Mechanical Properties of Polymers

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Materials Science Seminar

Definition of Polymers

- Polymers are materials consisting of very long molecules, made up of hundreds or thousands repeating chemical units (the monomer units), covalently bonded together.

- Organic glasses

- The long molecules are bonded together by
  - Ven der Waals
  - Hydrogen bonds
  - Covalent cross-links

Degree of Polymerization (DP):
the number of monomer units in a molecule.

Amorphous & Crystalline
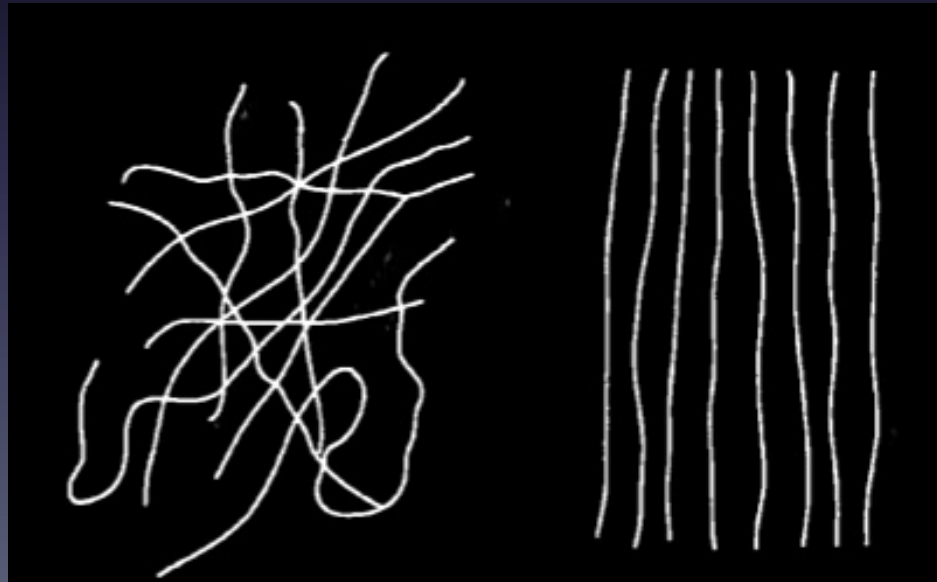
# Classes of Polymers

- Thermoplastics: such as PE. soften on heating

- Thermosets: such as epoxy. Harden when two components are heated together

- Elastomers or rubbers

- Natural polymers: such as cellulose, lignin, and protein

Thermoplastics

- Commonest: Polyethylene (PE)

- Often described as linear polymers (chains are not cross linked)

- T ⇧ secondary bonds melt, flow like viscous liquid

- Polystyrene (PS): amorphous
 PE: partly crystalline

- Sub-units (monomers) of most of them
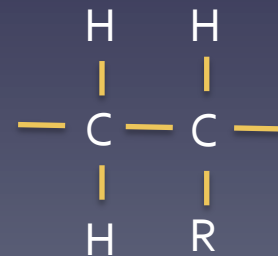
Thermosets

- Are made by mixing two components (resin and hardener) → react and harden at RT or on heating

- Heavily cross-linked → also called network polymers

- T ⇧ secondary bonds melt, E drops → rubber
- T ⇧⇧ → decomposes

Elastomers

- Almost linear polymers with occasional cross-links

- only in noncrystalline

- the backbone of the chain must be very long and have many kinks and bends.

```
      H           H
      |           |
 —  C  —  C  =  C  —
      |     |     |
      H     R     H
```
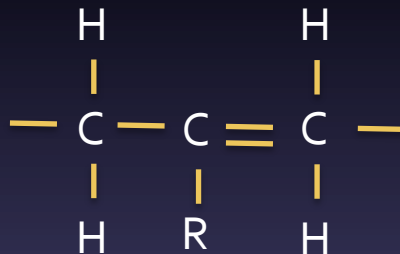
- At RT, secondary bonds have already melted

- Vulcanization

- Cross-links provide the memory of the material so that it returns to its original shape

Elastomers

- Helical pattern to the chain because of carbon-carbon double bonds

(a)   (b)
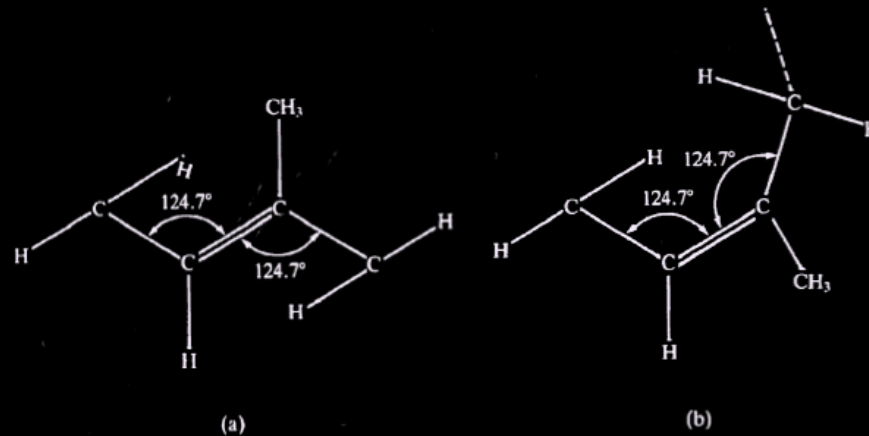
- Mechanical Model: a highly coiled skeleton of primary bonds (including cross-links) immersed in a viscous like medium.

- During application of a tensile load: coils are unwound to an extent

- Upon unloading, the cross-linking atoms act to restore the original dimensions.

- No links, no restoration

Elastomers

- Elastic behavior of rubbers is different from that of crystalline material

- Only at extensions where the chains approximately fully extended does the force begin to stretch primary bonds

- decrease in S → Increase in F (free energy)

- Potential energy is unchanged

- No primary bond stretching → small modulus

σ (MN/m^2)
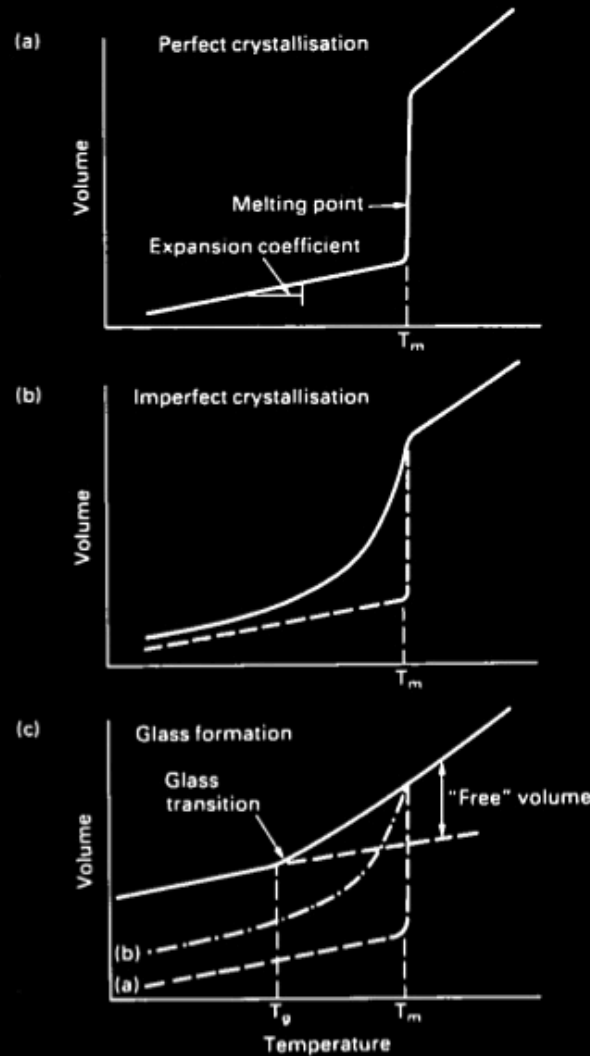
$\lambda (= \frac{l}{l_0} = 1 + e)$
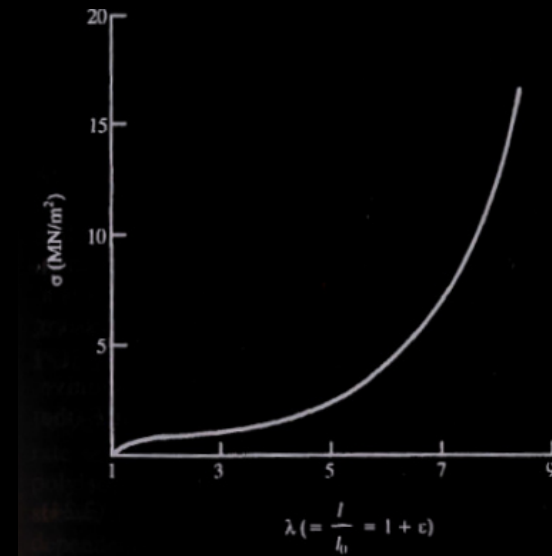
Elastomers

- Akin to ideal gases (no change in potential energy) but ...

- Incompressible

- Neo-Hookean $\mu = Nk_BT$
N : no. polymer chains/V

$$\sigma = \mu(\lambda^2 - \lambda^{-1})$$

Source: Courtney, Mechanical Behavior of Materials, 2000
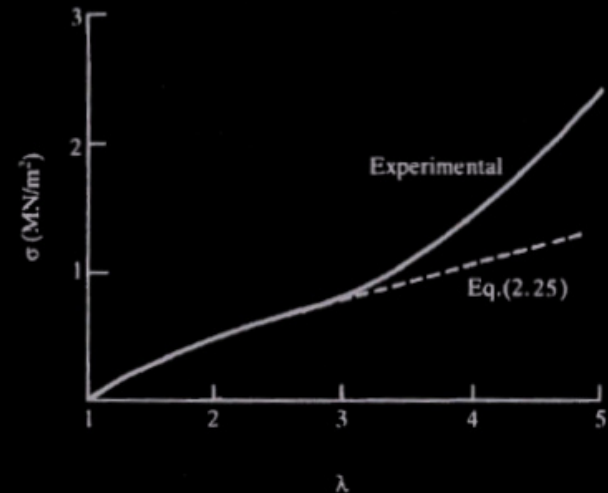
# Glass Transition Temperature

Deformation of Polymers

- Elastomers → Always elastic response
- Thermosets → viscoelastic response
- Thermoplastics → elastic or plastic

Change of Young's modulus for linear polymers

Linear-amorphous polymers (like PMMA & PS) show five regims of deformation

In general

$$E = \frac{\sigma}{\varepsilon(t, T)}$$

← Fixed loading time

Source: Ashby & Jones, Engineering Materials 2, 1998.
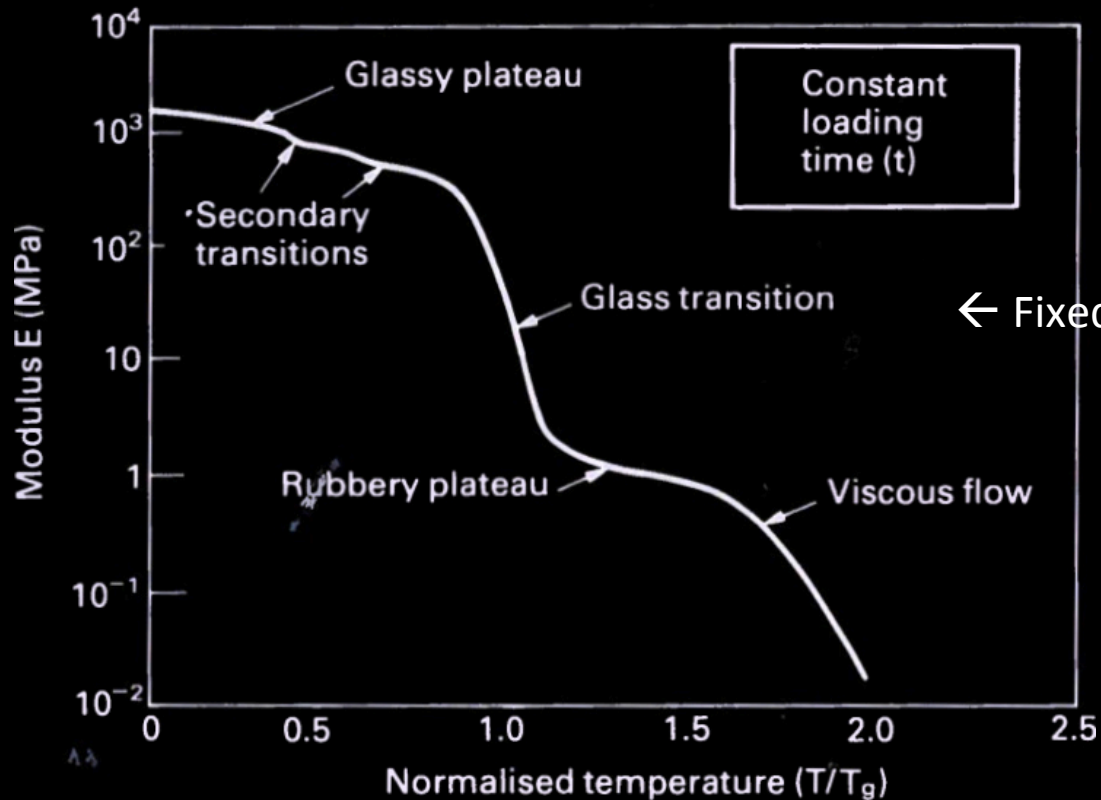
Glassy Regime and secondary relaxations

- T<<T$_g$

$$\varepsilon = f\frac{\sigma}{E_1} + (1-f)\frac{\sigma}{E_2} = \sigma\left[\frac{f}{E_1} + \frac{1-f}{E_2}\right]$$
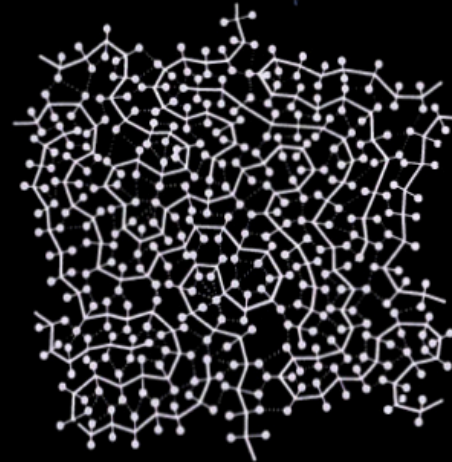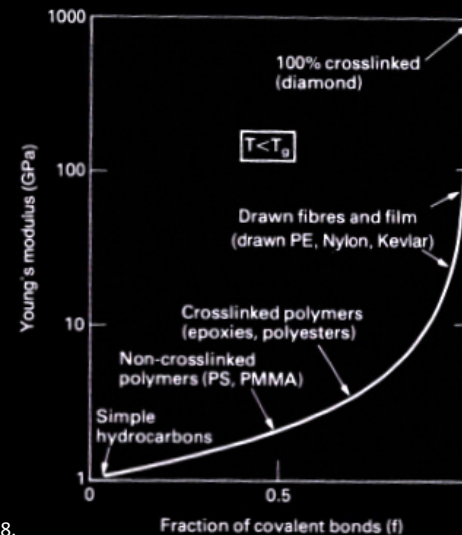
Fig. 23.2. A schematic of a linear-amorphous polymer, showing the strong covalent bonds (full lines) and the weak secondary bonds (dotted lines). When the polymer is loaded below T_g, it is the secondary bonds which stretch.

E$_1$~10^3 GPa
E$_2$~ 1 GPa

Young's modulus (GPa)

1000

100% crosslinked (diamond)

T<T$_g$

100

Drawn fibres and film (drawn PE, Nylon, Kevlar)

10

Crosslinked polymers (epoxies, polyesters)

Non-crosslinked polymers (PS, PMMA)

Simple hydrocarbons

1

0   0.5   1

Fraction of covalent bonds (f)

Glass or visco-elastic transition

- T>Tg Extra free volume lowers the packing density

- Still there are some non-sliding parts

- On unloading the elastic regions pull the polymer to its orgiginal shape

- Modeled by springs and dashpots

Fig. 23.4. Each molecule in a linear polymer can be thought of as being contained in a tube made up by its surroundings. When the polymer is loaded at or above T_g, each molecule can move (reptate) in its tube, giving strain.

Source: Ashby & Jones, Engineering Materials 2, 1998.

Higher Temperatures

- **Rubbery behavior**
  - DP$<10^3$ →polymer becomes sticky liquid
  - DP$>10^4$→long molecules intertwined like a jar of very long worms →rubbery behavior

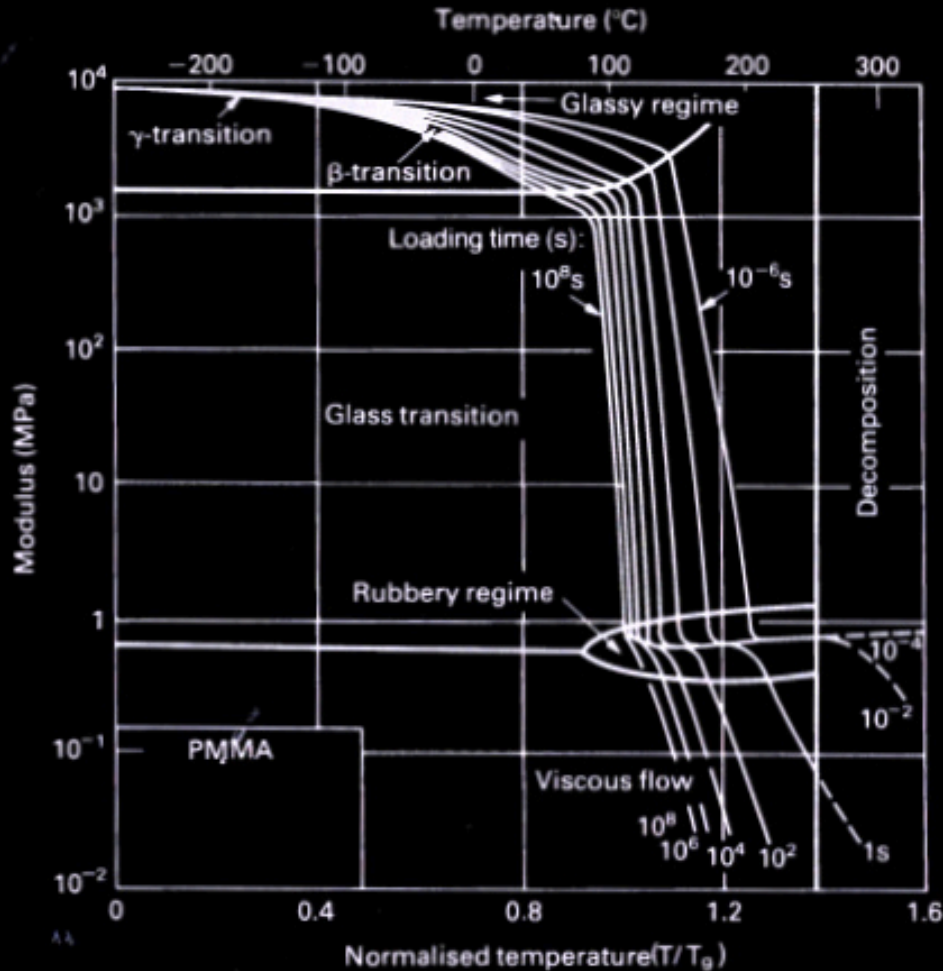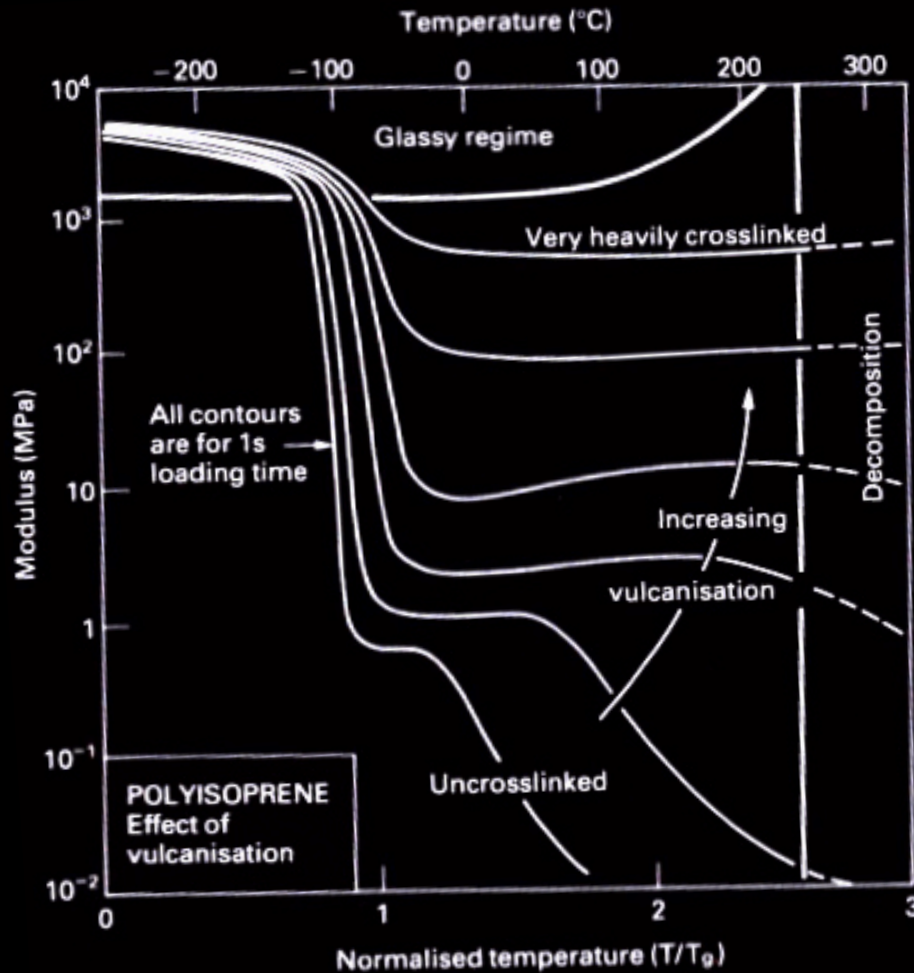- **Viscous flow**

$$\tau = \eta\dot{\gamma}$$

- **Decomposition**
  - the thermal energy exceeds the cohesive energy of some parts of the molecular chain, causing degradation or depolymerization.
  - PMMA → decomposes into monomer units
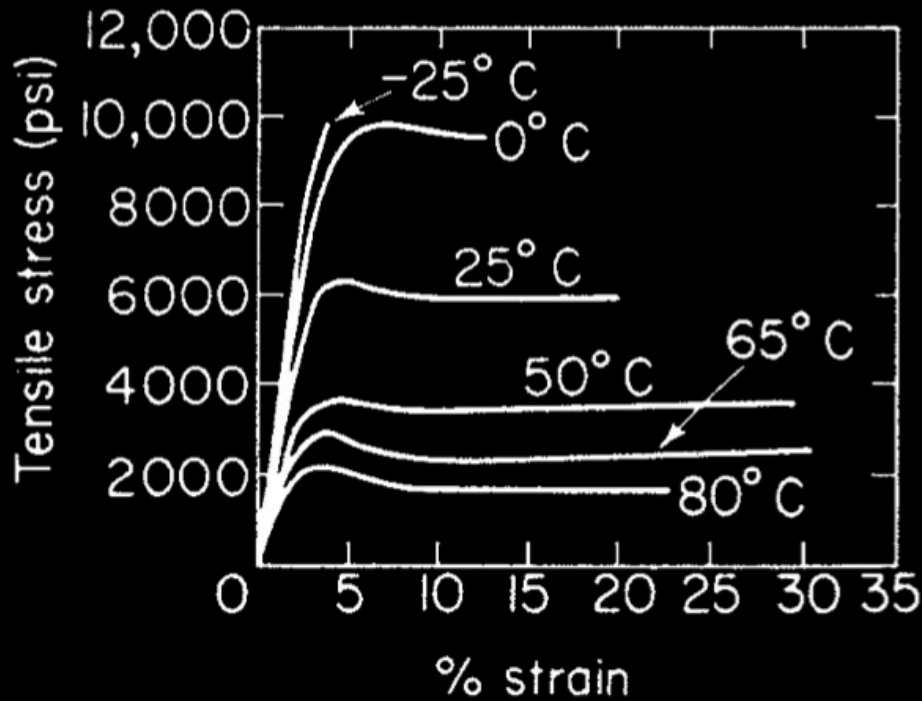 - PE →randomly degrade into many products

Modulus Diagram for Polymers

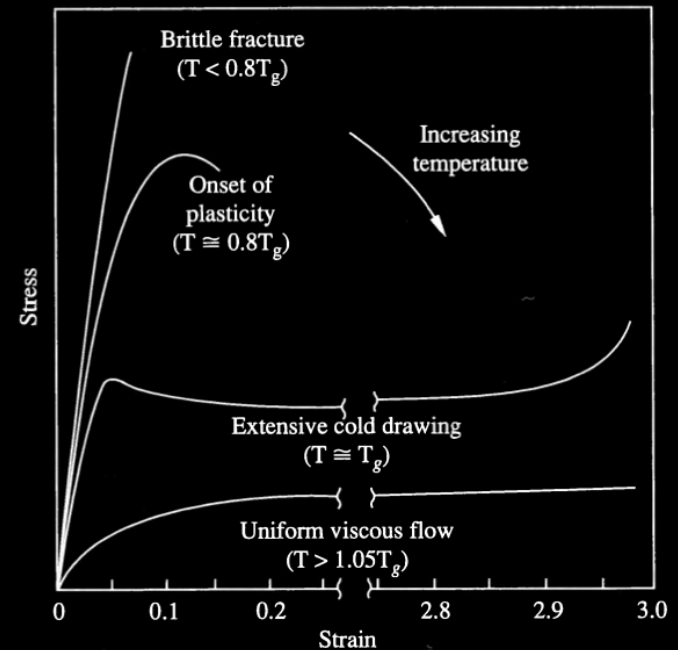# The influence of Cross-linking on a contour of the modulus diagram for polyisoprene

The effect of Temperature on Deformation

PMMA
Strength decreases and elongation
increases with higher temperature

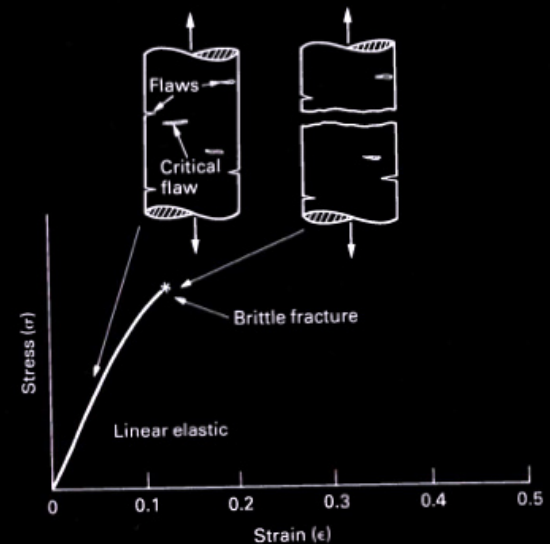Source:Carswell & Nason, ASTM Symposium on Plastics, Philadelphia, 1944

Source: Gibson & Ashby, Cellular solids-structure & properties, Pergamon Press, Oxford, 1988
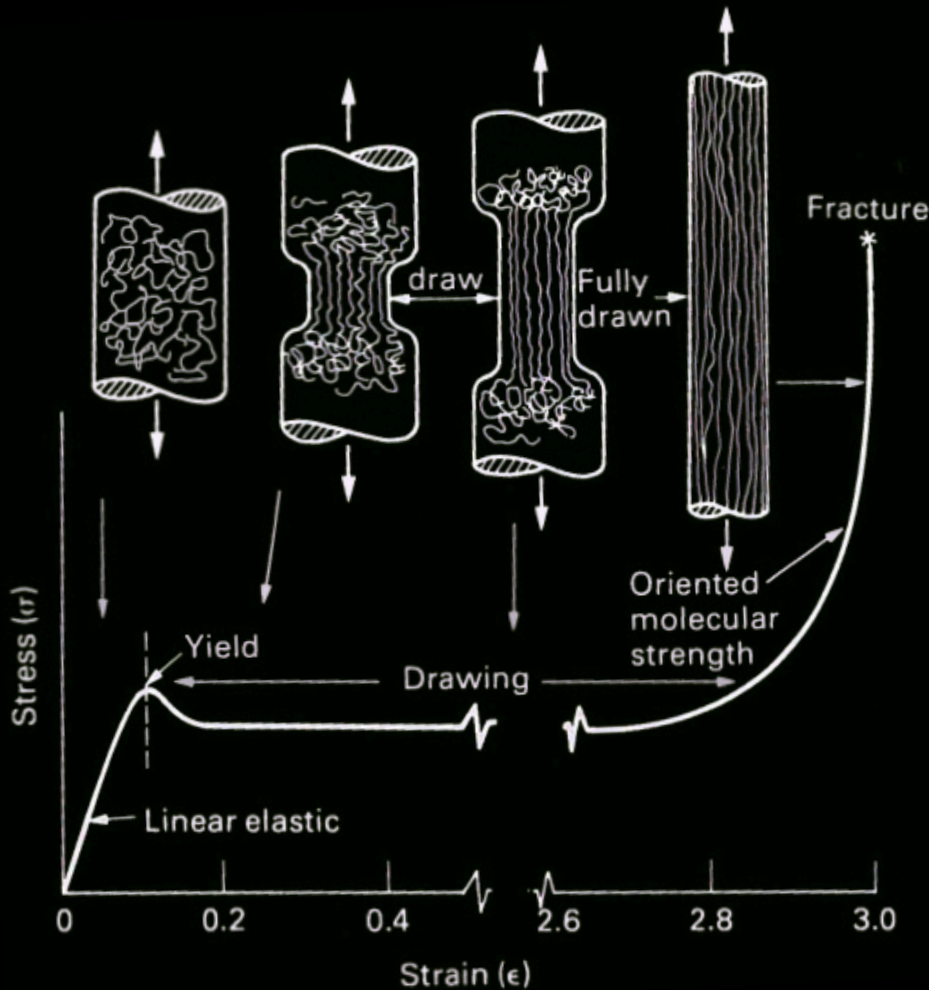
Brittle Fracture

- Polymers are brittle at $T < \sim 0.75 \, T_g$

- Pre existing cracks left by machining or abrasion or caused by environmental attack

$$\sigma = \frac{K_{IC}}{\sqrt{\pi a}}$$

- Fracture toughness $K_{IC} \sim 1 \, \text{MPa m}^{1/2}$

- Crack size $a \sim O(\mu m)$

- $\sigma \sim 1 \, \text{MPa}$

Cold Drawing

At ε ~ 0.1
The chains unfold (if folded) or draw out of the amorphous tangle (if glassy)

For λ sufficient enough (2-4) (ε=100-300%) : alignment of molecules
→ neck propagates until it is all drawn

Crazing

- Craze || maximum stress

- Propagates along a direction perpendicular to the principle axis

- Depends on T
(PE & PP draw at RT, PS does not, but it crazes)

- No crazing in compression
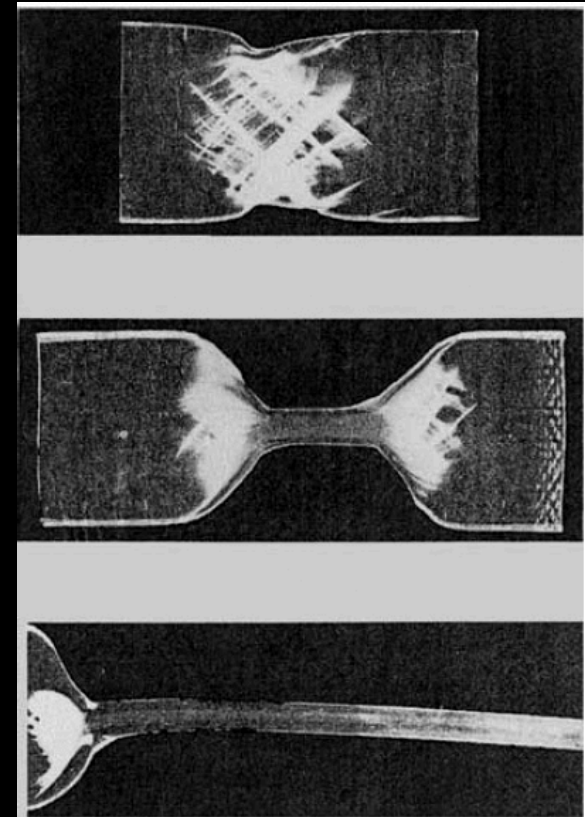
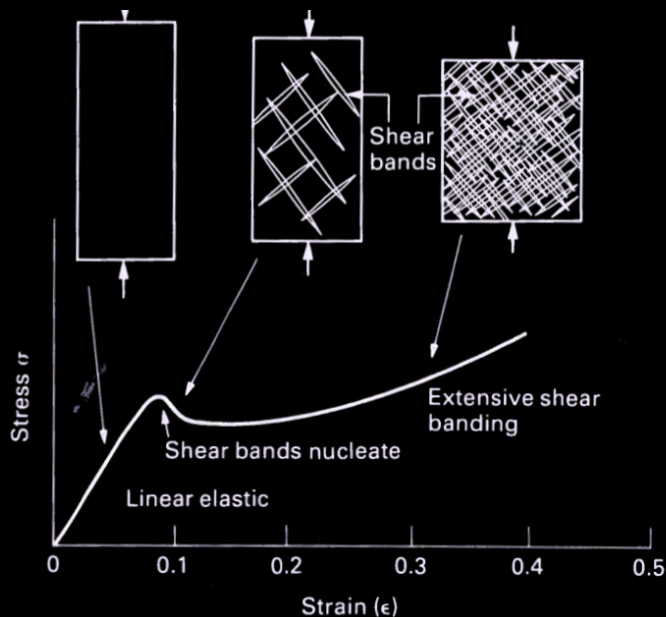- Precursor to fracture
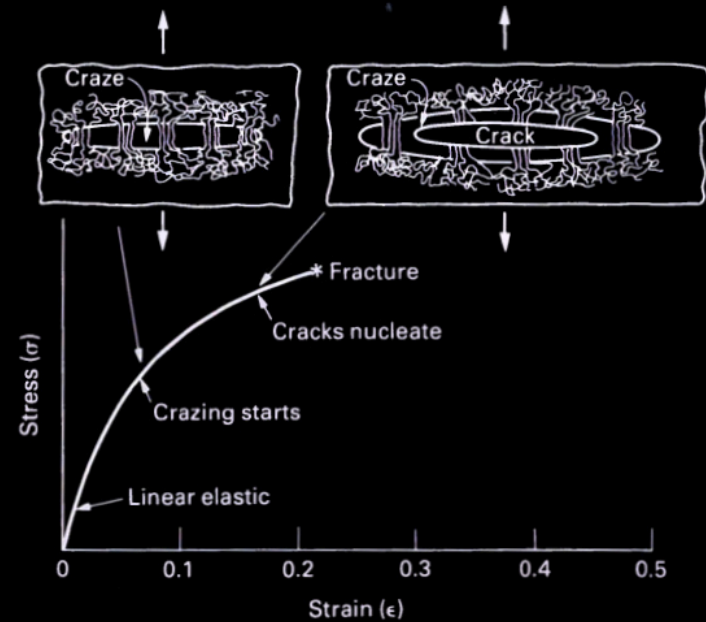
Shear Banding

Highly localized

In the direction of maximum shear stresses

More easily formed in tension

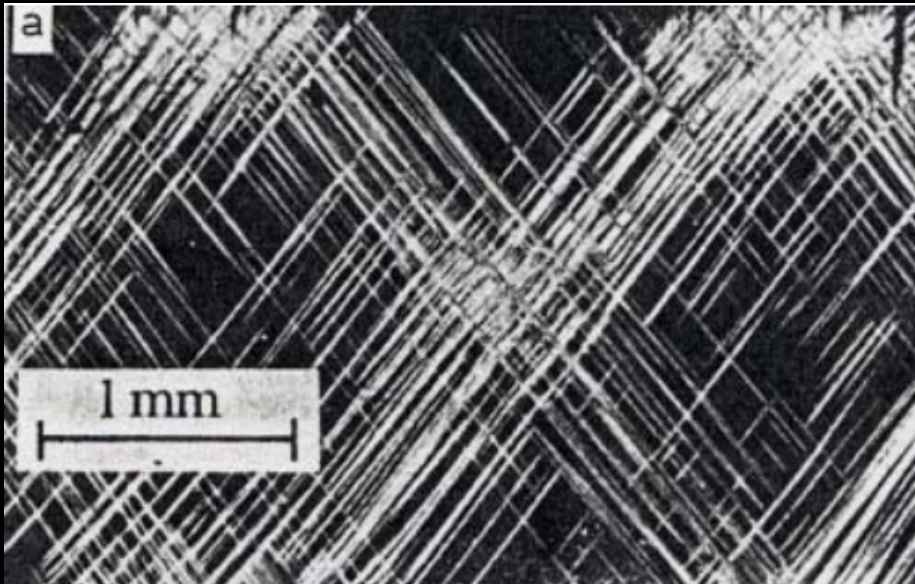Crazing and shear banding compete with each other

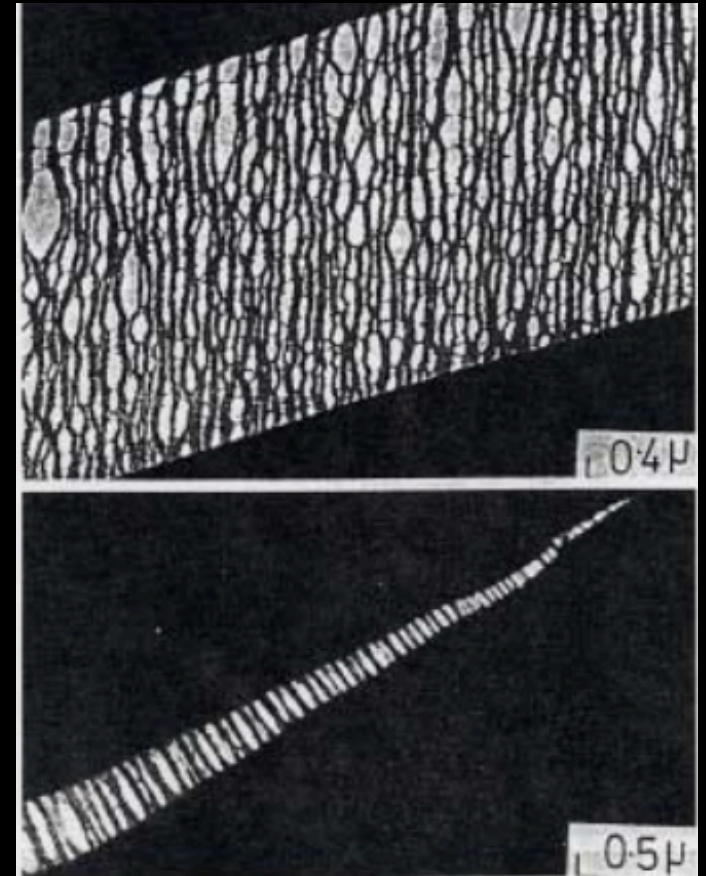Source:McClintock & Ashby, Mechanical Behavior of Materials, 1966

Source: Ashby & Jones, Engineering Materials 2, 1998.
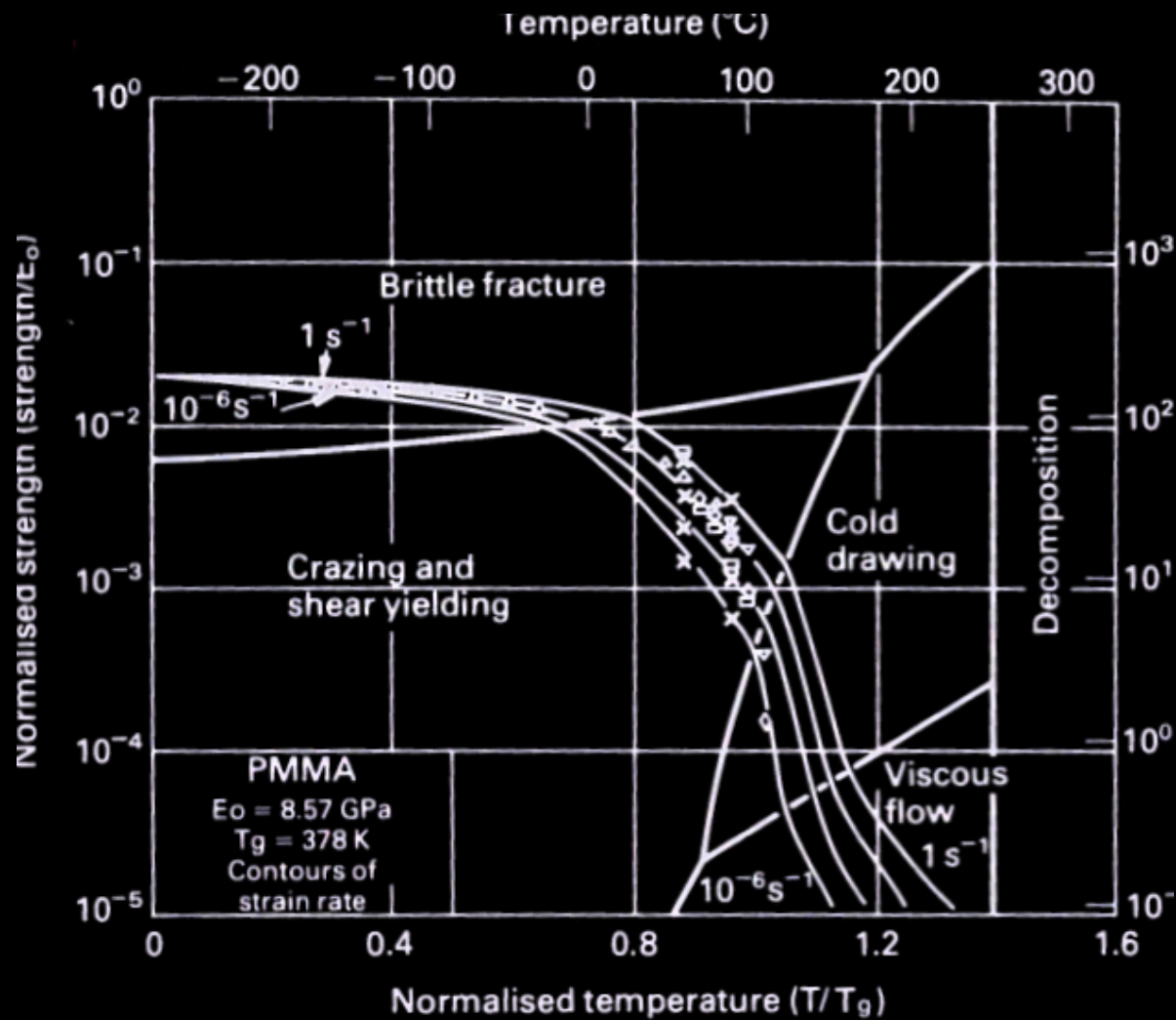
Glassy Polymers: Thermoplastics

Micro-shear bands

At-Polystyrene at 22° C under compression
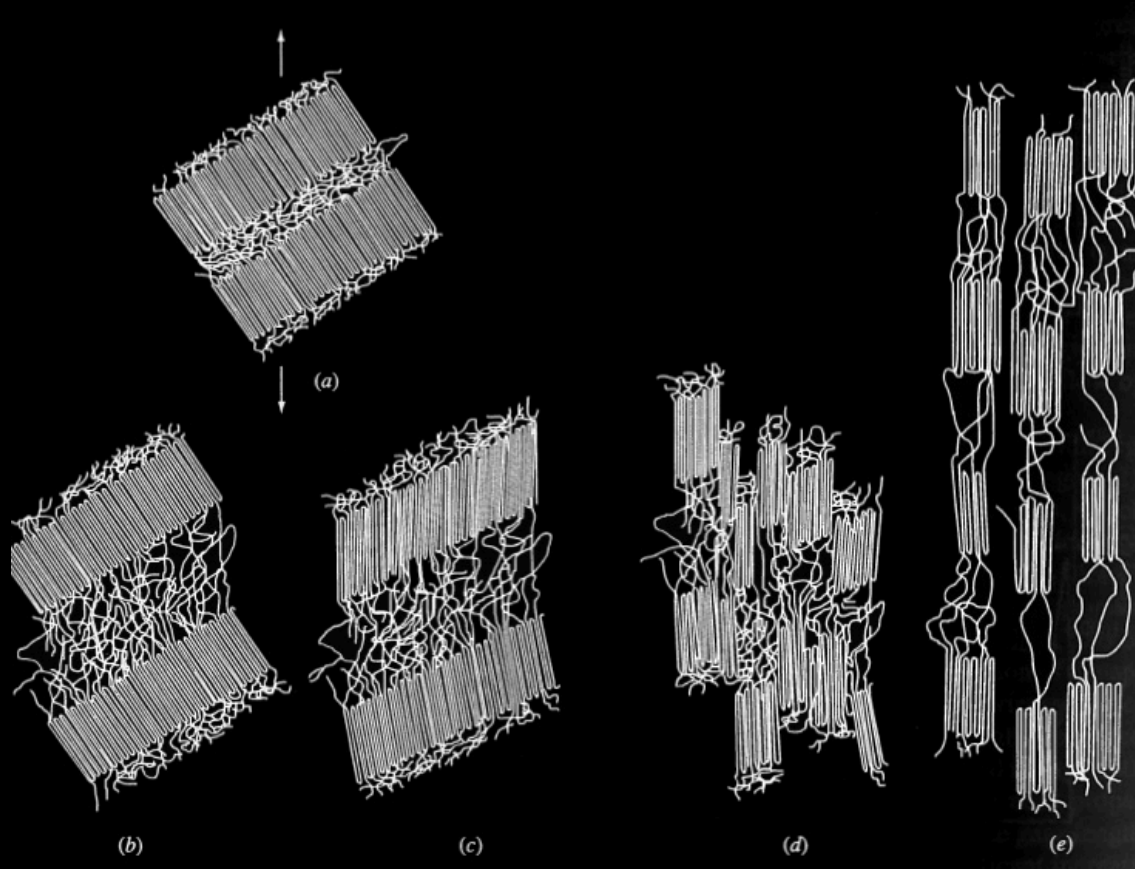(Optical Microscopy w/ Polarized Light)

Crazes
At-Polystyrene in tension
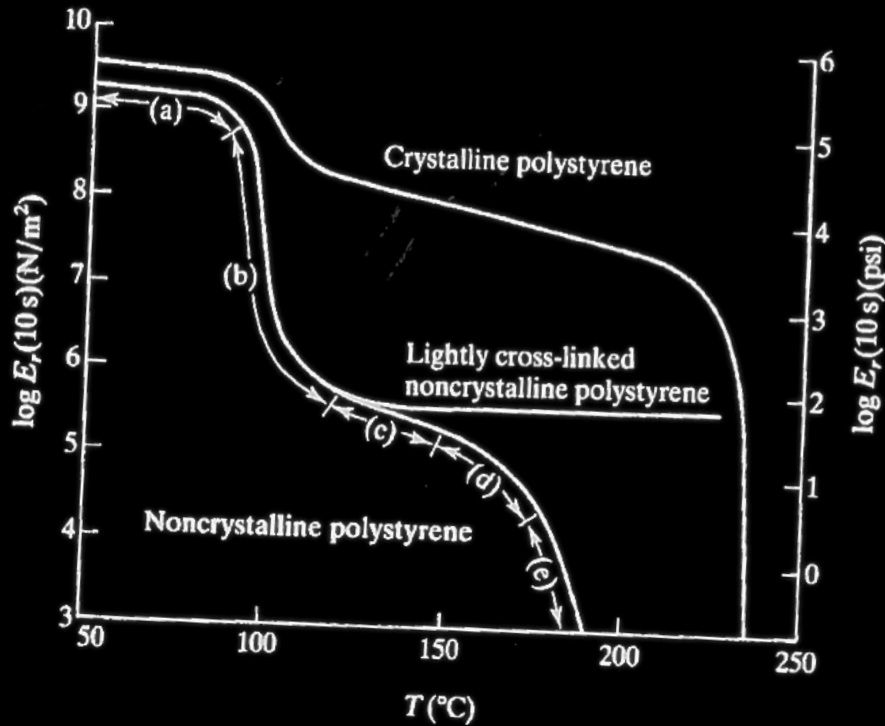(TEM)

Source: Ashby & Jones, Engineering Materials 2, 1998.

Deformation of Crystalline Polymers

- Crystalline polymers always contain some remnant non-crystalline material.

Crystallization

Crystallization increases the modulus too

Summary

- Polymers may be amorphous or semi-crystalline
- Deformation of polymers is highly affected by temperature, time, DP, etc.
- Elastomers deform elastically over a long range of temperature
- Linear polymers may be glassy, leathery, rubbery or viscous flow
- Plastic behavior of linear polymers may cause by cold drawing, crazing or shear banding
- Crystalline polymers always have remnants of amorphous polymers
- The tension and compression behavior of polymers can be quite different
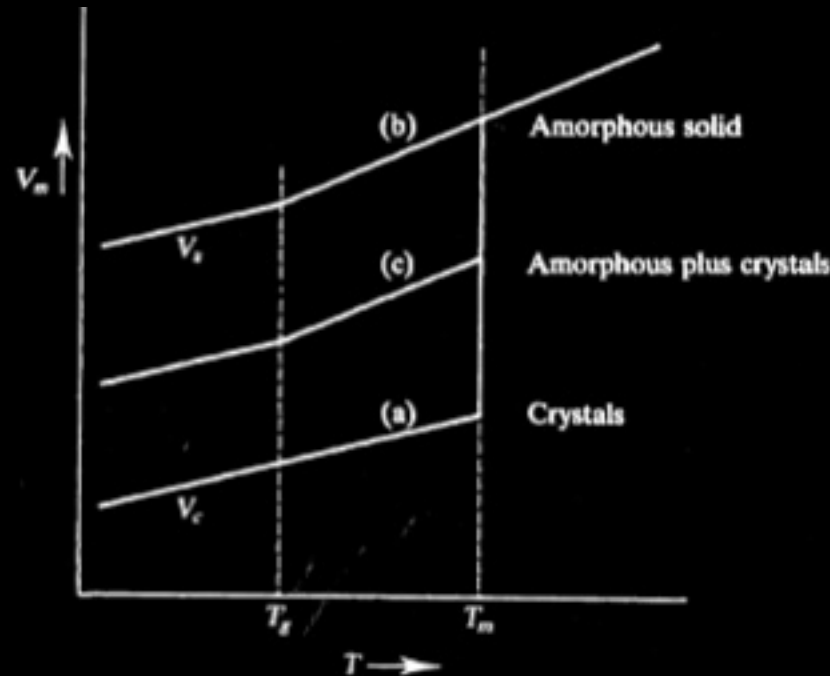
Glass Transition Temperature

Figure 8.2
Molar volume-temperature curves on cooling from above T_m to below it. If the material crystallizes (curve (a)), a discontinuity in molar volume occurs at T_m. If it does not (curve (b)), the thermal expansion coefficient ($\sim dV_m/dT$) is unchanged at T_m and the liquid structure remains below T_m. At T_g—the glass transition temperature—there is a discontinuity in the thermal expansion coefficient. Below T_g, the material demonstrates mechanical characteristics of a solid rather than a supercooled liquid. Some materials partially crystallize at T_m and their molar volume-temperature behavior on cooling is illustrated by curve (c). In certain materials (e.g., long-chain polymers) crystallization is easily avoided on cooling; in others (e.g., metals) very rapid cooling is required to prevent crystallization.