GLASS TRANSITION

Phenomenon associated with molecular mobility of chains in the amorphous state

Evidence of glass transition:

- orders of magnitude drop in modulus on heating across T_g
- slope change in specific volume vs. temperature curve
- brittle to ductile transition
- other changes .....

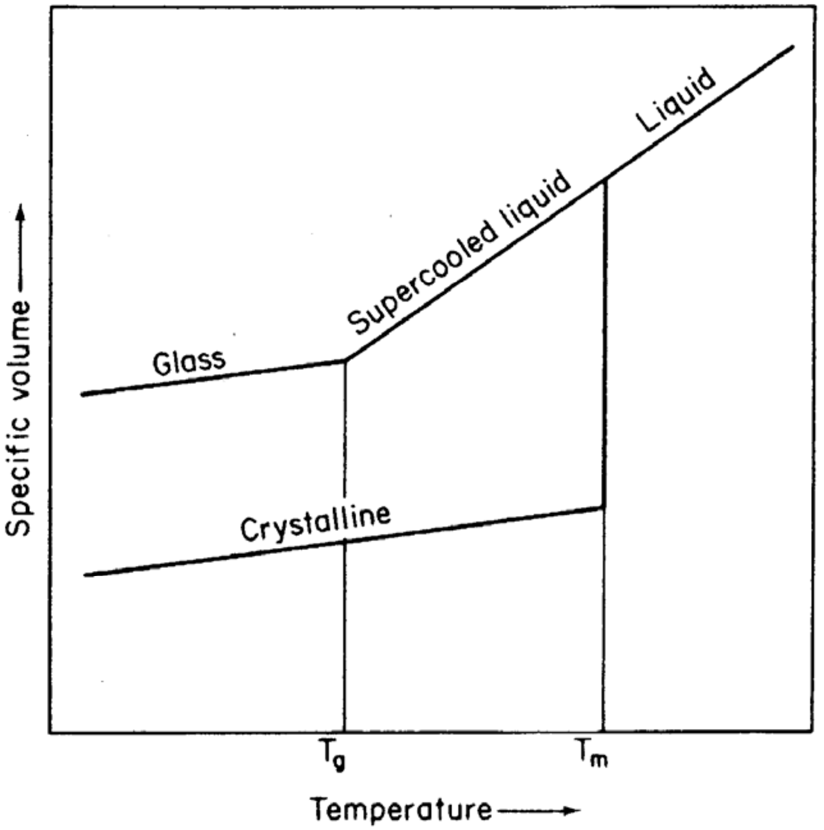


Figure 7–1. Schematic specific volume–temperature curves

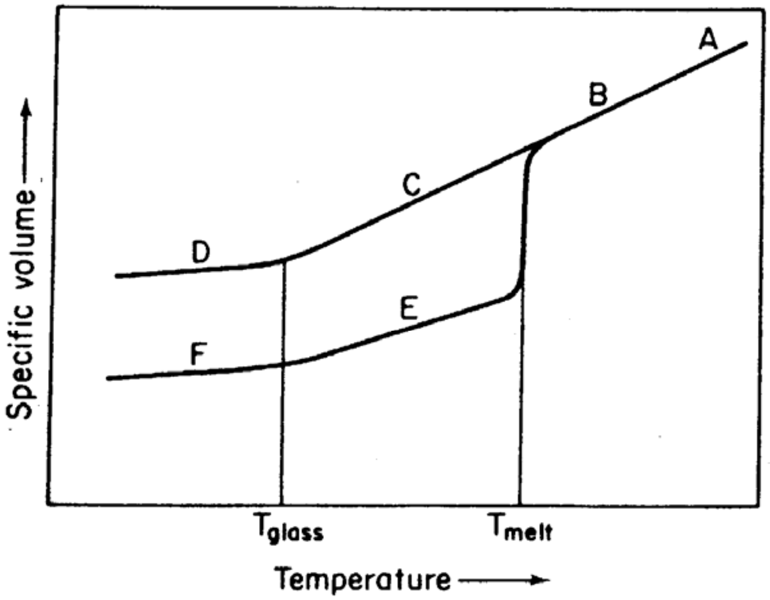


Figure 7–4. Specific volume–temperature curves for a semicrystalline polymer: (A) liquid region, (B) liquid with some elastic response, (C) rubbery region, (D) glassy region, (E) crystallites in a rubbery matrix, and (F) crystallites in a glassy matrix.

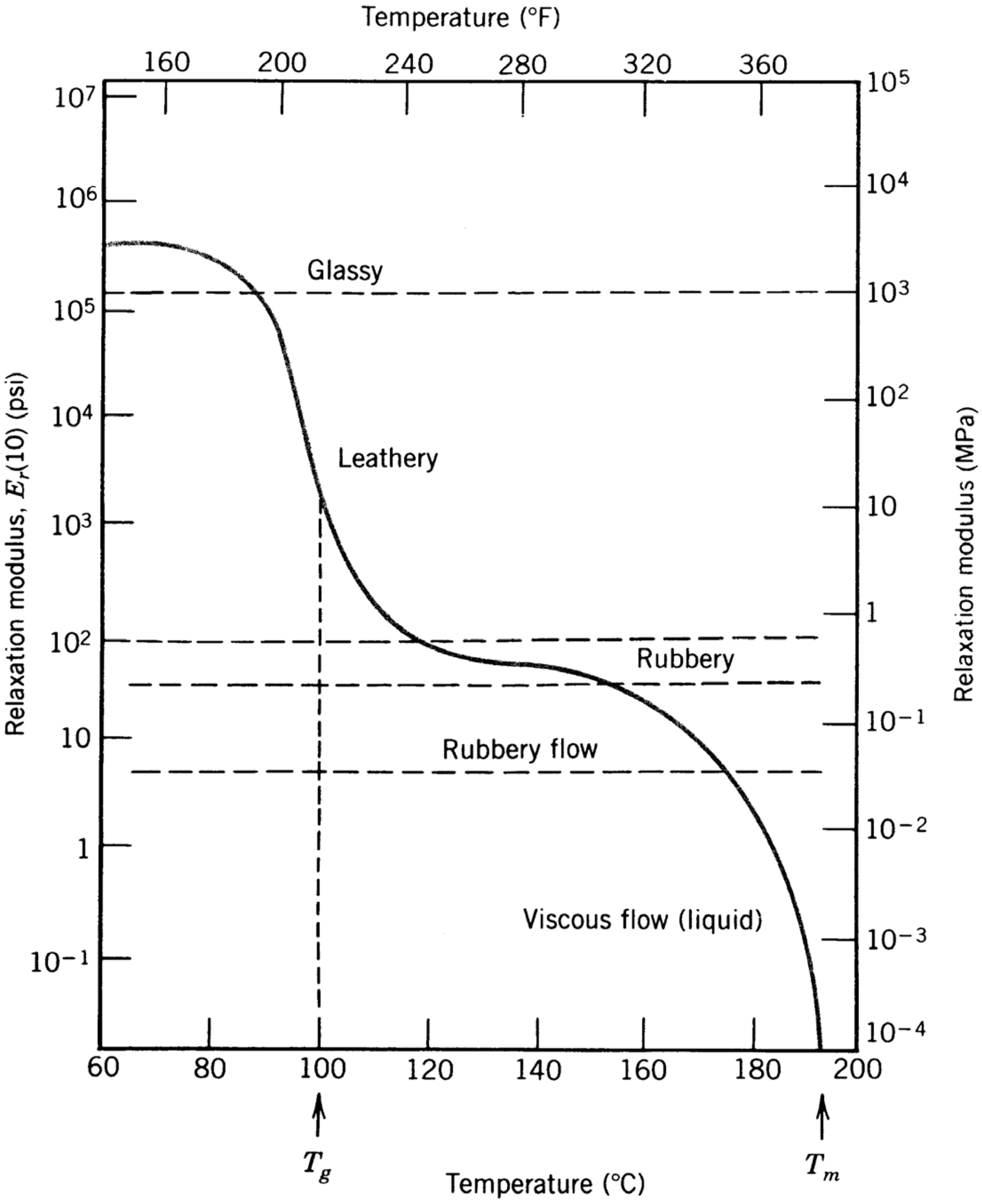
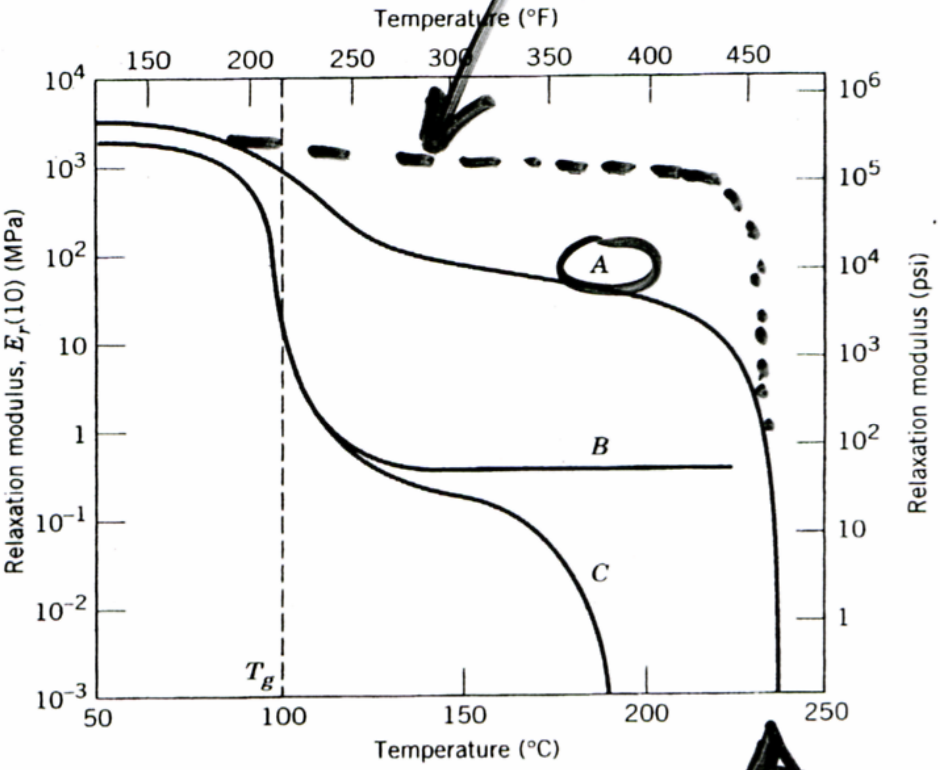

Temperature (°F)
160
200
240
280
320
360
10^7
10^6
10^5
10^4
10^3
10^2
10
1
10^{-1}
Relaxation modulus, $E_r(10)$ (psi)
10^5
10^4
10^3
10^2
10
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
Relaxation modulus (MPa)
Glassy
Leathery
Rubbery
Rubbery flow
Viscous flow (liquid)
60
80
100
120
140
160
180
200
T_g
T_m
Temperature (°C)

FIGURE 16.12

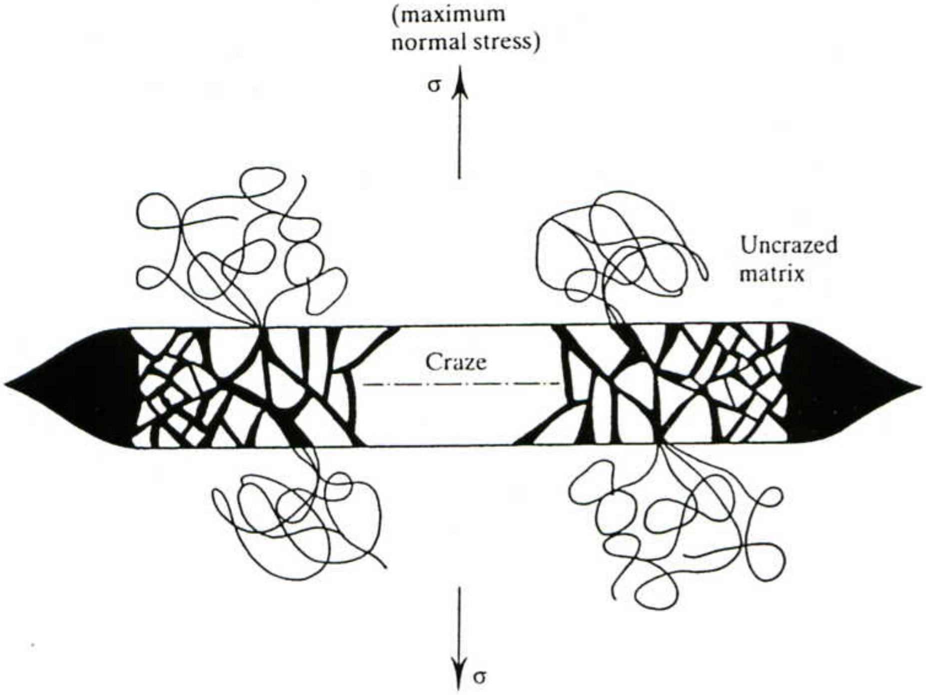
semicrystalline

100% crystalline

FIGURE 15.8 Logarithm of the relaxation modulus versus temperature for crystalline isotactic (curve *A*), lightly crosslinked atactic (curve *B*), and amorphous (curve *C*) polystyrene. (From A. V. Tobolsky, *Properties and Structures of Polymers.* Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



melting point for crystalline lamellae



Characteristics of crazes:

- highly planar ; highly reflective
- constituted of expanded material containing oriented fibrils interspersed with small (100-200 Å) interconnected voids (40-60%)
- crazes nucleate and grow along planes normal to the principal tensile stress direction ; won't occur under compression dominated stress states

Crazes (cont.)

- Craze thickness typically < 5 μm
- Craze material subjected to plastic strains > 50 %
- Craze deformation occurs without significant lateral contraction
- Crazes nucleate at points of high stress concentration (e.g., at the surface or at inclusions)
- Crazes result in overall weakening of a material ; precursor to fracture
- Continued application of stress → polymer fibril hardening & extension ; increase in void content
- Crazes observed in most glassy thermoplastics

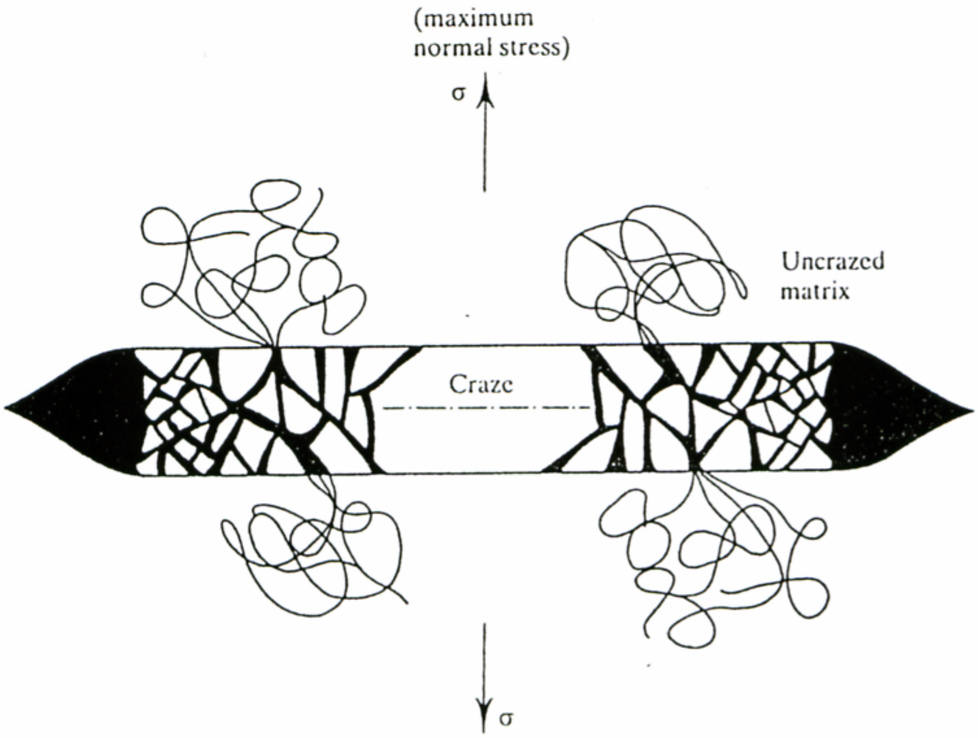


FIGURE 8.22 The molecular morphology in a craze. Crazing is an alternative mode of heterogeneous plastic deformation of organic glasses. The molecular alignment within the craze (the dark areas) is high; this portion of the craze material is strong. However, the craze also contains voids (light areas) and the density of the craze is less than that of the undeformed polymer. The differential volume between the regions causes a stress concentration and the craze propagates in a direction normal to the maximum principal stress direction. (*From S. S. Sternstein, Polymeric Materials. American Society for Metals, Metals Park, Ohio, 1975, p. 369.*)

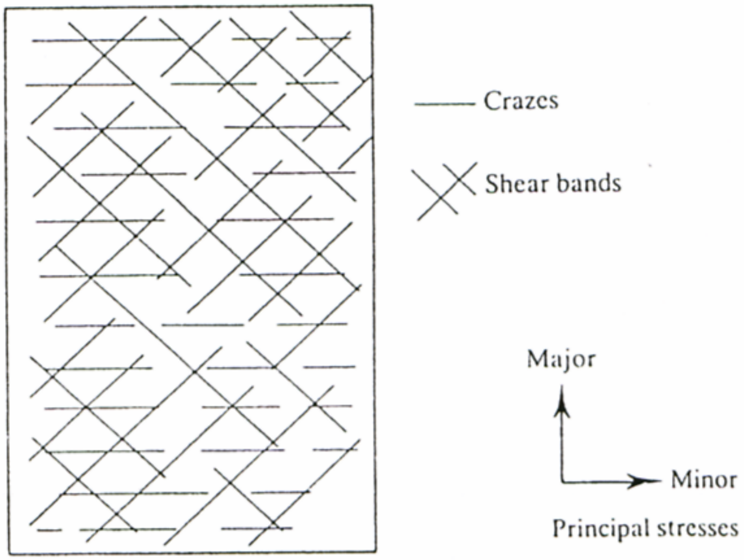


FIGURE 8.27 Schematic of the morphology of crazes and shear bands that formed simultaneously under appropriate stress conditions. The crazes are always normal to the maximum principal stress direction. Shear bands lie along planes nearly parallel to those with the maximum shear stress.