

Deformation of Non crystalline materials

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Deformation of Non-crystalline Materials

Learning Objectives

- To learn the primary deformation mechanisms when expose non-crystalline material in different stress and temperature environments
- To understand the micromechanics of flow behavior between crystalline and non-crystalline materials
- To distinguish the driving force(s) in a deformation process between crystalline and non-crystalline materials
- To examine the toughening and strengthening mechanisms in amorphous and non-crystalline materials
- To investigate the relationship between the applied stress and the initiation and propagation of shear bands
- To study the phenomenon of crazing, a type of plastic deformation, in glassy polymers

Differences between Crystalline and Non-crystalline Materials

- In crystalline materials, permanent deformation is generally related to identified defects such as dislocation, atom diffusion involving voids, vacancies, etc.
- The macroscopic deformation is similar in both crystalline and non-crystalline (i.e. behave in a brittle manner under high strain rate and low temperature)
- In non-crystalline materials, permanent deformation is often related to localized slip and/or viscous flow (low stress or high temperature)
- The non-crystalline arrangement is thermodynamically stable above material's T_m
- The crystalline just opposite (below the T_m is more stable)
- Crystalline arrangement is more ordered \Rightarrow less molar volume

Ordered Structure in Crystalline Material

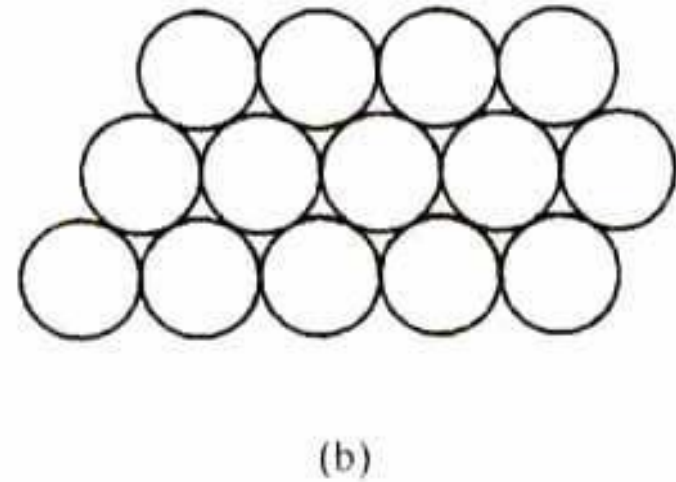
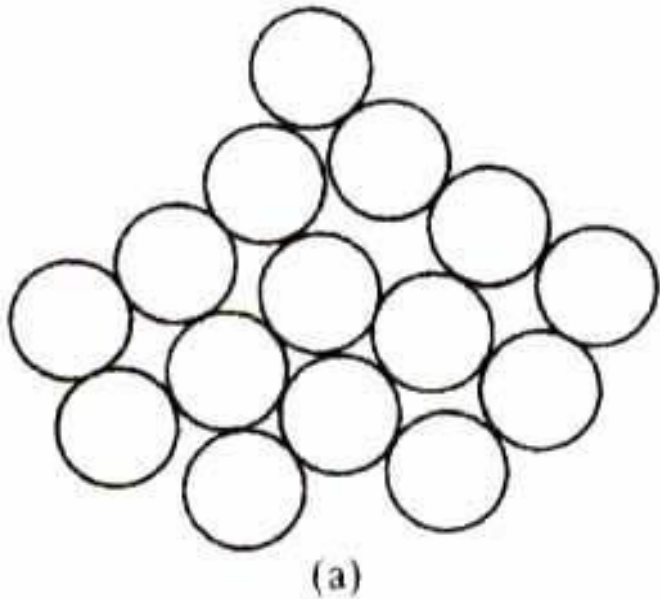


Figure 8.1

(a) Noncrystalline and (b) crystalline arrangements in a metal. The noncrystalline (amorphous) arrangement is thermodynamically stable above the melting point and the crystalline array below it. In almost all cases the more orderly crystalline arrangement is associated with a lower molar volume (i.e., a higher density).

Volume Change with respect to Cooling

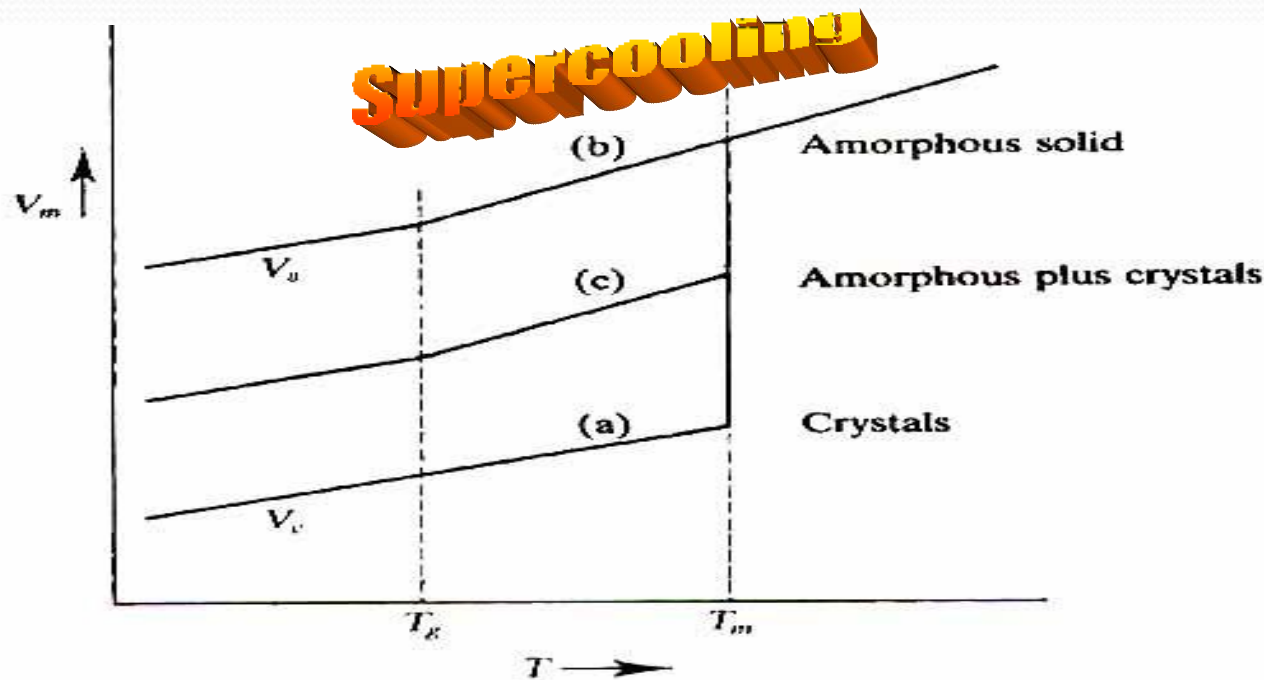


Figure 8.2

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.

Transformation from the Amorphous to Crystalline (Bond Breaking Is Required)

- Strong, directional, polar, covalent bonds between Silicon and oxygen atoms prevent the formation of crystallization.

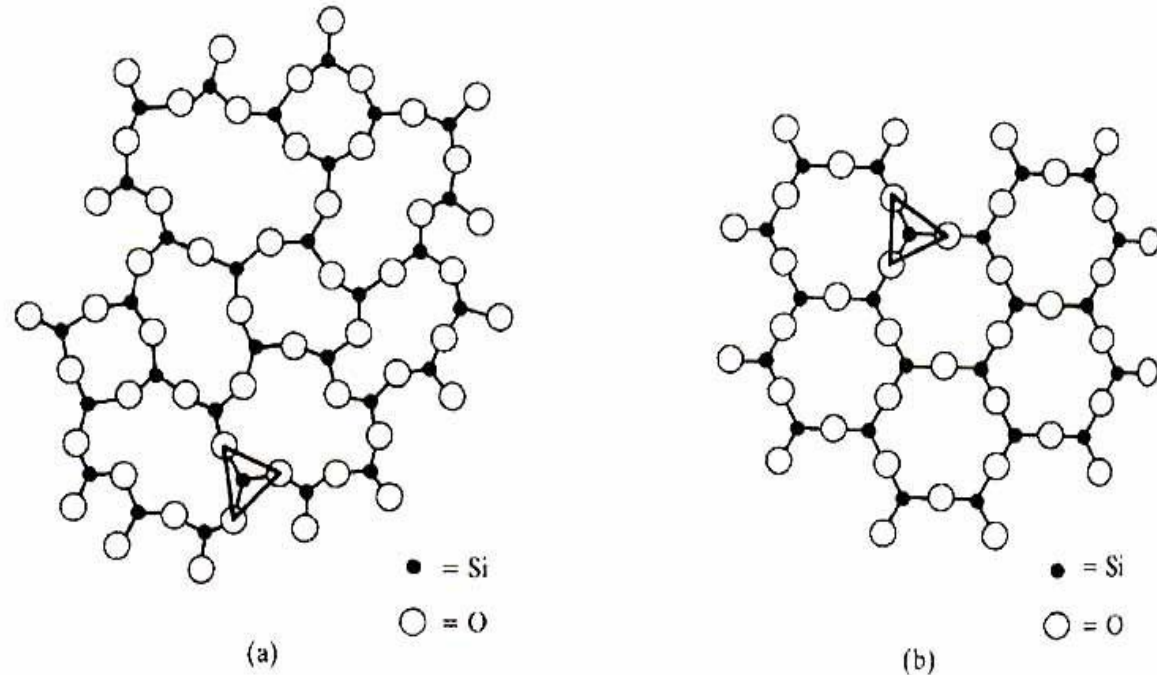


Figure 8.3

(a) Two-dimensional schematics of (a) noncrystalline and (b) crystalline arrangements in SiO_2 , the prototype of a silicate glass. The intertriangular (tetrahedral in three dimensions) O–Si bond is a strong polar-covalent one. The transformation of the structure in (a) to that in (b) necessitates breaking and reforming of these bonds and, as this is difficult, crystallization of pure SiO_2 glass is difficult. (From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*, Wiley, New York, 1976.)

A Long Distance Is Required for Crystallization to Take Place

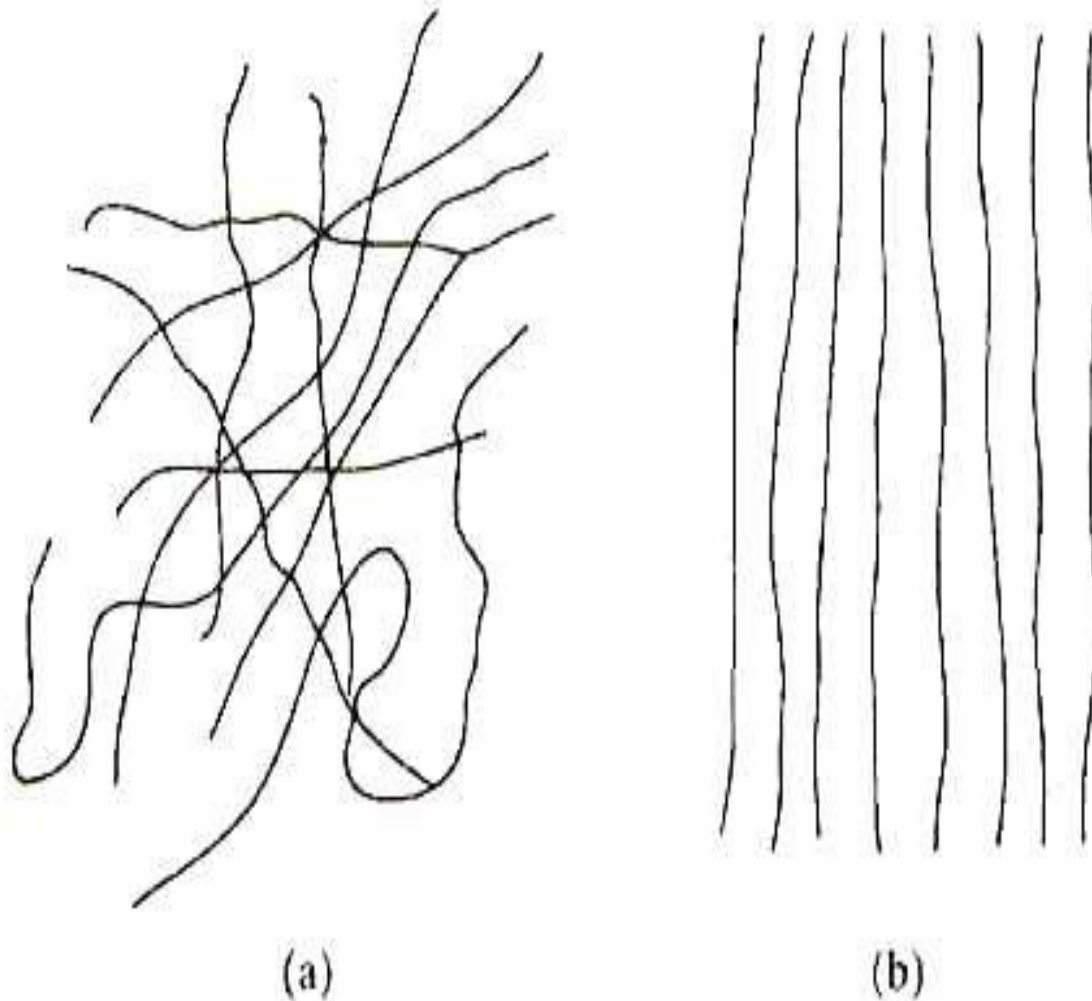


Figure 8.4

Schematics of (a) noncrystalline and (b) crystalline arrangements in a long-chain organic polymer. Although interchain bonding is weak, crystallization requires chain readjustments over distances large in comparison to interatomic dimensions. Thus, long-chain polymers, like silicate glasses, crystallize with difficulty, but for different reasons.

Concept of Free Volume

- Free volume is defined as $V_f = V_a - V_c$ where V_a is the amorphous volume and V_c is the crystalline volume
- The greater the free volume, the easier the molecular flow (or atomic flow)
- Free volume is an important concept to describe a deformation process in materials
- This concept is used in conjunction with T_g

Glass Transition Temperature and Molar Volume

- The ratio T_g/T_m can determine the ease of glass formation (ratio >0.67 is favorable)
- T_g relates to a reduction in atomic mobility
- Heating an amorphous material below its T_m can enhance the crystallization process

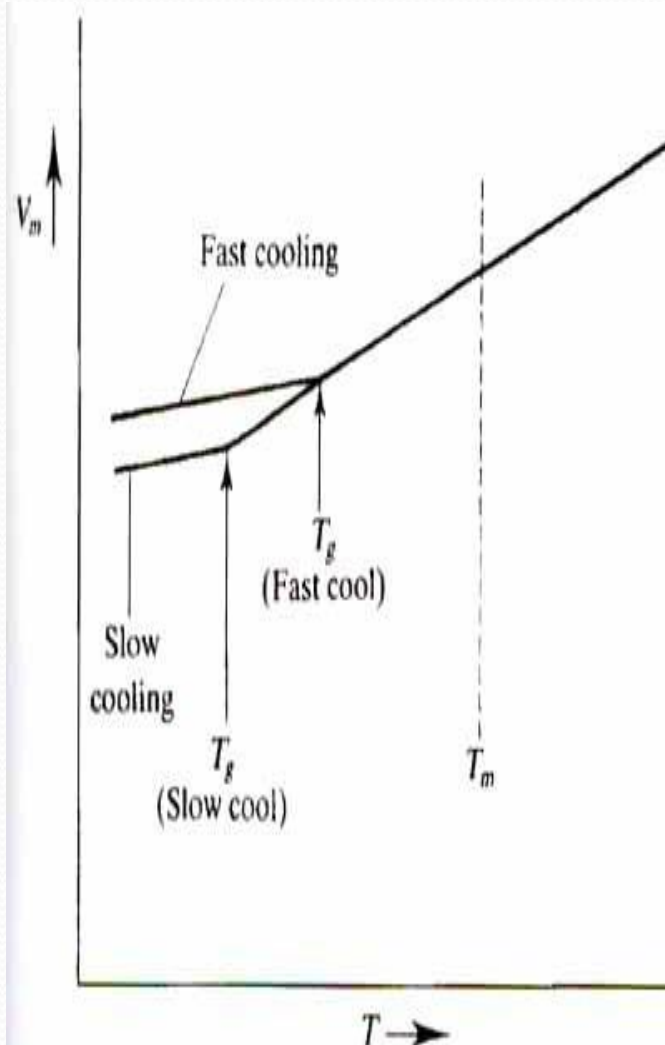


Figure 8.5

The glass transition temperature is a function of cooling rate; T_g increases with more rapid cooling. A material with a higher T_g also has a greater molar volume.

Viscous Flow (Newtonian Flow)

- Why viscous flow? Low stress or high temperature
- Shear stress is a function of shear strain rate ($\tau = \eta \dot{\gamma}$)
- The proportionality constant η is the material's constant, is independent of the applied stress, but is dependent on temperature
- The tensile stress is also a function of tensile strain rate, can be expressed as

$$\sigma = 3 \eta \dot{\epsilon}$$

Kinetic Principles Model (Stress Induced Flow)

- The energy decrease ($F\delta$) is associated with applied stress and jump distance δ (similar to dislocation glide at low temperatures)
- The force F can be expressed as (τA)
- The total energy decrease is $\tau A\delta = \tau V_{act}$ where V_{act} is the activation volume (similar to atomic volume)
- The net rate of atoms moving in a specified direction is expressed as

$$J_{net} = J_{L \rightarrow R} - J_{R \rightarrow L} = v \left[\exp\left(\frac{-\Delta U}{kT}\right) - \exp\left(\frac{-\Delta U - \tau V_{act}}{kT}\right) \right]$$

Reaction Rate Model

- This model assumes a stress-independent viscosity is directly related to the diffusion activation energy at high temperatures. The flow process is associated with activation energy due to atomic jump.
- At low temperatures and/or high stresses, the viscosity increases with stress.
- When τV_{act} is much greater than KT , η increases linearly with the stress. Activation energy is about the same.
- This model works well at high temperatures and low stresses in amorphous materials.
- This model is well suited for liquid materials such as gases and liquids having low viscosities (at high temperatures and low stresses)

Viscous Flow in Amorphous Materials

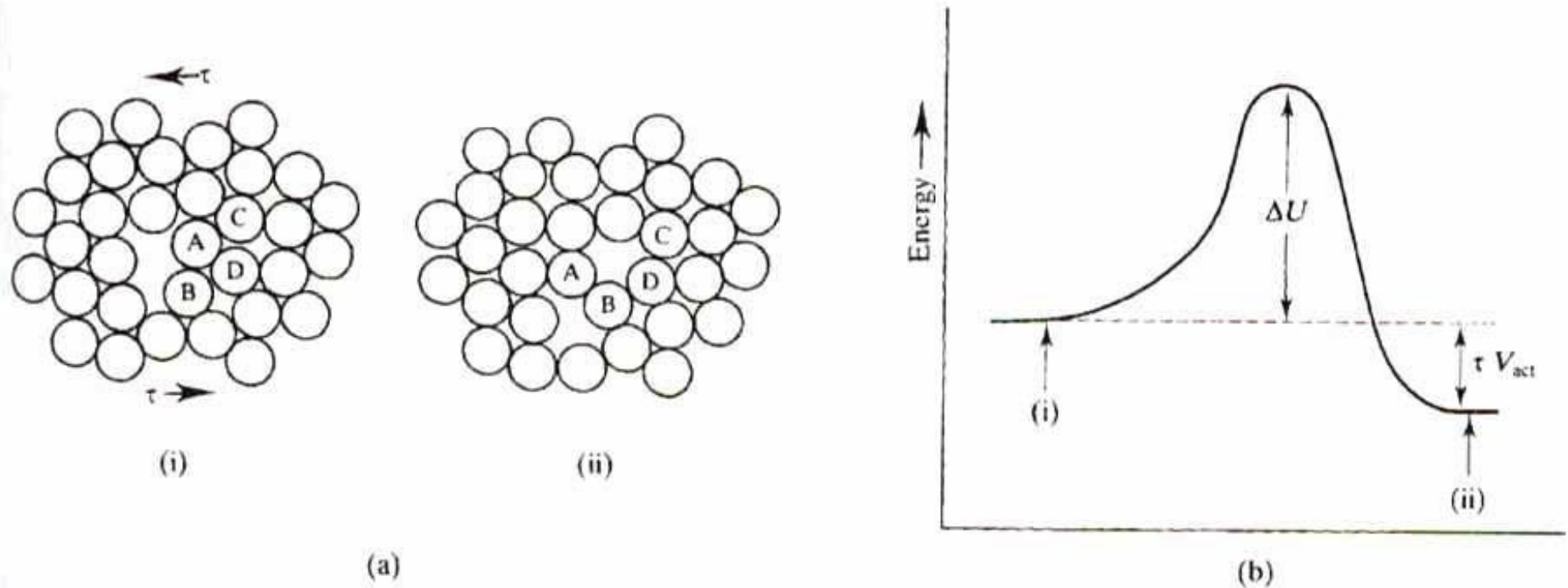


Figure 8.6
Viscous flow in an amorphous material. An applied shear stress (a(i)) induces flow of the upper portion of the material with respect to the lower. The flow is accomplished (a(ii)) by atomic or molecular jumps (e.g., atom A). As shown here, most such displacements occur in regions where the local atomic volume is highest. (b) Energy-reaction coordinate diagram for the process of (a). The atomic displacements require an activation energy (ΔU), but the displacements are stress-aided with an energy τV_{act} (V_{act} = activation volume). Kinetic principles (see text) determine the stress-strain rate relationship.

Model

- The proportionality constant (η) depends on the probability of an open volume in the vicinity of an atom (or molecule) that is ready to move affected by an applied stress.
- Thermal activation will create changes in local volume (reaction rate model)

Strain Components in Silicate

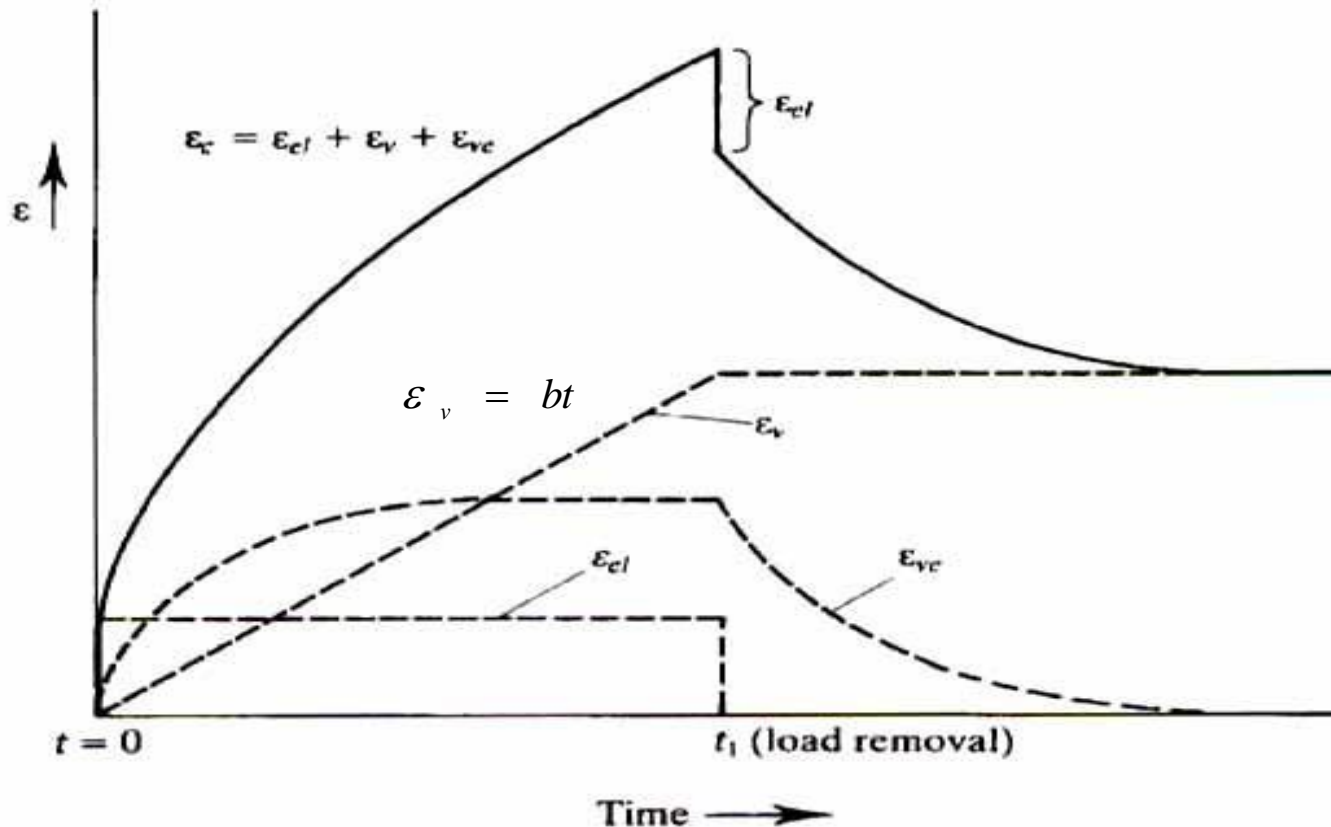


Figure 8.8

The creep strain of a silicate glass is composed of elastic, viscoelastic, and viscous strain components. Upon removal of the stress (at t_1), the elastic strain is instantaneously, and the viscoelastic component gradually, recovered. The relative contributions of the various strains are strongly temperature dependent. Viscous flow dominates at high temperature and elastic behavior at low, whereas viscoelastic and elastic deformation are comparable in the vicinity of T_g .

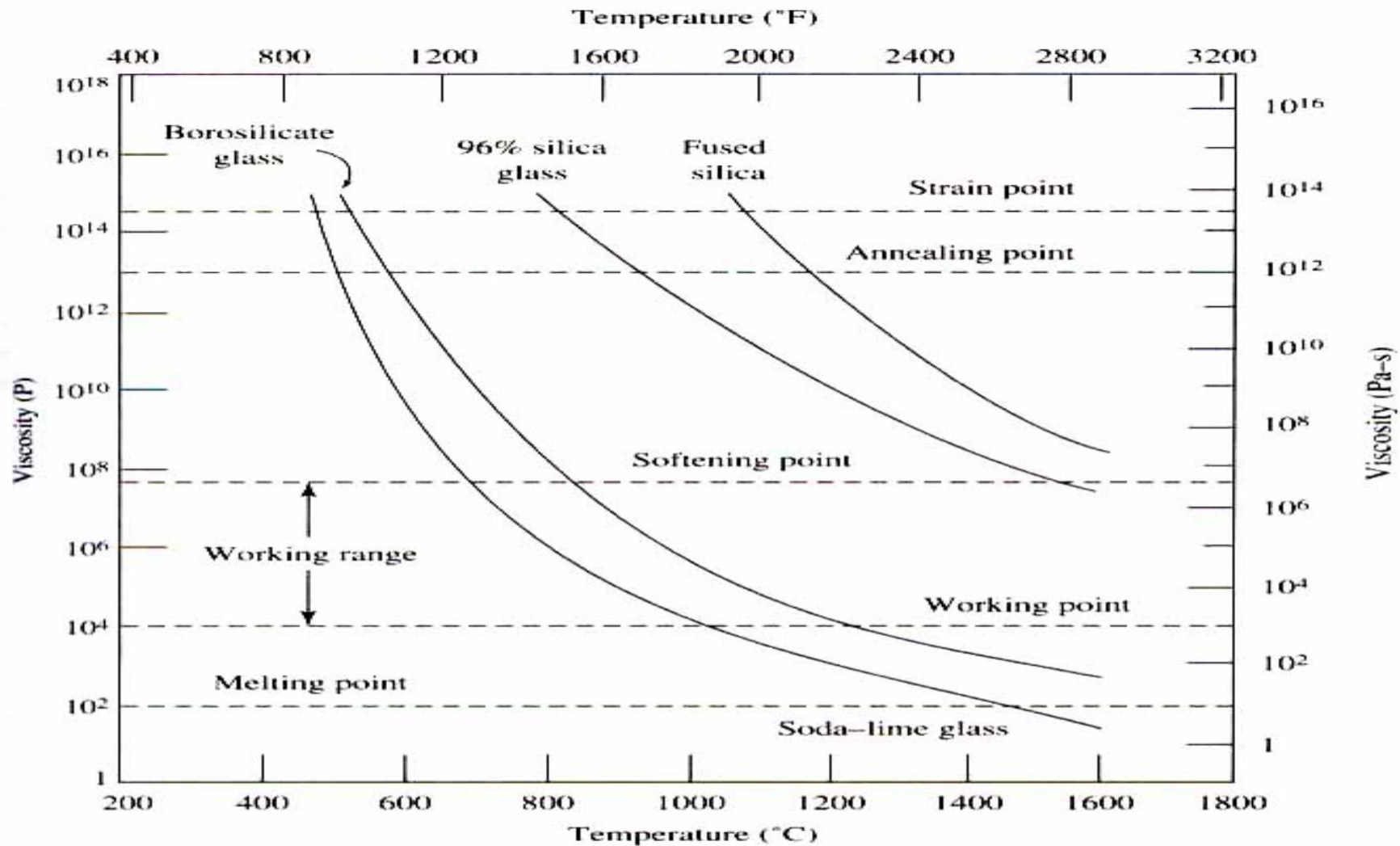


Figure 8.11

Viscosity (logarithmic scale) vs. temperature for fused silica and several other silicate glasses. Viscosity is reduced proportionally to the amount of modifier ions in the network. Fused silica (essentially pure SiO_2) does not soften until very high temperatures. The heavily modified soda-lime glass softens at a moderate temperature. The other glasses (compositions provided in the text) have modifying agent amounts intermediate to those in soda-lime and fused silica glass. The engineering significance of the various temperatures (melting point, working point, etc.) is described in the text. (From E. B. Shand, *Engineering Glass, Modern Materials, Vol. 6, Academic Press, New York, 1968, 262.*)

Deformation of Metallic Glasses

- What is metallic glass?
- Metals are produced in the amorphous state using extremely rapid cooling rates
- Metallic glasses offer excellent mechanical properties: similar bulk modulus (K), lower tensile modulus, but much higher UTS than crystalline counterparts
- The deformation process is affected by temperature, stress and strain rate.

- This is a deformation mechanism map
- Three distinct regions: elastic, viscoelastic and viscous regions
- Heterogeneous deformation at high stress and low temperature
- Homogeneous deformation at low stress and low temperature

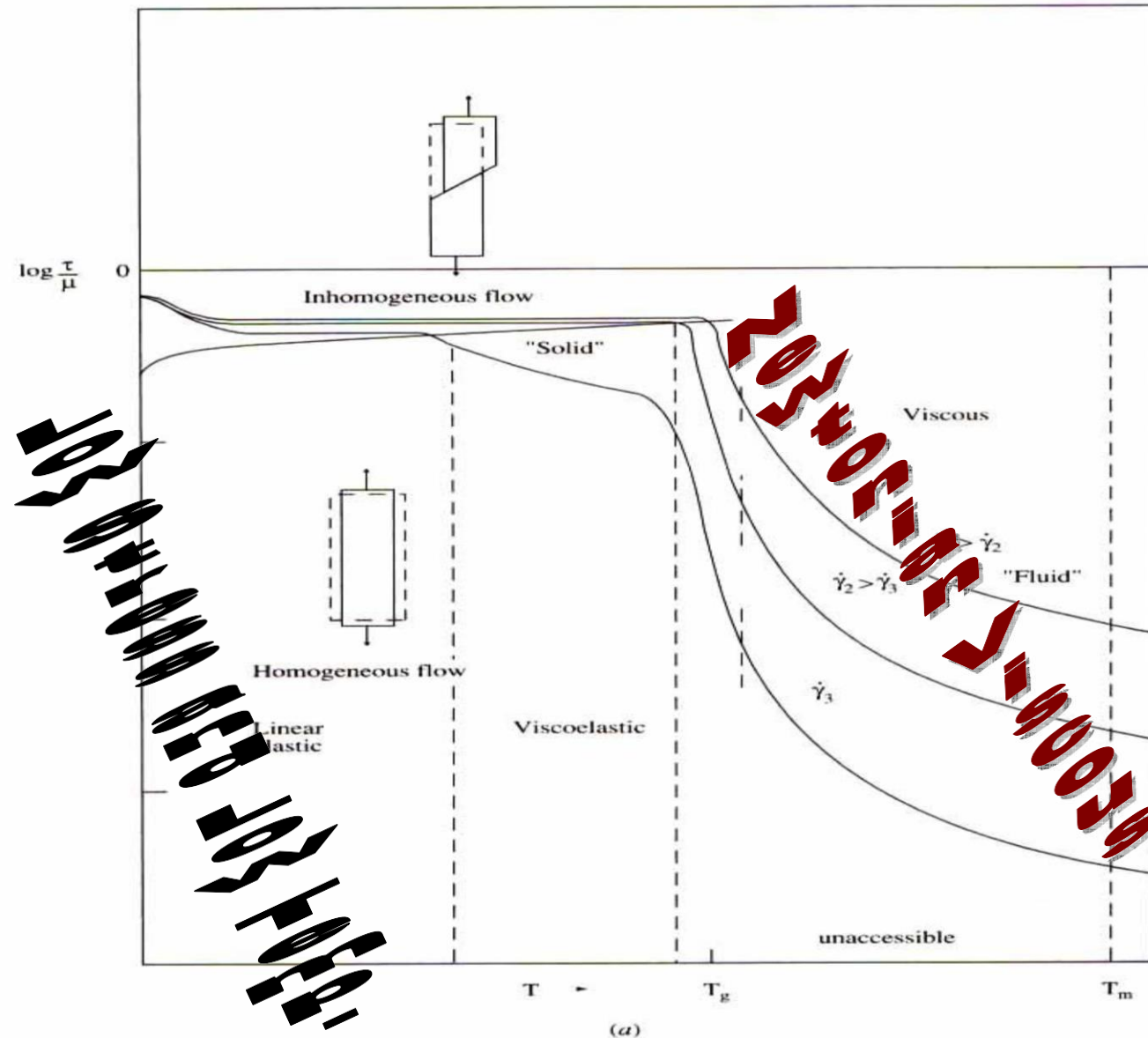
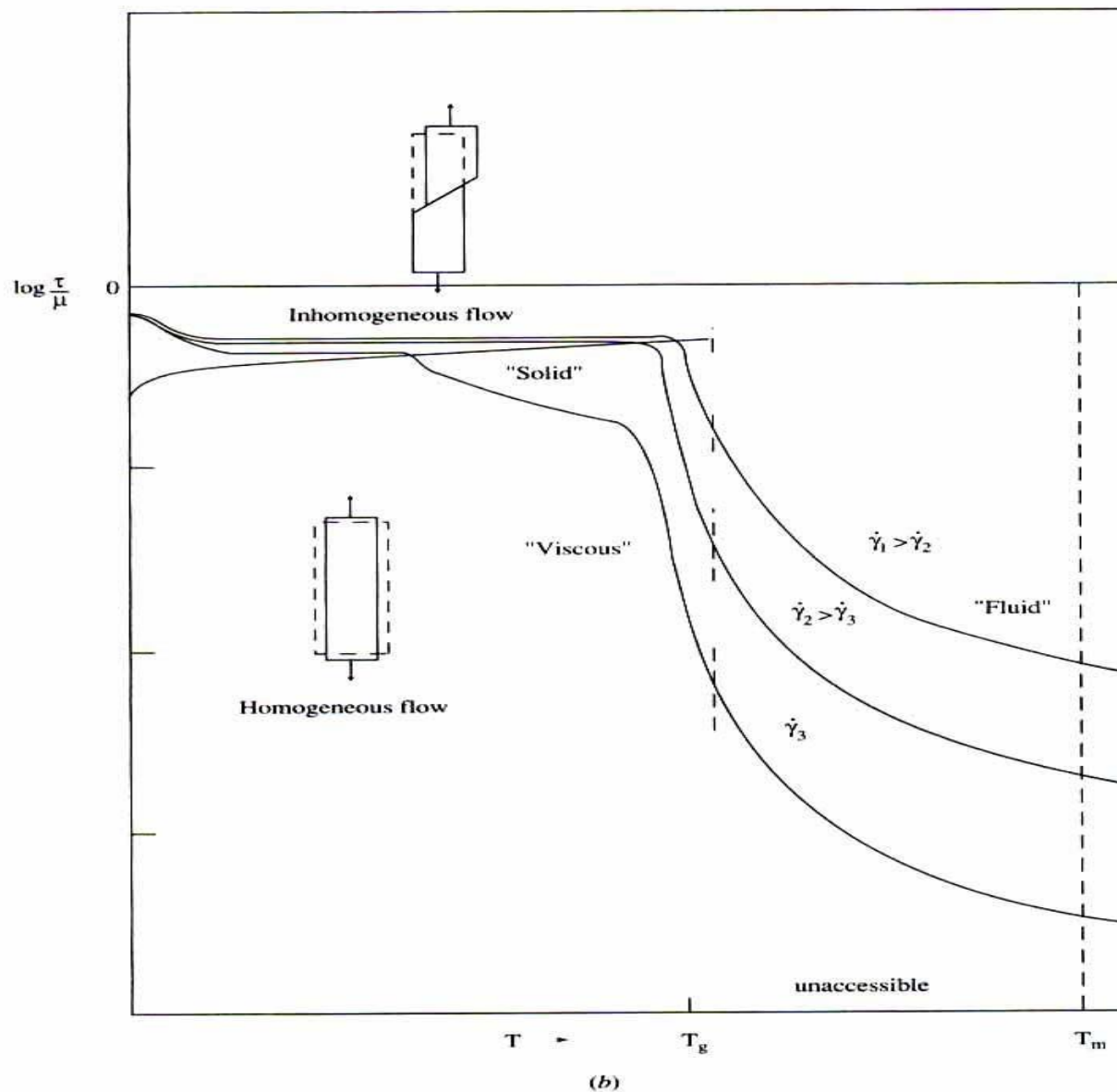


Figure 8.12

Schematic deformation mechanism maps for metallic glasses. (a) Includes linear elastic and viscoelastic regions; these are not shown in (b). At high temperatures (from the melting temperature downward to about T_g), the glass deforms in a Newtonian viscous manner. Further, permanent deformation is distributed uniformly throughout the material volume. At lower temperatures (less than about T_g) and low stresses,



- At high stresses and low temperatures, permanent deformation is associated with shear bands.

flow (whether elastic or permanent) is also homogeneous. However, at higher stresses at low temperatures, permanent deformation is heterogeneous and takes place by the formation of shear bands. Further, the strain-rate sensitivity of the flow stress is reduced at low temperatures. (Modified from A. Spaepen, "A Microscopic Mechanism for Steady State Inhomogeneous Flow in Metallic Glasses," *Acta Metall.*, 25, 407, Copyright 1977, with permission from Elsevier Science.)

Von Mises Yield Criterion

- Shear bands are initiated by both stress and temperature.
- The yielding criterion can be expressed as

$$\frac{1}{\sqrt{6}} [(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_1 - \sigma_3)^2]^{1/2} = s \geq \tau_Y$$

$$s + \alpha_p p \geq \tau_Y$$

$$p = \frac{(\sigma_1 + \sigma_2 + \sigma_3)}{3}$$

Crazing

- Glassy polymers are deformed by forming shear bands in the compression area
- Deformation in the tension side will develop necking phenomenon
- Crazing is promoted by a positive dilatatory stress (stress/atomic volume)
- The principal stress required to initiate craze yielding decreases as the 2nd principal stress increases (biaxial loading)
- Craze yield criterion is expressed as

$$\sigma_{\max} - \sigma_{\min} = C(T) + \frac{D(T)}{P}$$

where $C(T)$ and $D(T)$ are temperature constants

Two Yielding Criteria

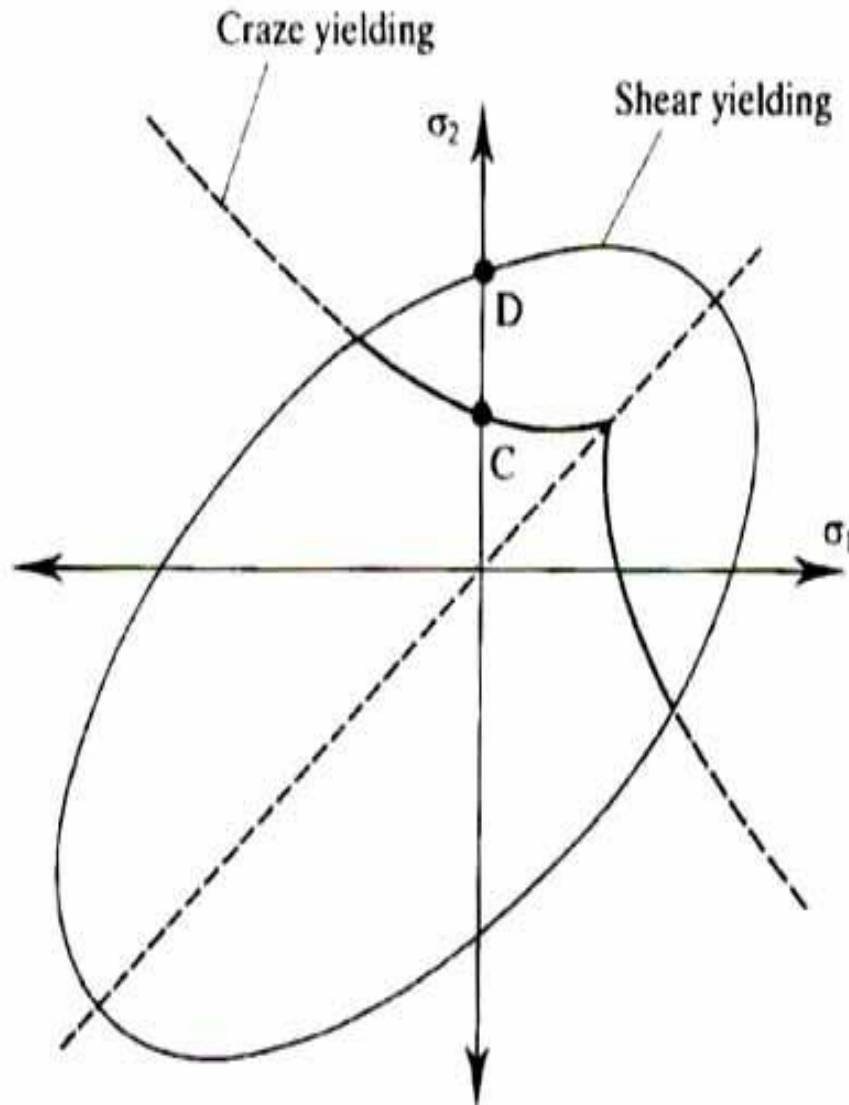
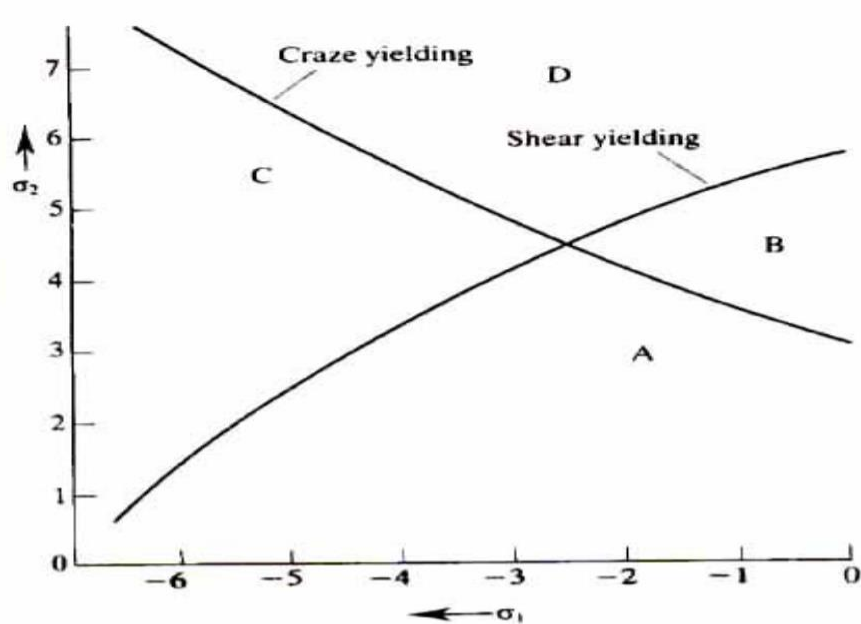
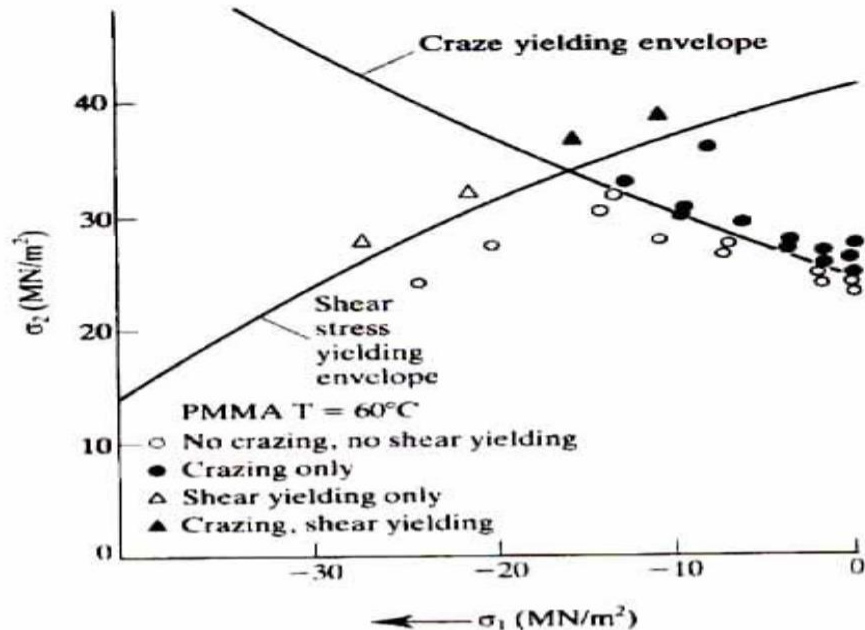


Figure 8.25

The biaxial loading yield loci for shear banding and crazing. Crazing dominates in the first ($\sigma_1, \sigma_2 > 0$) quadrant and in parts of the second and fourth ones ($\sigma_1 \geq 0, \sigma_2 \leq 0$ or vice versa). Only shear yielding is observed for biaxial compression ($\sigma_1, \sigma_2 < 0$). Points C and D are the uniaxial tensile stresses required to initiate crazing and shear yielding, respectively. (From S. S. Sternstein and L. Ongchin, *Polymer Preprints*, 10, 1117, 1969.)



(a)



(b)

Figure 8.26
(a) An expanded view of the second quadrant ($\sigma_1 < 0$, $\sigma_2 > 0$) of Fig. 8.25. Stress combinations lying in region A produce no yielding; in region B, craze yielding; in region C, shear yielding; and in region D both craze and shear yielding. **(b)** Experimental verification of the scheme of (a) for PMMA. (From S. S. Sternstein and F. A. Myers, *J. Macromolec. Sc.*, B8, 539, 1973.)

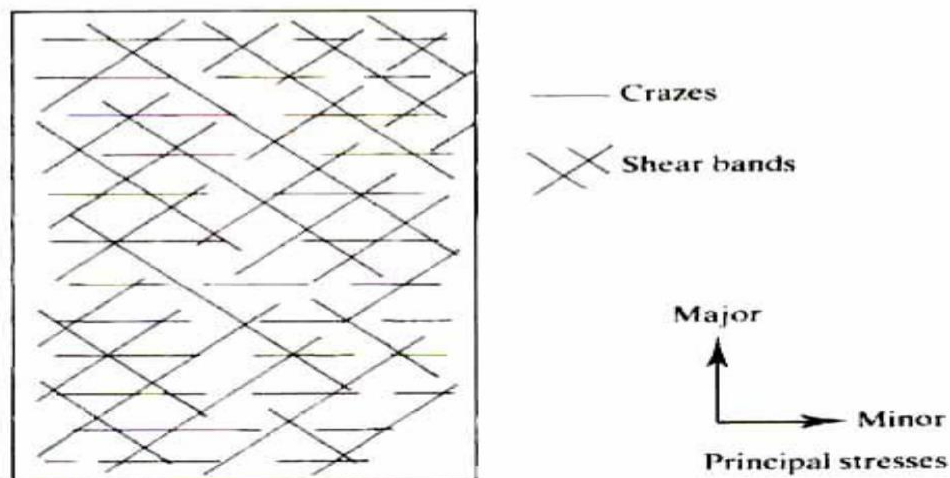


Figure 8.27
Schematic of craze-shear band morphology when both deformation modes are operative. The maximum principal stress is always perpendicular to the long dimension of the craze. Shear bands lie along planes nearly parallel to those characterized by the maximum shear stress.

EXAMPLE PROBLEM 8.1. A hypothetical polymer yields by shear banding in room-temperature compression at a stress of 29 MPa. For room-temperature tension, shear banding initiates at a stress of 21 MPa. Develop an expression for the shear yielding criterion for this material applying to room-temperature biaxial loading ($\sigma_3 = 0$, $\sigma_{1,2} \geq, \leq 0$).

Solution. The shear yield condition (Eq. (8.15)) is

$$S + \alpha_p p = \tau_y$$

Let the tensile yield strength (21 MPa) be designated by σ_T and the compressive yield strength (29 MPa) by σ_c . In the following two equations the respective yield strengths are written in terms of their *magnitudes*:

$$\frac{1}{\sqrt{6}}[2\sigma_T^2]^{1/2} + \frac{1}{3}\alpha_p\sigma_T = \tau_y \quad \text{or} \quad \sigma_T\left[\frac{1}{\sqrt{3}} + \frac{1}{3}\alpha_p\right] = \tau_y \quad (1)$$

$$\frac{1}{\sqrt{6}}[2\sigma_c^2]^{1/2} - \frac{1}{3}\alpha_p\sigma_c = \tau_y \quad \text{or} \quad \sigma_c\left[\frac{1}{\sqrt{3}} - \frac{1}{3}\alpha_p\right] = \tau_y \quad (2)$$

We have two equations (those above) and two unknowns (τ_y and α_p). Equating Eqs. (1) and (2) and rearranging we find

$$\frac{1}{3}\alpha_p = \frac{1}{\sqrt{3}}\left[\frac{\sigma_c - \sigma_T}{\sigma_c + \sigma_T}\right] = \frac{1}{\sqrt{3}}\left[\frac{8}{50}\right] = 0.0924$$

To find τ_y use Eq. (1) (or Eq. (2), it doesn't matter which)

$$21 \text{ MPa} \left[\frac{1}{\sqrt{3}} + 0.0924\right] = 14.07 \text{ MPa} = \tau_y$$

Thus, for biaxial loading the shear yielding criterion for the polymer is expressed as

$$\frac{1}{\sqrt{6}}[(\sigma_1 - \sigma_2)^2 + \sigma_1^2 + \sigma_2^2]^{1/2} + 0.0924(\sigma_1 + \sigma_2) = 14.07 \text{ MPa}$$

when the respective stresses are expressed in MPa.

Summary

- Viscous flow is due to permanent displacement of atoms in different locations within the material.
- Glass transition temperature is an important factor to the deformation in non-crystalline material.
- Stress, temperature and free volume are key factors to a deformation mechanism.
- Shear band is another deformation mechanism in non-crystalline material – crazing.



THANK
YOU