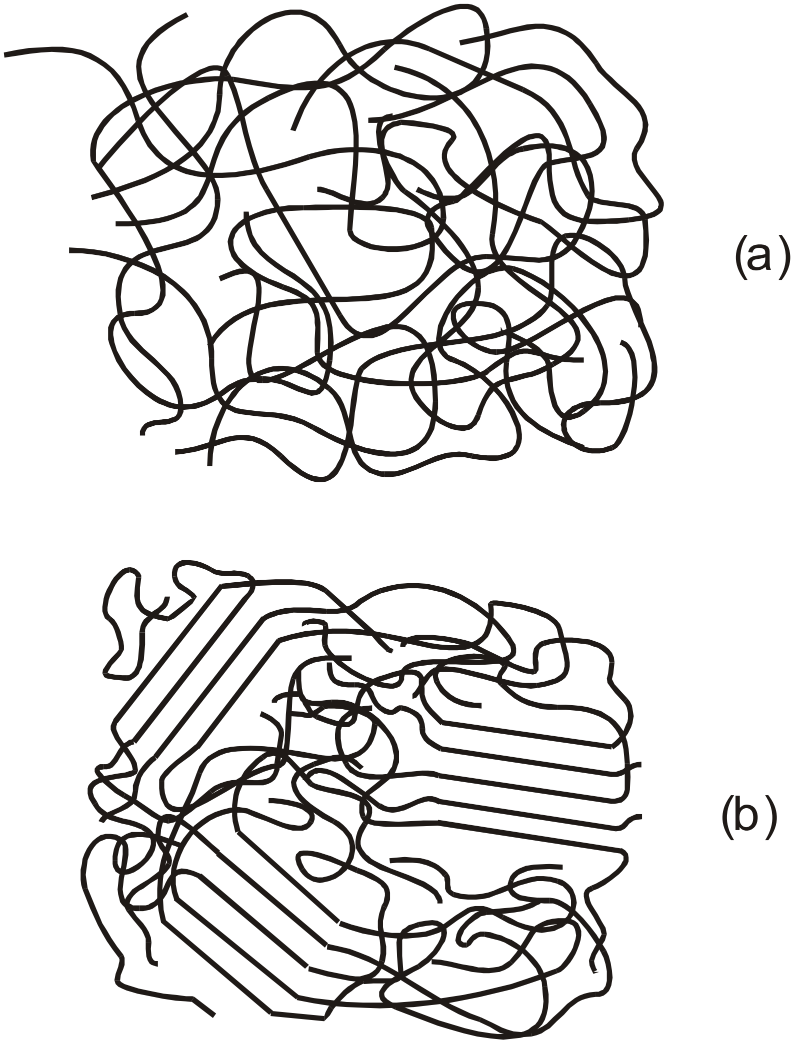


Fig. 4 (a) amorphous polymer (observe the entanglements among the polymer chains) and (b) semicrystalline polymer

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 (and experiment), **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.

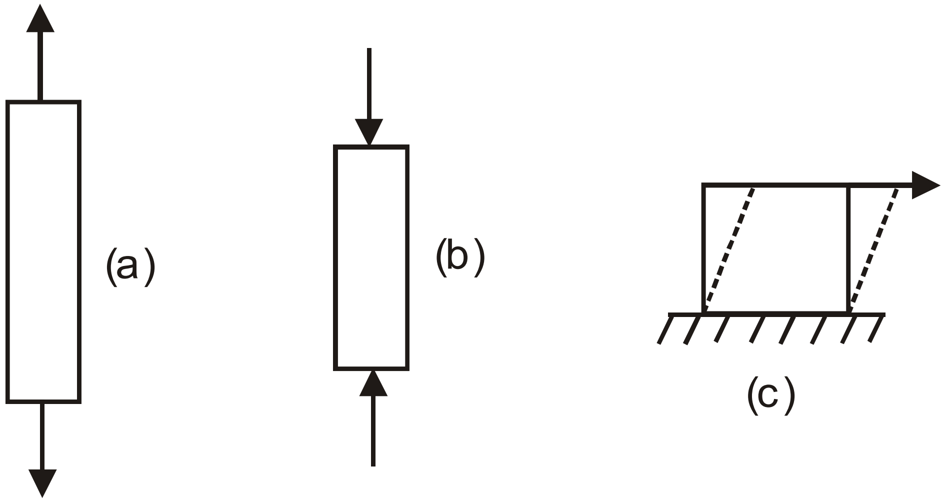


Fig. 5 Examples of Types of forces: (a) Tensile force (b) Compressive force (c) Shear force

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** (σ); it is defined as the force (F) divided by the cross-sectional area (A) of the material (units $N/m^2 = Pa$). The deformation is quantified by the **strain** (ε) which is defined as the length change (Δl) 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

$$\sigma = E\,\varepsilon \tag{2.1}$$

where $\sigma = F/A$, $\varepsilon = \Delta l/l_0$ and E is the **Young's modulus** (units $N/m^2 = Pa$).

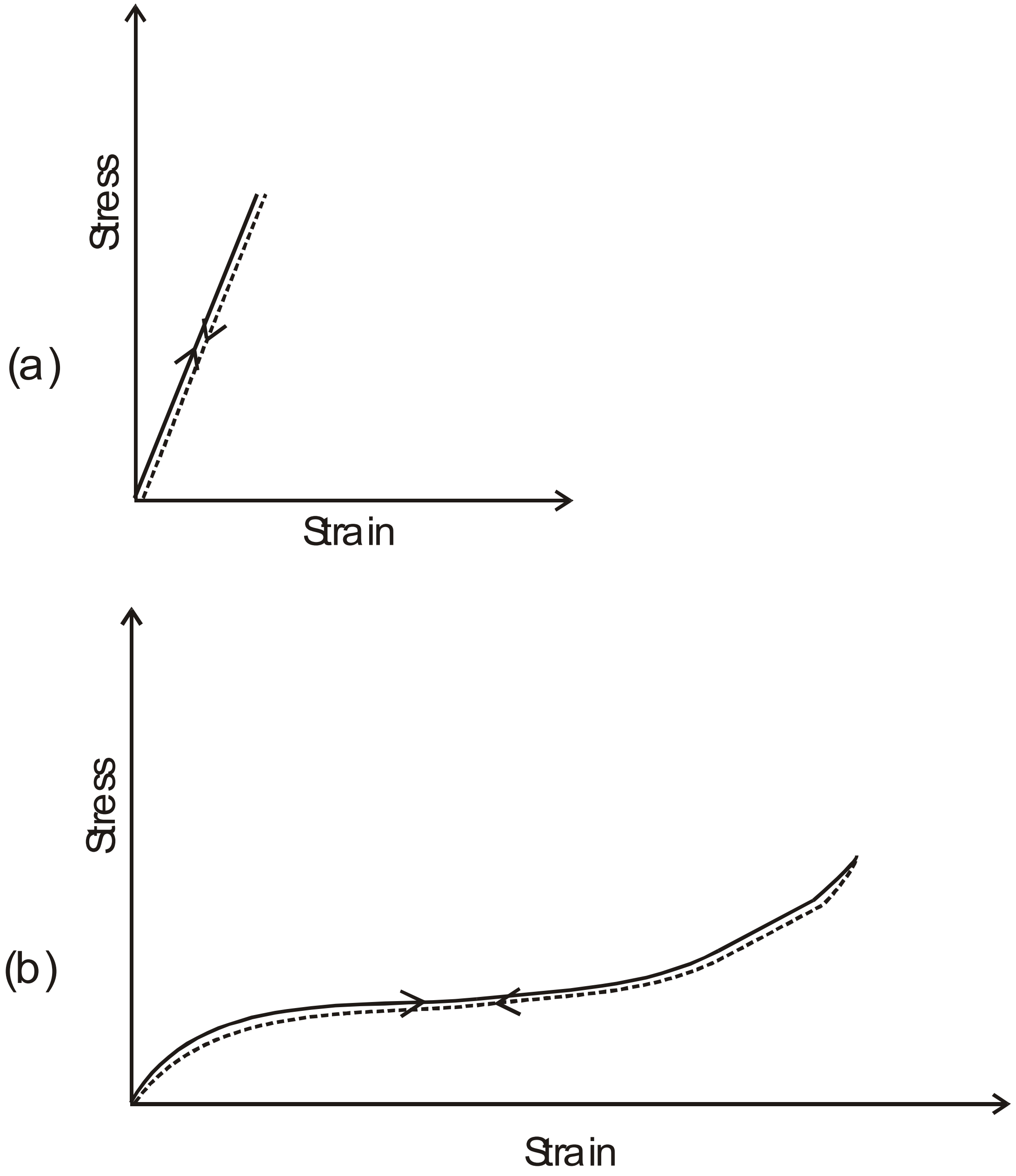


Fig. 6 Elastic behaviour: (a) at low strains for all materials
(b) at low stresses (but large elongations) for elastomers (e.g. rubber elasticity)

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%). 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%) 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 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.

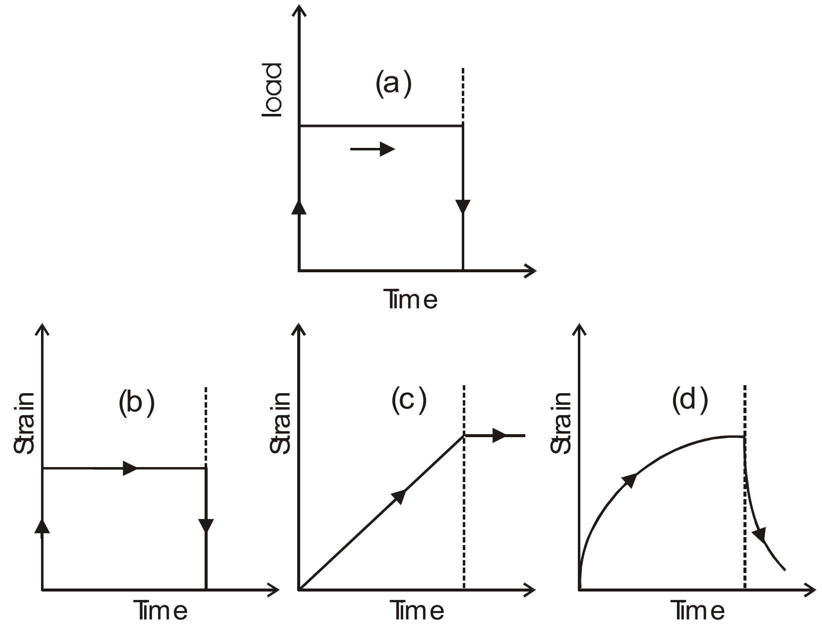


Fig. 7 Mechanical response (deformation) of a material subjected to a constant load for a finite time interval (up to the dotted line). (a) load application (b) solid - elastic behaviour (c) liquid - viscous flow behaviour (d) polymer - viscoelastic behaviour

We can use combinations of springs (linear elastic behaviour) and dashpots (linear 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 σ is distributed both to the spring σ_1 and to the dashpot σ_2

$$\sigma = \sigma_1 + \sigma_2 \qquad (2.2)$$

The deformation is the same

$$\varepsilon = \varepsilon_1 = \varepsilon_2 \qquad (2.3)$$

We know that $\sigma_1 = E\,\varepsilon_1$ (2.4)

For a viscous liquid

$$\sigma_2 = \eta\, d\varepsilon_2/dt \qquad (2.5)$$

Where η is the viscosity.

Thus, $\sigma = E\,\varepsilon + \eta\, d\varepsilon/dt$ (2.6)

Solving the differential equation for constant stress (Creep test), we obtain

$$\varepsilon(t) = \frac{\sigma}{E}\left(1 - e^{-\frac{E}{\eta}t}\right) \qquad (2.7)$$

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

$$\varepsilon(t) = \varepsilon_0 e^{-\frac{E}{\eta}t} \qquad (2.8)$$

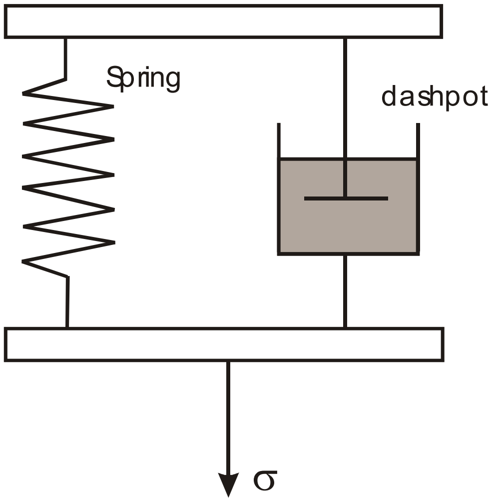


Fig. 8 Voigt element.Combination of a spring and a dashpot in parallel

Equations 2.7 and 2.8 qualitatively agree 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

$$\varepsilon(t) = K\sigma t^n \qquad (2.9)$$

where n, K are constants for a given polymer and $0 \le n \le 1$. 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 break**, respectively.

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

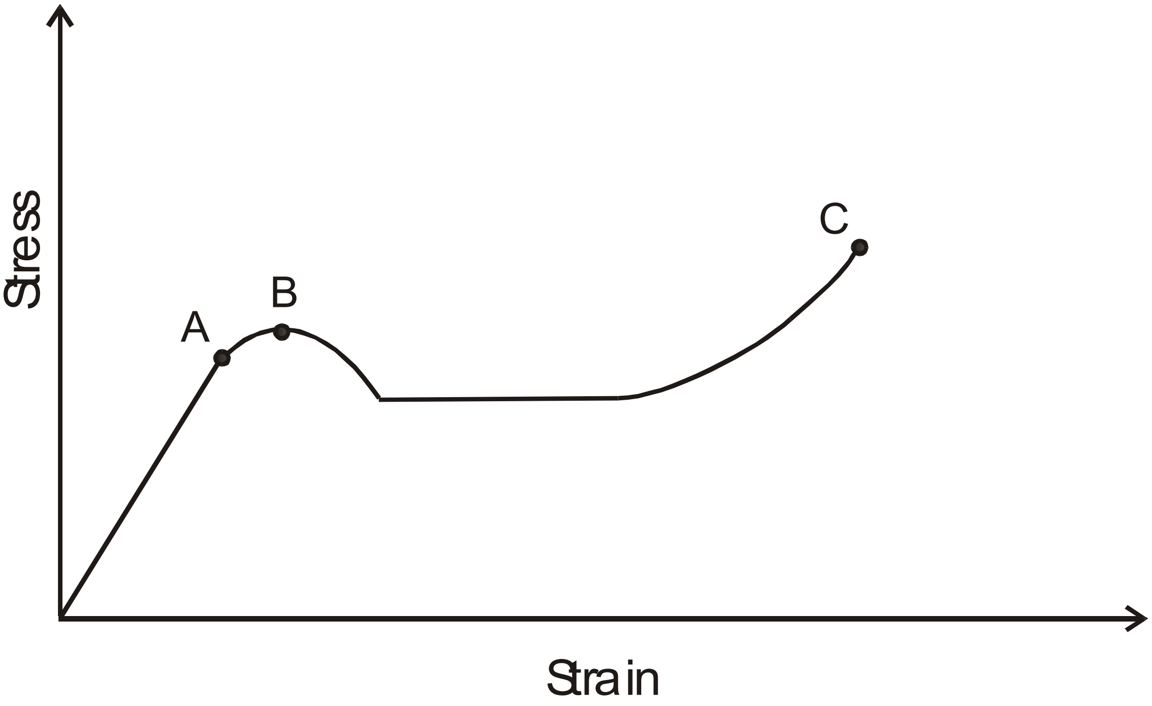


Fig. 9 Typical stress-strain curve of a polymeric material. A is the proportional point, B the yield point and C the rupture (break) point

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, de-coupling 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.

Bibliography

Fundamentals of Polymer Science: An Introductory Text
P. C. Painter and M. Coleman
Second edition, Technomic Publishing, **1997**

Plastics: Materials and Processing
A. B. Strong
Second edition, Prentice-Hall, **2000**

Mechanical Behaviour of Materials
M. A. Meyers and K. K. Chawla
Prentice-Hall, **1999**

Materials Science and Engineering: An introduction
W. D. Callister, Jr.
Fifth edition, Wiley, **2000**

Polymer Materials: An Introduction for Technologists and Scientists
Christopher Hall
Second edition, Macmillan Education, **1989**

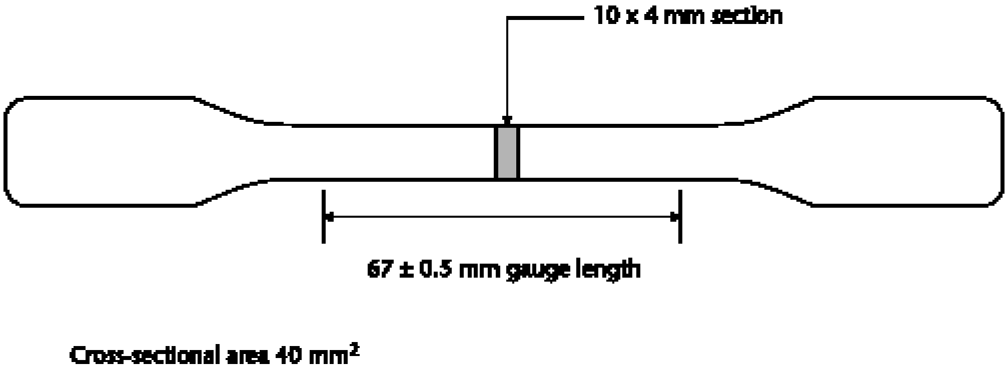
Experimental Procedure

This practical involves the tensile testing of high density polyethylene specimens (semicrystalline thermoplastic polymer) and glass-filled nylon specimens (composite material).

Information on the specimens (issued by the manufacturer)

1) The low density polyethylene has branched polymer chains and therefore the structure of this grade of polyethylene is largely amorphous. It has a density of approximately 0.92 and a melting temperature of 115°C. The merits of the polymer are its low cost, flexibility at temperatures down to –120°C, high toughness and chemical inertness to a wide range of liquids and solids. The major applications of low density polyethylene are therefore in packaging, toys, housewares and insulation for electrical cables. **High density polyethylene (PL1)** has a higher degree of crystallinity than the low density grade, resulting in improved strength and stiffness. The density is approximately 0.96 and melting temperature 135°C. The improved mechanical properties, coupled with chemical inertness and resistance to permeation, make this type of polymer ideal for blowmoulded containers, dustbins, milk crates, tissue film, pipe and structural panels.
Gauge width: 10.0 mm
Gauge thickness: 4.0 mm
Gauge length: 67.0 mm
Cross sectional area: 40 mm^2
Extension rate: 26 mm/min
Colour: PL1(red),
Limit of proportionality (N/mm^2): 15
Maximum strength (N/mm^2): 25
Elongation (%): >100

2) Nylon 66 is a tough, semi-crystalline polymer that is widely used in all branches of industry for load-bearing applications. In particular, its abrasion resistance and low surface friction make it suitable for gears, cams and bearings. In the automative industry it is employed in door locks, filters, ball joints, bearings in suspension and steering systems. Domestic applications include curtain rail fittings, door furniture, food mixers and vacuum cleaners. **Glass fibres can be added to Nylon 66 (PL6)** to increase the strength and stiffness, but at the expense of elongation and toughness. The glass addition also improves dimensional stability. The users of glass-filled nylon are similar to those of the unfilled grade but with the added capabiltiy of being operated at higher stress levels, or under conditions where
creep resistance is required.
Gauge width 10.0 mm
Gauge thickness 4.0 mm
Gauge length 67.0 mm
Cross sectional area 40 mm2
Extension rate: 26mm/min
Colour: PL6 (black)
Limit of proportionality (N/mm^2): 125
Maximum strength (N/mm^2): 125
Elongation (%): 0



1. Tensile Testing

Details of how to use the tensile tester, and which parameters should be used for each material are given in the laboratory.
Before tensile testing measure the original width and thickness of the specimens. To obtain elongation at break (%), place two gauge marks a known distance apart on the parallel waisted section of each specimen, and measure their separation after testing.
From the tensile testing you should obtain the following values:

- Young's modulus
- Proportionality limit
- Yield strength
- Elongation at yield
- Ultimate strength
- Elongation at break
- Reduction in area at break

2. Microscopy

The demonstrators/lecturers will show you how to use the optical microscopes in order to get information of the microstructure of the materials tested.
Optical microscopy has to be performed
a) on the failed sample using the stereo microscope:
- Before the test
- After the test (close to and away from the failed region)
b) and/or on already prepared microscopy samples using the high magnification optical microscopy.

Write up

You should write a group report. The report should have the structure of a technical report (as you probably remember from last year).

In particular,

- Describe accurately and explain/ interpret all experimental findings and all features (strange or not strange) of the obtained experimental curves. Do not be afraid to be original but give adequate explanations.
- Observe carefully the experimental tensile-test curves, the microscopic images of the failed specimen. Try to find connections between the observed mechanical behaviour and the microstructure.
- Consult the handout and the recommended bibliography.