

# Characteristics & Applications of Polymers

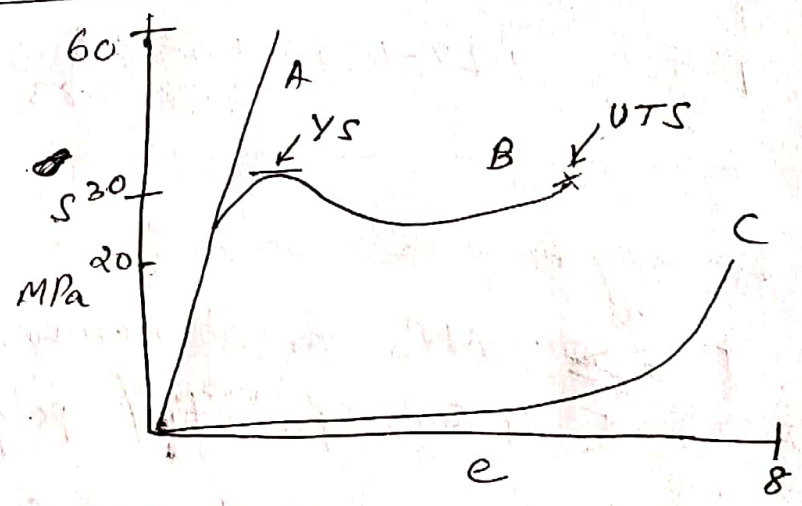
## Mechanical behaviour of polymers

### Stress-strain behaviour

The mechanical ~~charac~~ parameters are found using ASTM Std D 638 "standard test method for tensile properties of plastics".

### Modulus of elas.

The stress strain behaviour for Brittle (A), plastic (B) and highly elastic (elastomeric) (C) polymers.



A → fractures while deforming elastically.

B → initially deforms elastically, followed by yielding and a region of plastic deformation

C → totally elastic, this rubber-like elasticity (large recoverable strains produced at low stress levels) → is displayed by elastomers.

$\sigma_y$  may be  $<$  or  $>$   $\sigma_{UTS}$

Room Temp.	Sp. gr.	$E$ (GPa)	$\sigma_{UTS}$ (MPa)	$\sigma_y$ (MPa)	% El. at break
LDPE	0.917-0.932	0.17-0.28	8.3-31.4	9-14.5	100-650
HDPE	0.952-0.965	1.06-1.09	22.1-31.0	26.2-33.1	10-1200
PVC	1.3-1.58	2.4-4.1	40.7-51.7	40.7-44.8	40-80
Nylon 6,6	1.13-1.15	1.58-3.8	75.9-94.5	44.8-82.8	15-300
PET	1.29-1.4	2.8-4.1	48.3-72.4	59.3	30-300
Polycarbonate	1.2	2.38	62.8-72.4	62.1	110-150
PF	1.24-1.32	<del>1.58-3.8</del> 2.76-4.83	<del>75.9-94</del> 34.5-62.1	-	1.5-2.0

~~$E_s$  may be great~~

$E \leq 7$  MPa for elastomers

$E \leq 4$  GPa for <sup>very</sup> stiff polymers.

Metals  $E = 48$  to  $410$  GPa

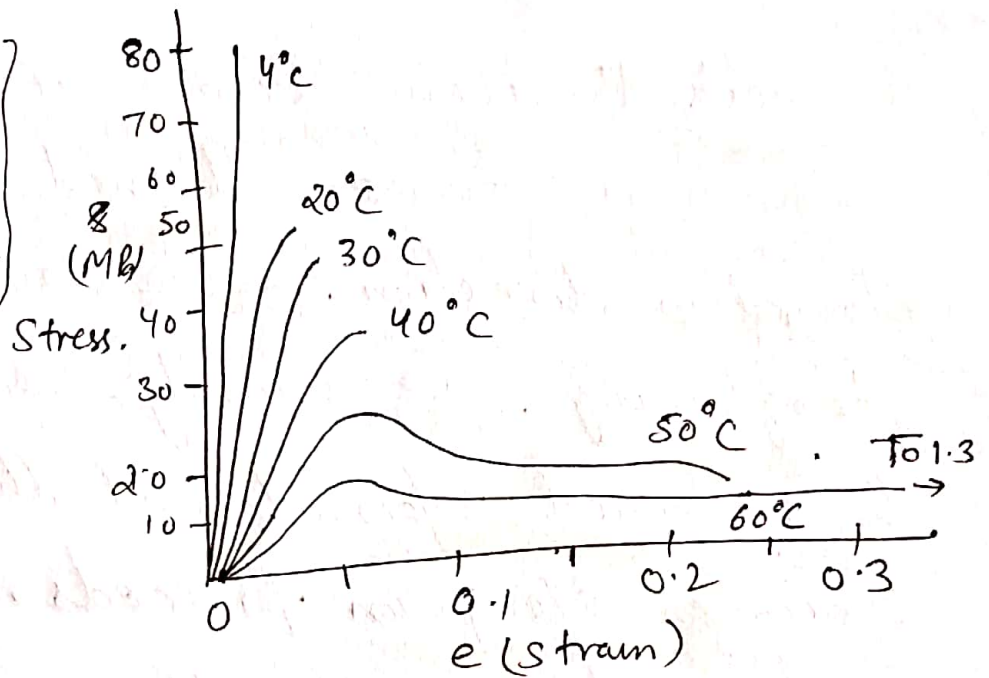
$\sigma_{UTS}$  max for polymers = 100 MPa  
metals = 4100 MPa

Metals % El<sub>max</sub>  $< 100\%$ .

Polymers % El<sub>max</sub>  $\geq 1000\%$ .

Mechanical characteristics of polymers are much more sensitive to temperature changes near room temp.

The influence of temperature on the  $\sigma$ - $\epsilon$  characteristics of poly methyl methacrylate (Plexiglass)



Increasing the temperature produces

- ① a decrease in elastic modulus
- ② a reduction in tensile strength
- ③ an enhancement of ductility [at 4°C - brittle] <sup>totally</sup>  
[at 50 & 60°C - considerable plastic deformation]

Decreasing the strain rate  $\sim$  increasing the temp.

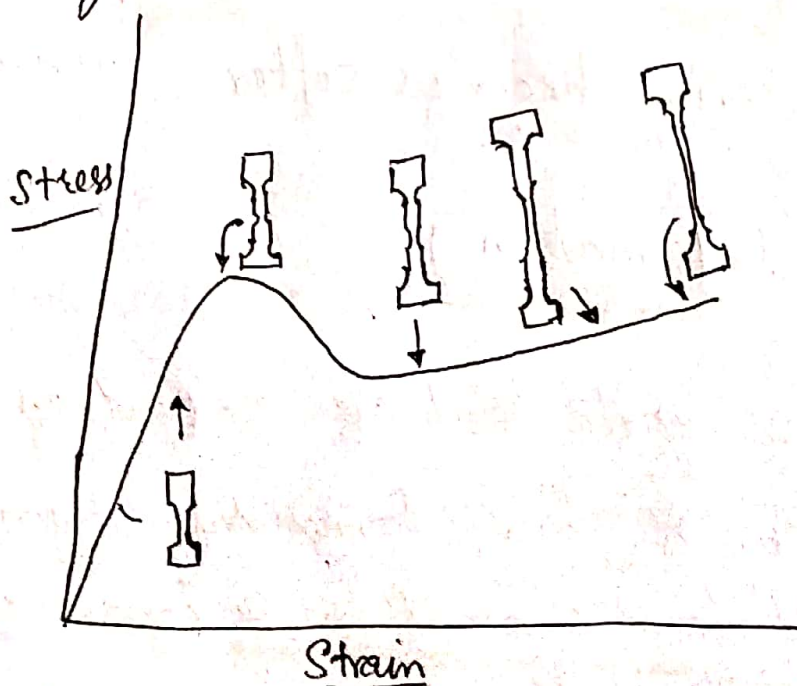
$\phi$  i.e. material becomes softer & more ductile.  
-eg.  $10 \text{ s}^{-1}$  to  $0.0001 \text{ s}^{-1}$

### Macroscopic deformation

Upper & lower yield points are evident on the curve, followed by a near horizontal region. At the upper yield point, a small neck forms within the gauge section of the specimen. ~~the~~ Within

the neck the chain becomes oriented. (i.e. the chain axes become aligned parallel to the elongation direction, a ~~con~~ leading to localized strengthening. Consequently, there is a resistance to continued deformation at this point, and specimen elongation proceeds by the propagation of this neck region along the gauge length.

The chain orientation phenomenon accompanies this neck extension. This tensile behaviour may be contrasted to that found for ductile metals, wherein once a neck has formed, all subsequent deformation is confined to within the neck region.



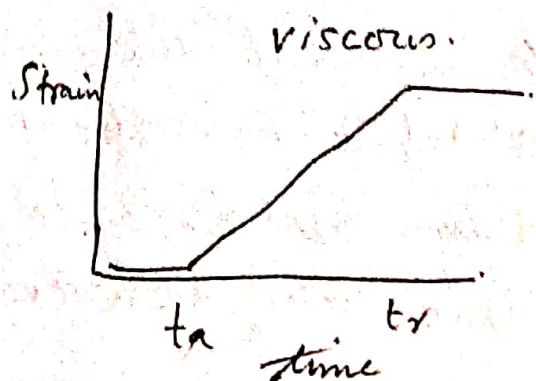
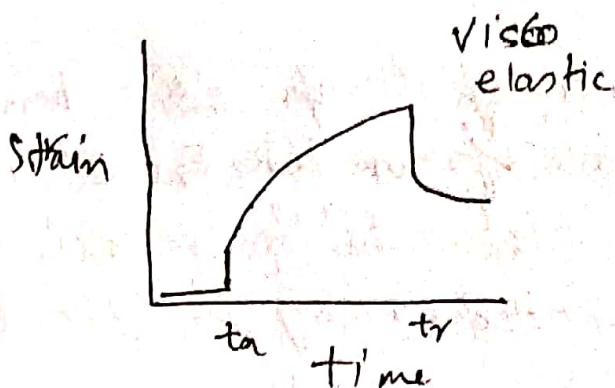
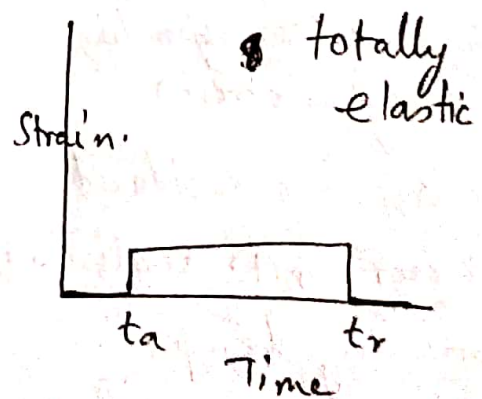
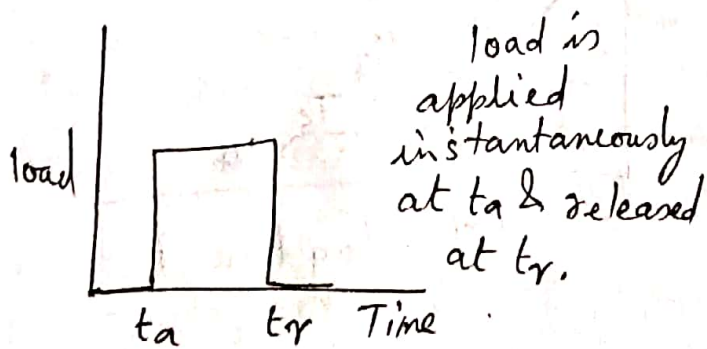
Schematic tensile stress-strain curve for a semicrystalline polymer.

Specimen contours at several stages of deformation are included.

## Viscoelastic deformation.

An amorphous polymer may behave like a glass at low temperatures, a rubbery solid at intermediate temperatures ( $> T_g$ ) and a viscous liquid as the temperature is further raised.

For relatively small deformations, the mechanical behavior at low temperatures may be elastic i.e. conforms to Hooke's law ( $\sigma = \epsilon \cdot E$ ). At the highest temperatures, viscous or liquid like behaviour ~~is~~ prevails. For intermediate temperatures the polymer is a rubbery solid that exhibits the combined mechanical char. of these two extremes; the condition is termed viscoelasticity.



## viscoelastic relaxation modulus

Stress relaxation measurement — A specimen is initially strained rapidly in tension to a predetermined and relatively low strain level. The stress necessary to maintain this strain is measured as a fn of time, while temp. is held constant. Stress is found to decrease with time due to molecular relaxation processes that take place within the polymer. We may define

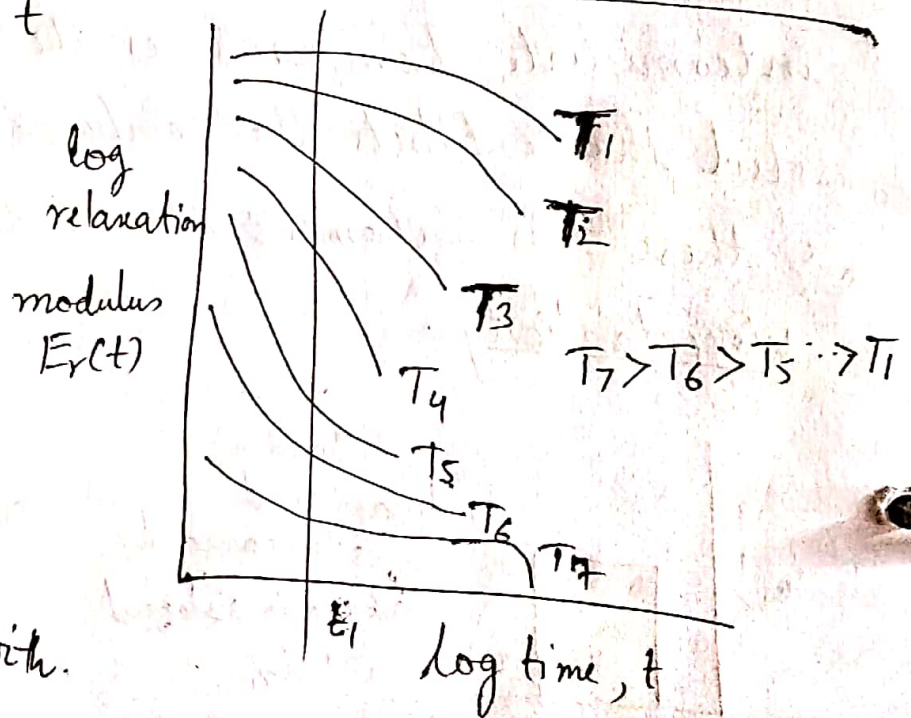
$$\text{Relaxation modulus } E_r(t) = \frac{\sigma(t)}{\epsilon_0} \quad (\text{for viscoelastic polymers.})$$

$E$  &  $\sigma$  are time dependent.

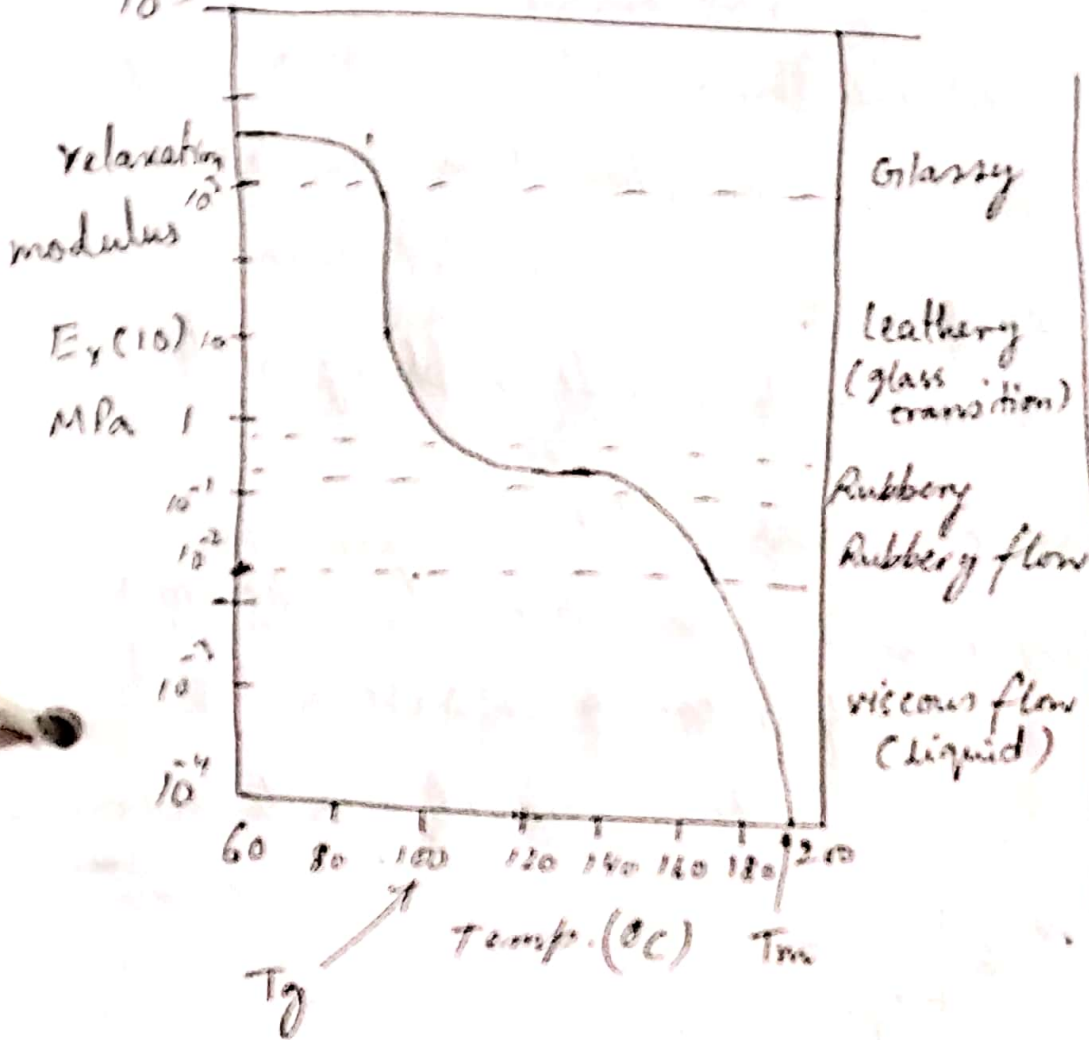
Log of  $E_r(t)$  vs log  $t$   
for a viscoelastic polymer.

① Magnitude of  $E_r(t)$  decreases with time (corresponding to decay in stress)

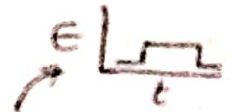
② Curves are displaced to lower  $E_r(t)$  levels with increasing temp.



To represent the influence of temp. data points are taken at a specific time from the  $E_r(t)$  vs log time plot for a polymer that exhibits viscoelastic behaviour and then cross-plotted as log  $E_r(t)$  vs temp.



log of  $E_r(t)$  vs  $T_c$   
 for amorphous (atactic) polystyrene  
 $t_i = 10^5$



{ Glassy region → material rigid & brittle. — low temp.

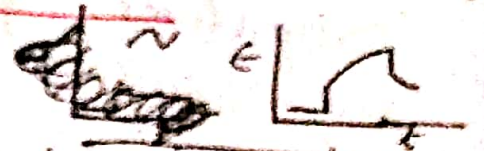
{  $E_r(t)$  is virtually independent of temperature.

— Temp. increased further —

{  $E_r(t)$  drops by  $10^3$  within a  $20^\circ\text{C}$  temp. span

• — leathery or glass transition region

{  $T_g = 100^\circ\text{C}$ . Deformation is leathery or time dependant and not totally recoverable on release on an applied load.



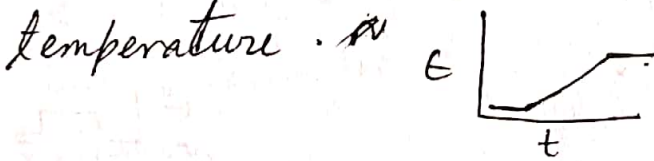
{ Within the rubbery plateau temp region, the material deforms in a rubbery manner, here, both elastic & viscous components are present, and deformation is easy to produce because  $E_r(t)$  is relatively low.

— temp. rises further —

Rubbery flow ~~& viscous flow~~ Polymer is a very viscous liquid ~~and~~ that exhibits both elastic & viscous flow components. The material experiences a gradual transition to a soft rubbery state.

— temp. rises further —

Viscous flow region = The material experiences a gradual transition to a soft rubbery viscous liquid. The modulus decreases dramatically with increasing temperature.



Chain . From a molecular standpoint, chain motion intensifies so greatly that for  $\mu$  viscous flow, the chain segments experience vibration and rotational motion largely independent of <sup>one</sup> each other. At these temperatures, any deformation is entirely viscous and essentially no elastic behaviour occurs.

The deformation behaviour of a viscous polymer is specified in terms of viscosity, a measure of a material's resistance to flow by shear forces.



## Visco elastic Creep

Many polymeric materials are susceptible to time dependent deformation when the stress level is maintained constant; such deformation is termed viscoelastic creep.

This type of deformation may be significant at room temperature and under modest stresses that lie below the yield strength of the material.

eg. automobile tires may develop flat spots on their contact surfaces when the automobile is parked for prolonged time periods.

Creep test results ~~at~~ under isothermal conditions.

# Creep modulus  $E_c(t)$ , defined by

$$E_c(t) = \frac{\sigma_0}{\epsilon(t)}$$

wherein  $\sigma_0$  is the constant applied stress and  $\epsilon(t)$  is the time dependent strain. The creep modulus is also temperature sensitive and diminishes with increasing temperature.

~~See~~ # wrt the influence of molecular structure on the creep characteristics, as a general rule the susceptibility to creep decreases [i.e.  $E_c(t)$  decreases increases] as the degree of crystallinity increases.

# Fracture of Polymers

The fracture strengths of polymeric materials are low (wrt those of metals & ceramics). Generally, the mode of fracture in thermosetting polymers (heavily crosslinked networks) is brittle.

In simple terms, during the fracture process, cracks form at regions where there is a localized stress concentration (i.e. scratches, notches & sharp flaws).

⊗ The stress is amplified at the tips of these cracks leading to crack propagation and fracture.

Covalent bonds in the network or crosslinked structure are severed during fracture.


For thermoplastic polymers, both ductile and brittle modes are possible, and many of these materials are capable of experiencing a ~~ductile~~ ductile to brittle transition. Factors that favor a brittle fracture are a reduction in temperature, an increase in strain rate, the presence of a sharp notch, increased specimen thickness, and any modification of the polymer structure that raises  $T_g$ .

Glassy thermoplastics are brittle below their  $T_g$  temperatures. However, as the temperature is raised,

they become ductile in the vicinity of their  $T_g$ 's and experience plastic yielding before fracture.

PMMA  $\begin{cases} 4^\circ\text{C} & \text{brittle} \\ 60^\circ\text{C} & \text{ductile} \end{cases}$

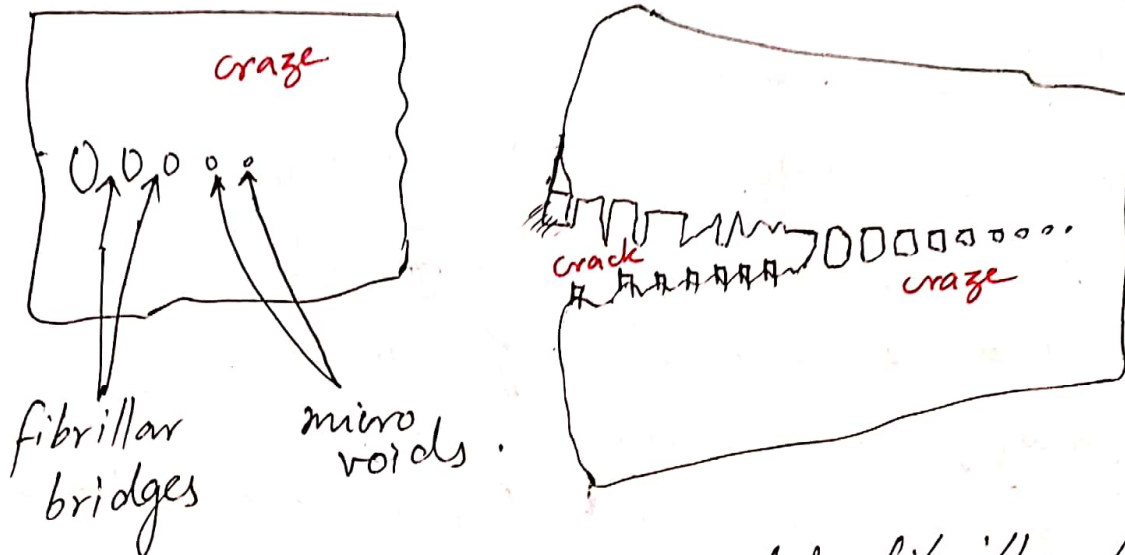
A phenomenon that frequently precedes fracture in some thermoplastic polymers is crazing. Associated with crazes are regions of very localized plastic deformation, which leads to the formation of small & interconnected microvoids. Fibrillar bridges form between these microvoids wherein micro molecular chains become oriented.



If the applied tensile load is ~~a~~ sufficient, these bridges elongate and break, causing the microvoids to grow & coalesce. As the microvoids coalesce, cracks begin to form. A craze is different from a crack in that it can support a load across its face. Furthermore, this process of craze growth prior to cracking absorbs fracture energy and effectively increases the fracture toughness of the polymer. In glassy polymers, the cracks propagate with little craze formation resulting in low fracture toughness. Crazes form at highly stretched regions associated with scratches, flaws, and molecular inhomogeneities; in addition, the propagate

perpendicularly to the applied tensile stress, and typically are  $5\ \mu\text{m}$  or less thick.

### Principles of fracture



- (a) A craze showing microvoids & fibrillar bridges
- (b) a craze followed by a crack.

Susceptibility of brittle & quasi-brittle polymers to fracture when a crack is present may be expressed in terms of the plane strain fracture toughness.

The magnitude of  $K_{Ic}$  will depend on characteristics of the polymer (i.e. molecular wt., % crystallinity, etc) as well as temperature, strain rate, and the external environment.

## 14.6 Miscellaneous mechanical characteristics:-

### Impact Strength

The degree of resistance of a polymeric material to impact loading.

- Izod / Charpy test.
- brittle/ductile fracture displayed depending on the temperature, specimen size, strain rate and mode of loading.
- Both semicrystalline & amorphous polymers are brittle at low temp.s  $\Rightarrow$  both have relatively low impact strengths. They experience a DBT over a relatively narrow temp. range (like steel) Impact strength undergoes a gradual decrease at still higher temp.s as the polymer begins to soften. Ordinarily the ~~two~~ <sup>ambient</sup> impact strength is high at the ~~room~~ temp. and a DBTT that lies below room temp.

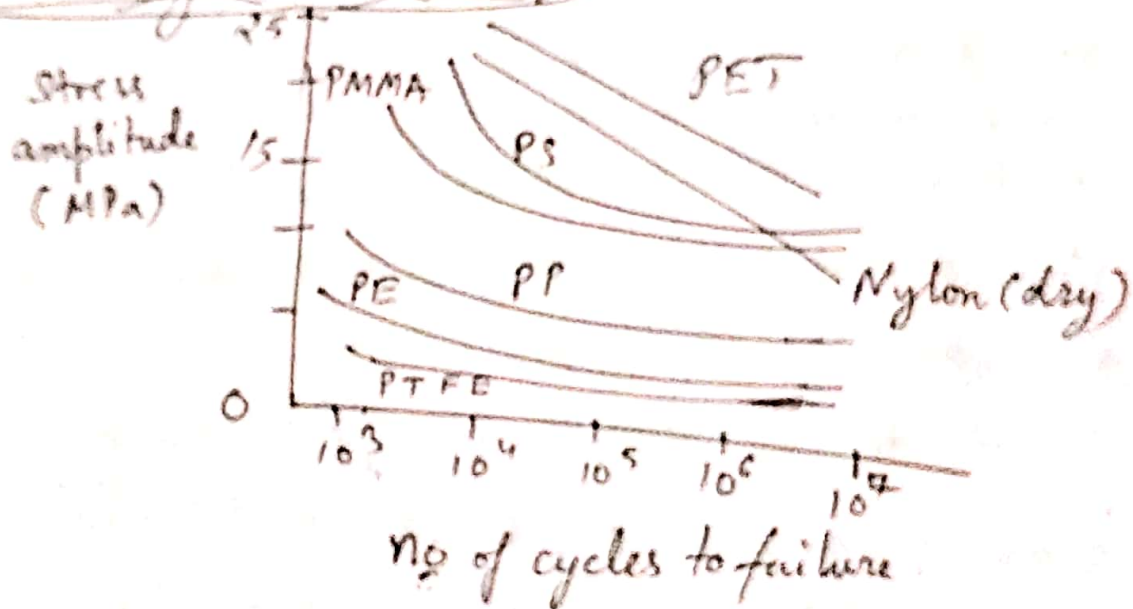
Fatigue - Polymers experience fatigue failure under conditions of cyclic loading. \*

- fatigue occurs at stress levels that are low relative to the yield strength.
- Some polymers have a fatigue limit (a stress level at which the stress at failure becomes independent of the no of cycles)
- fatigue strength & fatigue limits of polymers are much

lower than for metals.

- The fatigue behaviour of polymers is much more sensitive to loading frequency than for metals.
- Cycling polymers at high frequency & / or relatively large stresses can cause localized heating; consequently failure may be due to a softening of the material rather than as a result of typical fatigue processes.

### Tear strength & hardness



### Tear strength & hardness

Other mechanical properties ~~are~~ that are sometimes influential in the suitability of a polymer for some particular application include tear resistance & hardness.

- The ability to resist tearing is important for some plastics (e.g. thin films in packaging)

Tear strength  $\rightarrow$  the mechanical parameter that is measured is the energy required to tear apart a cut specimen that has a standard geometry. The magnitude of tensile & tear strengths are related.

Hardness - resistance to scratch, penetrate, <sup>marring</sup> ~~mark~~ and so on  
Rockwell test, Durometer <sup>test</sup>, Barcol test (indentation techniques)

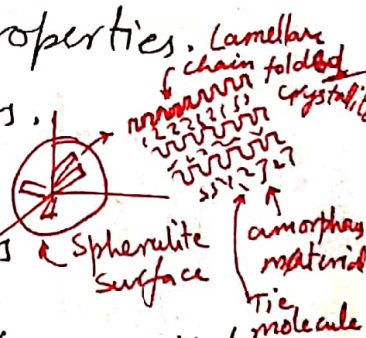
## Mechanisms of deformation and for strengthening of polymers

Deformation models for semicrystalline and elastomeric polymers ~~deserve~~ are studied.

- stiffness & strength of semicrystalline materials.
- elastic & plastic deformation mechanisms.
- methods used to stiffen & strengthen these materials
- elastomers & their unusual elastic properties.
- deformation mechanism of elastomers.

### (14.7) Deformation of semicrystalline polymers

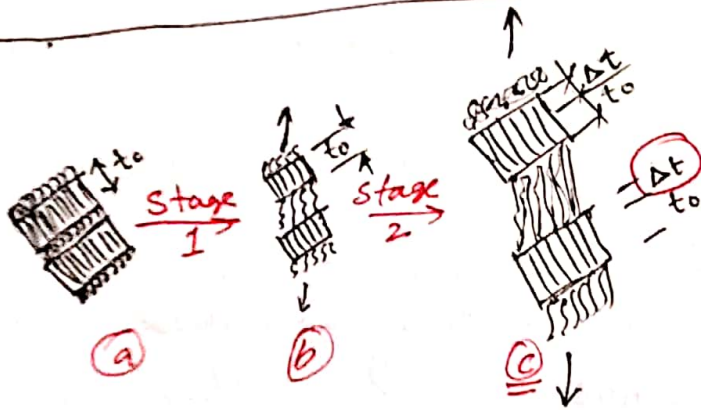
Many semicrystalline polymers in bulk form will have the spherulitic structure. Each spherulite consists of numerous chain-folded ribbons, or lamellae, that radiate outward from the center. Separating these lamellae are areas of amorphous material; adjacent lamellae are connected by tie chains that



pass through these amorphous regions.

## \* Mechanism of elastic deformation

As with other material types, Elastic deformation of polymers occurs at relatively low stress levels on the  $\sigma$ - $\epsilon$  curve. The onset of elastic deformation for semicrystalline polymers results from chain molecules in amorphous regions elongating in the direction of the applied tensile stress.



stages in the elastic deformation of a semicrystalline polymer.

(a) Two adjacent chain folded lamellae and interlamellar amorphous

material before deformation.

(b) Elongation of amorphous tie chains during the first stage of deformation.

(c) Increase in lamellar crystalline thickness (which is reversible) due to bending and stretching of chains in crystalline regions.

The process is represented in fig. Continued deformation in the 2nd stage occurs by changes in both amorphous and lamellar crystalline regions.



Amorphous chains continue to ~~be~~ align and become elongated. In addition, there is bending and stretching of the strong chain covalent bonds within the lamellar crystallites. This leads to a slight & reversible increase in the lamellar crystallite thickness as indicated by  $\Delta t$ .

Since semicrystalline polymers are composed of both crystalline & amorphous regions, they may in a sense be considered as composite materials. As such the elastic modulus may be taken as some combination of the moduli of crystalline & amorphous phases.

### \* Mechanism of plastic deformation

The transition ~~of~~ from elastic to plastic deformation occurs in stage 3 of fig ~~(identical to stage 2)~~. But stage a of fig (b) is same as stage c of previous fig.

During stage 3 adjacent chains in the lamellae slide past one another. This results in the tilting of the lamellae so that the chain folds become more align aligned with the tensile axis. Any chain displacement is resisted by relatively weak secondary or van der Waals bonds.

Crystalline block segments separate from the lamellae, in stage 4 with the segments attached to ~~the~~ one another by tie chains. In the final stage (stage 5)

the blocks and tie chains become oriented in the direction of the tensile axis. Thus, appreciable tensile deformation of semicrystalline polymers produces a highly oriented structure. This process of orientation is referred to as drawing and is commonly used to improve the mechanical properties of polymer fibers & films.

During deformation the spherulites experience shape changes for moderate levels of elongation. However, for large deformations, the spherulitic structure is virtually destroyed.

Also, to a degree the processes represented in Fig. are reversible. That is, if deformation is terminated at some arbitrary stage, and the specimen is heated to an elevated temperature near its melting point (i.e. is annealed), the material ~~is~~ will ~~be~~ recrystallize to again form a spherulitic structure. Furthermore, the specimen will tend to shrink back, in part, to the dimensions it had prior to deformation. The extent of this shape & structural recovery

will depend on the annealing temperature and also the degree of elongation.

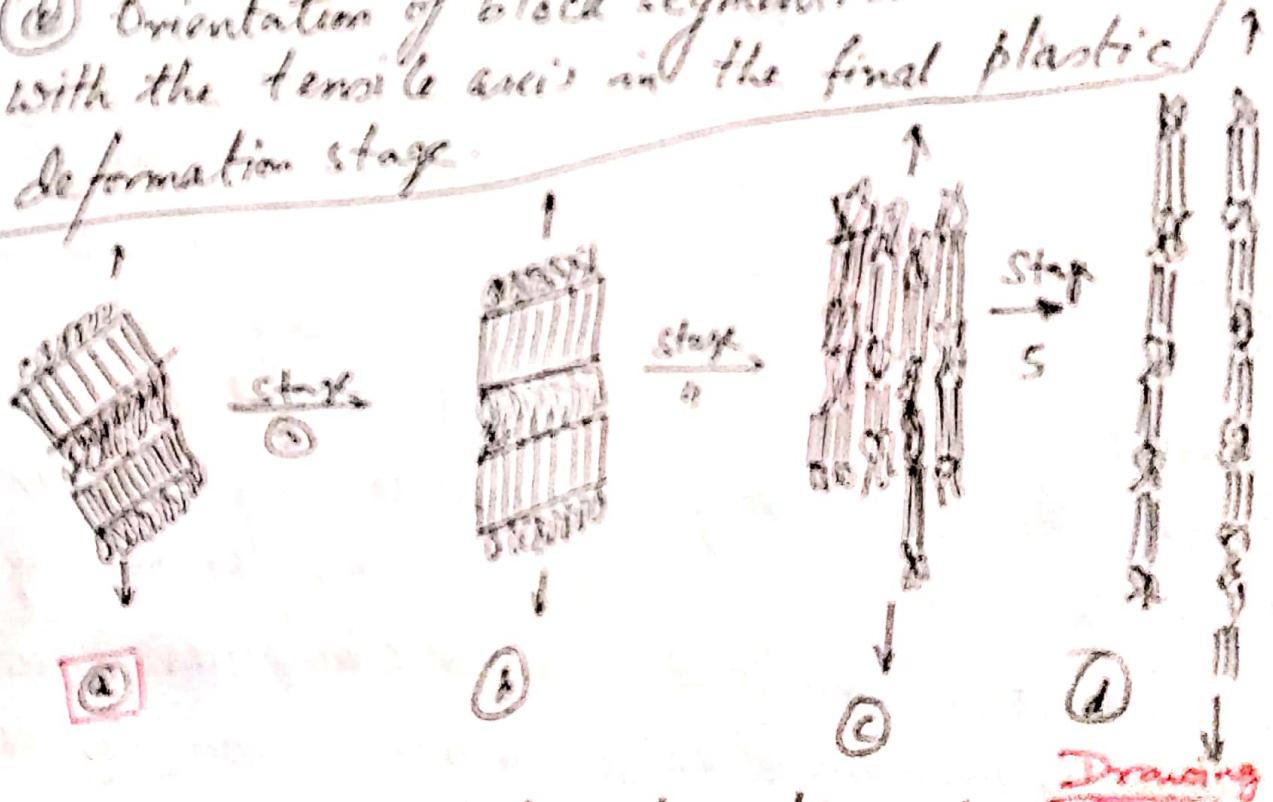
Stages in the plastic deformation of a semicrystalline polymer

- (a) Two ~~adj~~ adjacent chain-folded lamellae and interlamellar amorphous after elastic deformation

- (b) Tilting of lamellar chain folds.

- (c) Separation of crystalline block segments.

- (d) Orientation of block segments & tie chains with the tensile axis in the final plastic deformation stage.



Stages in the plastic deformation of a semi-crystalline polymer. (a) Two adjacent chain folded lamellae and interlamellar amorphous material after elastic deformation. (b) Tilting of lamellar chain folds (c) Separation of crystalline block segments. (d) Orientation of block segments and tie chains with the tensile axis in the final plastic deformation stage.