

1. A polymer has the plateau shear modulus,  $G_N^0$ , of 1.0 MPa at 27 °C. Answer the following questions.

(a) Estimate the Young's modulus of this polymer at the glassy state.

$$E = 2(1+\nu)G = 2(1+0.4)(1000 G_N^0) = 2.8 \text{ GPa} \sim 3 \text{ GPa}$$

(b) What would be the plateau shear modulus, when the molecular weight is doubled up?  
The value of plateau shear modulus (height of plateau) does not change by varying molecular weight.

(c) What would be the slope of  $\log \eta - \log M_w$  plot of this polymer sample when it is melted? Explain your answer with a calculation.

[You may need this:  $R = 8.3 \times 10^7 \text{ dyn cm/mol K}$ ]

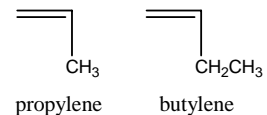
3.4, The molecular weight of 500000 is much higher than  $M_e$  or  $M_c$ .

$$M_e = \rho RT / G_N^0 = (1)(8.3 \times 10^7)(300) / (1 \times 10^6) = 24900 \sim 25000$$

$$M_c \sim 2 - 3 M_e. M_c \sim 50000 - 75000$$

2. Choose one in the bracket, and explain why using "free volume."

(a) The glass transition temperature of polybutylene is [lower, higher] than that of polypropylene.



lower. Larger substituent gives higher (fractional) free volume and thus lower  $T_g$ .

(b) As the molecular weight of a polymer increases, glass transition temperature [increases, decreases] up to a certain molecular weight.

increases. As molecular weight increases, concentration of chain ends, which have larger free volume, decreases, and  $T_g$  increases.

(c) As the crosslinking density of a network polymer increases, glass transition temperature [increases, decreases].

increases. As the crosslinking points restrict the motions of amorphous chains and lower the free volume (for motion),  $T_g$  increases.

3. You observed that zero-shear viscosity of polystyrene ( $T_g = 100 \text{ °C}$ ) decreases by 5% by raising the temperature from 200 °C to 210 °C.

(a) What would be the % change in zero-shear viscosity, when the temperature is raised from 210 °C to 230 °C?

For the temperatures higher than  $T_g + 100 \text{ K}$ , you may and actually better use Arrhenius relation, and you may use the same constant for this temperature range not far away.

$$\ln [\eta(483) / \eta(473)] = \ln 0.95 = E/R (1/483 - 1/473)$$

$$\ln [\eta(503) / \eta(483)] = E/R (1/503 - 1/483) = \ln 0.908 \quad \underline{9.2\% \text{ decrease}}$$

(b) What would be the % change in zero-shear viscosity, when the temperature is raised from 150 °C to 160 °C?

You cannot use the same Arrhenius activation energy, and you better use WLF equation at this low temperature.

$$\log [\eta(160) / \eta(T_g)] - \log [\eta(150) / \eta(T_g)] = \log [\eta(160) / \eta(150)] = -0.793$$

$$\eta(160) / \eta(150) = 0.161 \quad \underline{84\% \text{ decrease}}$$

4. Answer the following questions briefly in your own words.

(a) Why is rubber called an 'entropy spring'?

When rubber is stretched, it does with the decrease in entropy and without change in internal energy. The retracting force depends only on the change in entropy.

(b) What is the 'Kauzmann paradox,' and how is the paradox resolved?

Aging of amorphous polymers to the equilibrium liquid line, entropy could be lower than the entropy of the crystal, and could be negative at the temperature higher than 0 K.

This paradox can be resolved by Gibbs-DiMarzio theory, which state the metastable glassy state with zero configurational entropy at a temperature lower than  $T_g$ .

(c) What is the 'two-thirds rule,' and why is it observed for polymers?

$$T_g = 2/3 T_m \text{ (in K)}$$

Both  $T_g$  and  $T_m$  depend on chain stiffness and intermolecular interaction.

5. Fill the blanks. No need to explain. [Each right answer counts 3 points]

The reason why fracture stress of polymers is much lower than (a) theoretical strength (theoretical fracture stress), which is about one-tenth of its modulus, is the existence of flaw like crack, inclusion, or notch.

In front of a crack, there are two factors that lead to brittle fracture, (b) stress concentration and (c) plastic constraint. In front of a sharp crack (b) makes the stress very high, but the stress is cut-off by (d) yield strength (yield stress), which let the material in front of a crack undergo plastic deformation. This is the reason why measured (e) fracture energy ( $G_c$ ) is much higher than that expected based on the (f) surface energy created by crack propagation.

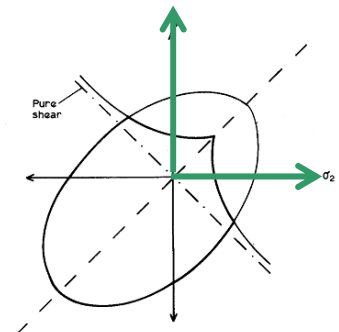
However, the plastic deformation in front of a crack is restricted by (c), which is the result of triaxial stress state in front of a crack and let the material yield at a higher stress than its inherent (d). If the effective (d) is higher than its (g) craze stress (fracture stress), the polymer fractures in a brittle manner. At surface or edge of a fracture test specimen, the stress state is in (h) plane stress condition, and a larger volume of material yields. At inside of a specimen, (c) cut the (i) plastic zone radius (size) to about one-third of that at surface. This is the reason for (j) ductile-brittle transition when specimen thickness varies.

6. The drawing below shows yield and crazing criteria of polymers.

(a) Is this polymer ductile or brittle upon uniaxial tension? Explain your answer using a drawing.

brittle

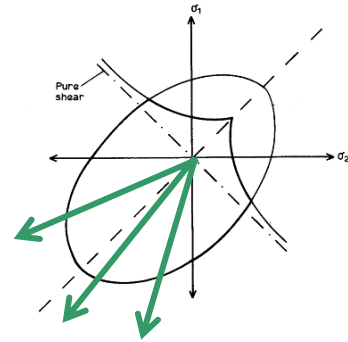
The craze stress is smaller than the yield stress in UTT, and the polymer fractures in a brittle manner.



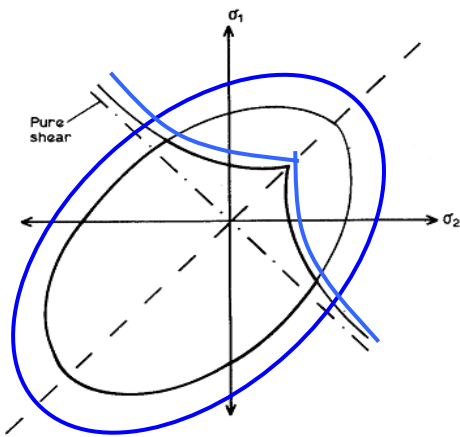
(b) Is this polymer ductile or brittle upon biaxial compression? Explain your answer using a drawing.

ductile

Crazing does not occur during biaxial compression.



(c) Show how the drawing changes when the strain rate increases.



With increasing strain rate, both yield stress and craze stress increase. Yield stress increases faster than craze stress does.