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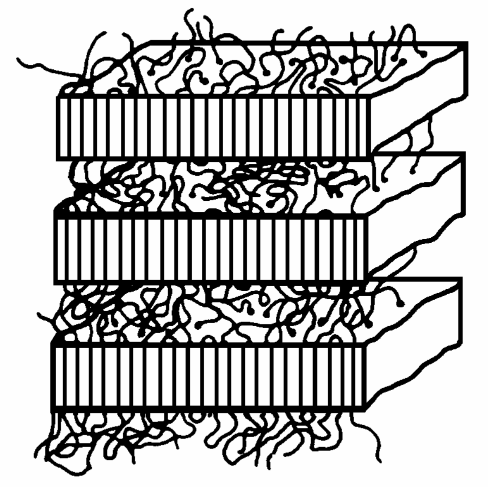
# *Characterisation of Polymers*

## Unoriented Semicrystalline Polymers

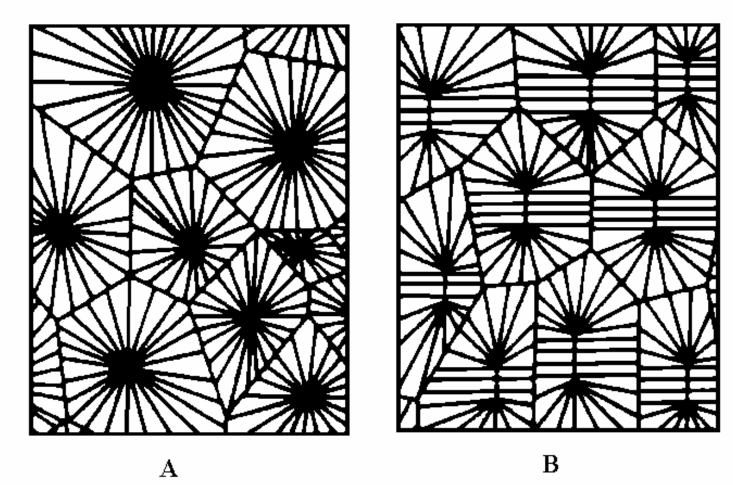
In semicrystalline polymers, there are three levels of microstructures which are important in property control. The *0.1* to *1.0nm* level represents interactions between neighbouring chain segments. The behaviour of the amorphous phase is controlled by interactions at this level. Within the crystalline phase, defects cause local increases in interchain spacing. The increased interchain spacing makes easier the sliding of chain stands past their neighbours, thereby lowering the shear strength of the crystals.

The crystalline phase of semicrystalline polymers consists of thin plates or ribbons, with the chains oriented along the thin dimension. The plates stack one above the other, and are separated by layers of amorphous material (see figure). The thickness of the crystal and amorphous layers are of the order of *100Å* and this then constitutes the second important level of microstructure. The amorphous layer consists of chain-end cilia, totally included chains, and chains which are incorporated in two or more crystals (tie chains). The tie chains determine the mechanical continuity of the system and thereby control the level of the elastic modulus and can greatly affect the yield strength. At this second microstructural level, the thin, ribbonlike crystals usually exhibit a regular twist about their long axis.

At the largest microstructural level are colonies of crystallites when crystallisation takes place under conditions of little or no applied strain and crystal nucleation begins at various sites in the melt. The transformation proceeds spherically from those centers, through the radial growth of ribbonlike crystals and the parallel formation of new ribbons to fill the growing spherical space. These spherulites grow until they impinge on each other, forming a polygonal array in the solid. A schematic diagrams for the crystallite colonies are shown in the figure. The dimensions of spherulites range from *0.1* to $1000\mu m$.



Sketch of the basic crystallite microstructure of semicrystalline polymers.



Crystallite colonies: A) spherulites, B) elongated spherulites.

## Oriented Polymers

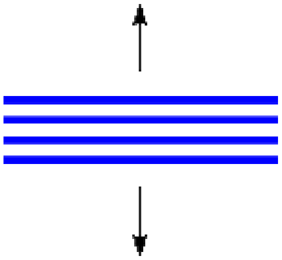
If a plastic is stretched by drawing or other mechanical processes, the molecules will tend to align themselves in the direction of the stress, this is referred to as orientation.  Molecular orientation leads to anisotropy of mechanical properties.

In order to obtain improved properties in some polymers, sheets are uniaxially or biaxially oriented during the extrusion process.  Both crystalline and amorphous polymers can be oriented.  For crystalline polymers, unique combinations of properties can be achieved by carefully matching levels of mechanical stress with heating and cooling rates.  Crystallites thus formed can be formed from highly oriented molecules, yielding dramatic reduction in haze level and equally impressive increases in ultimate tensile strength.

Molecular orientation in products can be classified into several categories:

- Low magnitude: this type of orientation is predominantly uniaxial and is especially notable in injection moulded thermoplastics, but is also evident in some extrusion processes including extrusion blow moulding.  This type of orientation occurs unavoidably, but can be controlled within limits during processing.
- High magnitude: in processes such as tape drawing (uniaxial), thermoforming and stretch blow moulding (biaxial orientation), orientation of higher magnitude is induced deliberately under high strain-rate tensile stress.
- Ultra-high orientation: highly oriented products are yet to gain significant commercial importance.

Oriented fibers are strong when you pull in the fiber direction.



But they're weak at right angles to the fiber direction.

## Mechanical Properties of Polymers

Strength, toughness, and ductility are all mechanical properties. But what do these words really mean? How do we measure how "strong" a polymer is? What is the difference between a "strong" polymer and a "tough" polymer?

## Strength

Strength is a mechanical property that you should be able to relate to, but you might not know exactly what we mean by the word "strong" when we're talking about polymers. First, there is more than one kind of strength. There is *tensile* strength. A polymer has tensile strength if it is strong when one pulls on it like this:

Tensile strength is important for a material that is going to be stretched or under tension. Fibers need good tensile strength.

Then there is *compressional* strength. A polymer sample has compressional strength if it is strong when one tries to compress it. Concrete is an example of a material with good compressional strength. Anything that has to support weight from underneath has to have good compressional strength.

There is also *flexural* strength. A polymer sample has flexural strength if it is strong when one tries to bend it.

There are other kinds of strength like torsional and impact strength. A sample *torsional* strength if it is strong when one tries to twist it. A sample has impact strength if it is strong when one hits hit sharply and suddenly, as with a hammer.

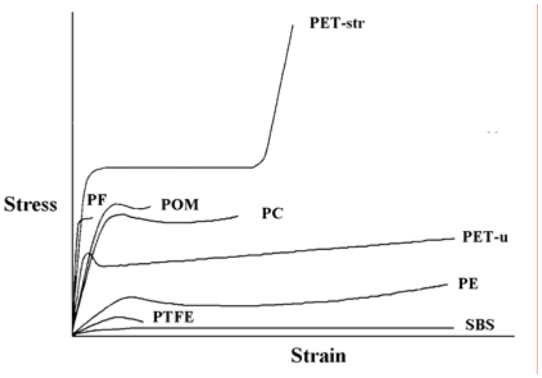
The initial steps of materials selection for component specification and design involve a careful consideration of a range of mechanical properties, together with additional factors such as processability and cost-effectiveness of given design. Mechanical properties range from the soft, relatively compliant and elastic thermoplastic through hard, viscoelastic solids to some reinforced plastics. When a mechanical load is applied to a polymeric material, its response may be either a change in shape and dimensions or fracture. The former response is often reversible but may take place with little deformation (brittle failure), or alternatively, considerable strain could be imposed on the specimen and it may experience gross yielding (ductility).

Mechanical properties of polymers are most commonly evaluated by tensile tests in which a rectangular or dumb-bell shaped test specimen is drawn with constant speed. The type of test specimen depends on the properties of polymers: different test specimens are used for plastics with moderate elongation at break, high elongation at break and thermosetting mouldings.

The tensile–elongation curve of a semicrystalline polymer with lamellar structure may have four distinct parts.

- The initial almost reversible elastic part.
- The yield area
- The necking area which transforms the lamella into a fibrous structure.
- The drawing area of the newly formed fibrous structure ending with the fracture of the sample.

The deformation is homogeneous during the initial reversible elastic part and in the final drawing area with the whole sample in lamellar or fibrous structure respectively. It is inhomogeneous during the yield and necking areas where the neck separates the material with lamellar structure from that with fibrous structure.



Stress-strain curves of polymers at room temperature. PC = Bisphenol A polycarbonate; PE = polyethylene; PET = polyethylene terephthalate, u = unstretched or str = biaxially oriented; PF = phenol-formaldehyde thermoset; POM = polyoxymethylene; PTFE = polytetraflouroethylene; SBS = polystyrene-block-polybutadiene-block-polystyrenebvbv.

The yield point is the first point on the stress/strain curve at which an increase in extension occurs without an increase in load, it is the first maximum of the stress-strain curve. The yield point is sometimes called the upper yield point. Brittle polymers break before they reach a yield point. Tough polymers continue to extend and the stress either remains constant or decreases with increasing strain. The decrease of stress with strain is called stress softening. The total area under the stress-strain curve measures the absorbed energy; it describes the toughness of the specimen. A subsequent increase of stress with strain is called stress hardening. At break polymers exhibit an ultimate strength.

The failure of polymeric solids can occur in a brittle or a ductile manner, or in various combinations of the two. The specific fracture mechanism depends on three types of variables: chain chemistry, molecular weight and degree of imperfection; thermomechanical history; and loading conditions, including the ambient temperature.

## Tensile Testing

Tensile properties -of extruded and injection moulded polymer samples are measured on an Instron Universal testing machine at room temperature. Standard dumb-bell test pieces were stamped from extruded polymer sheets using a cutting die made to *BS2782* specifications.

The experimental procedure used is in accordance with *BS2782: Part 3*: Method *320A*. During the tensile test, standard test pieces are deformed at a constant rate of *100mm/min* with an initial gauge length of *60mm*.

The width and thickness of the central parallel portion of the dumb-bell shaped test pieces are measured at several points using a digital micrometer. The mean cross-sectional area is then used.

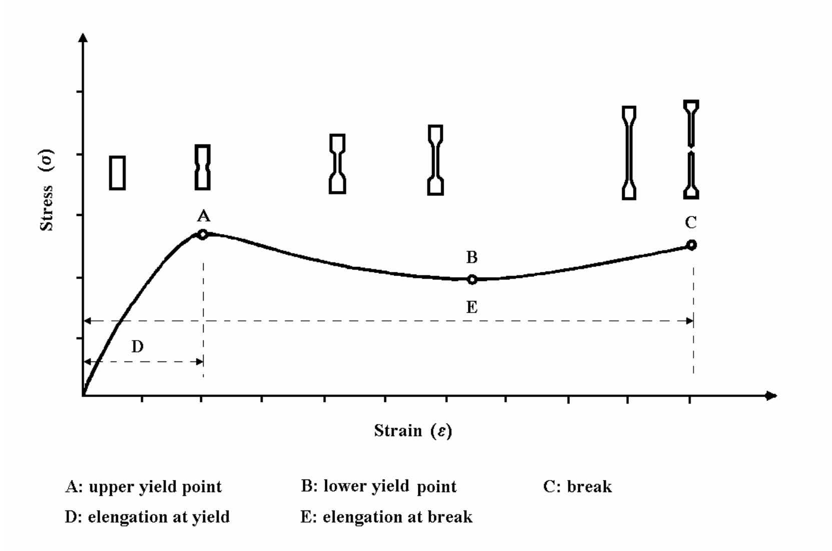
The test pieces are mounted in the grips and axially aligned with the direction of pull. The grips were separated at a constant rate until fracture occurred in the sample. At least five samples were tested in each case. A typical load/deflection cure is shown in the figure.

The following definitions were used to determine the tensile properties:

Tensile stress: the tensile force carried by test piece per unit area of the original cross-sectional area.

Strain: the ratio of the change in sample length to the original sample length suspended between the machine jaws.

Yield point: the first marked inflection on the curve at which an increase in extension is not accompanied by an increase in force. Below this point samples behave elastically and obey Hooke’s law.



A typical example of stress-strain curve obtained during the tensile testing of polymers.

Using the above definitions the following tensile properties were calculated:

Yield strength: the stress developed in the sample at the yield point.

$$\text{Yield strength } (N/mm^2),\ \sigma_y = \frac{F_y}{A}$$

Where $F_y$ is force at yield ($N$) and $A$ is original mean cross-sectional area of the test piece ($mm^2$)

Tensile strength: is the maximum tensile stress which the test piece is capable of supporting.

$$\text{Tensile strength } (N/mm^2),\ \sigma_b = \frac{F_b}{A}$$

Where $F_b$ is force at break ($N$).

Percentage elongation: the elongation produced in the gauge length of the test piece by a tensile stress. It is expressed as a percentage of the original gauge length.

Percentage elongation at break: the elongation at break produced in the gauge length of the test piece, expressed as a percentage of the original gauge length.

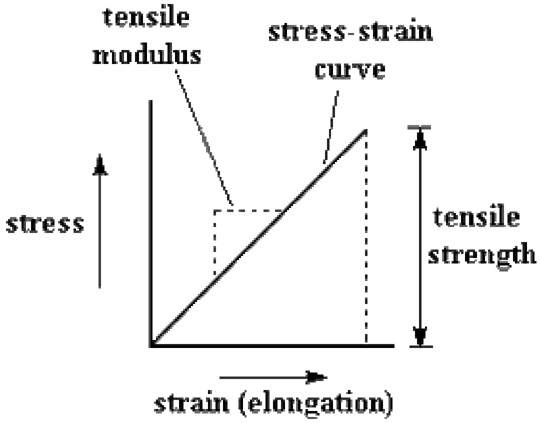
$$\%\ \text{Elongation at break},\ \varepsilon_b = \frac{(L - L_o)_b}{L_o} * 100$$

Where ($L$-$L_o$) is the change in sample length at break ($mm$) and $L_o$ is the original sample length suspended between the jaws.

Secant modulus: the ratio of stress to corresponding strain at a given point on the force/deflection curve.

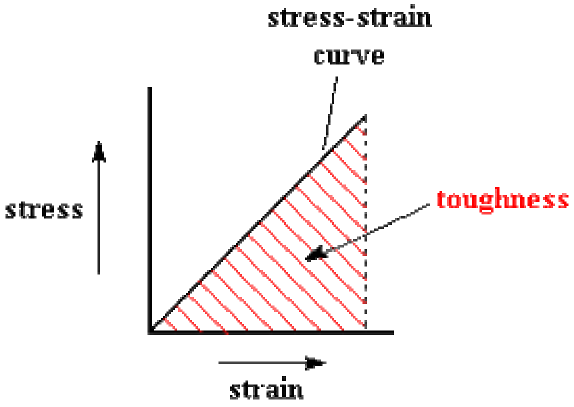
Secant modules ($N/mm^2$), $E_{sc} = \dfrac{F_e}{\varepsilon A}$

Where $F_e$ is force required to produce a strain of magnitude ε.

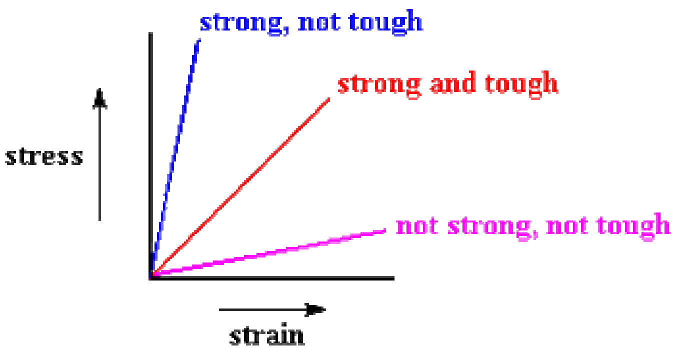


## Toughness

That plot of stress versus strain can give us another very valuable piece of information. If one measures the area underneath the stress-strain curve, colored red in the graph below, the number you get is something we call *toughness*.



Toughness is really a measure of the energy a sample can absorb before it breaks. How is toughness different from strength? From a physics point of view, the answer is that strength tells how much force is needed to break a sample, and toughness tells how much energy is needed to break a sample. But that doesn't really tell you what the practical differences are.



## Observed Roles of Microstructure in Polymer Failure

A semicrystalline polymer must be though of as a microstructurally and mechanically complex system, in which all components are subject to control. The figure below illustrates the levels of microstructure considered in describing the deformation of semicrystalline polymers. At the spherulite level, cracks develop at boundaries and nodal points. Simultaneously, spherulites deform by the bending, rotation, or destruction of their interior ribbons. At the crystal size and amorphous zone size level, amorphous zones stretch and lamellae shear past each other. At the interatomic level, packing defects allow locally easy shearing to take place, giving rise to the yielding of the crystal.

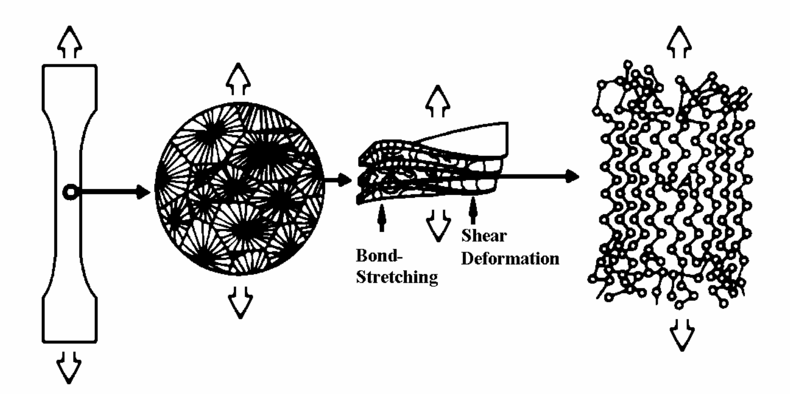
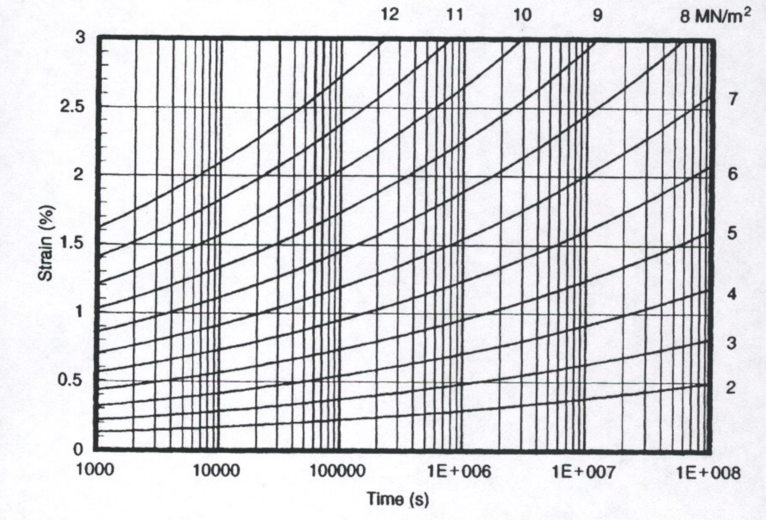
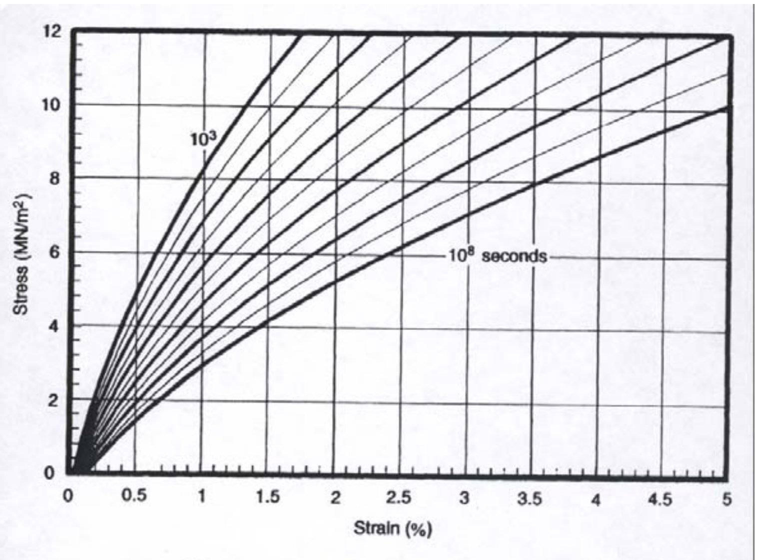


Illustration of levels of microstructure considered in describing the failure behavior of semicrystalline polymers

*Example 1:* A polypropylene beam is 100 mm long, simply supported at each end is subjected to a load W at its mid-span. If the maximum permissible strain in the material is to be 1.5 %, calculate the largest load which may be applied so that the deflection of the beam does not exceed 5 mm in a service life of 1 year. For the beam I = 28 mm$^4$.



Creep curves for polypropylene at 20°C (density 909 kg/m$^3$)



Stress−strain curves for polypropylene

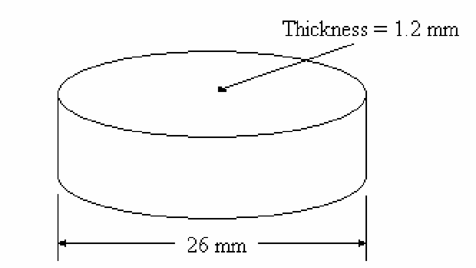
*Example 2:* A glass bottle of sparkling water has an acetal cap as shown. If the carbonation pressure is 375 kN/m$^2$, estimate the deflection at the centre of the cap after 1 month. The value of the Poissons ratio for acetal may be taken as 0.33. The top of the bottle cap is effectively a plat with clamped edges. The central deflection in such a situation is given by:

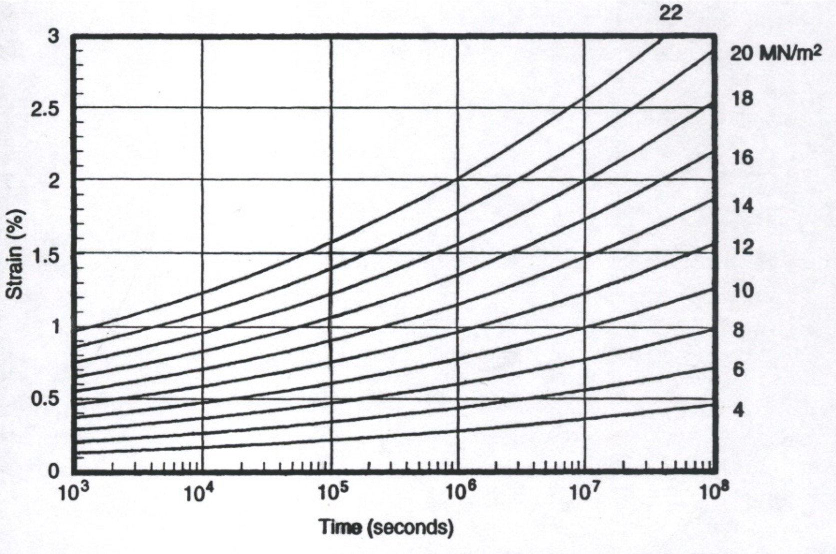
$$\delta = \frac{pR^4}{64D}$$

where

$$D = \frac{Eh^3}{12\left(1-\nu^2\right)}$$

h is the thickness.





Creep curves for acetal (20°C)

## Melt Flow Rate: Melt Indexers

Measurement of polymer flow has become one of the most important tests for processors. Injection molders, extruders, and blow-molders are increasingly using this procedure to insure that incoming materials meet their specifications, consistently.

**First:** melt flow tests tell whether a material can be processed.

**Second:** a material's flow indicates whether it's properties will be consistent with those required. An increased or decreased melt flow, as compared to specifications, can indicate incorrect molecular weight, degradation, cross-linking, etc.

A processor may discover errors in compounding that can result in a loss of mechanical strength, impact or chemical resistance. These errors could have an adverse effect on the final product's performance and final quality

### Melt Indexers

The most common method for testing Melt Flow Rate (MFR), sometimes called the Melt Flow Index (MFI), is to use a Melt Flow Indexer. The basic procedure for testing is to determine the weight of a polymer extruded in a fixed period of time, under standardized conditions of temperature, geometry, and force.

The standards are established and can be found in ASTM D1238, or ISO 1133. The ASTM and ISO methods are technically equivalent.

- A specific amount of material is placed in a heated barrel
- The material is heated to a specified temperature
- The material is forced through a very specific sized die with a specified force

The MFR is the Mass of material, in grams, that passes through the die in 10 min. So the MFR has a unit measurement of g/10min.