

1. In mechanical models that consist of spring and dashpot;
    - (a) Show that a Maxwell model cannot describe creep behavior correctly.

In the Maxwell model, the spring and the dashpot are in series, and are subject to the same stress.  
Then the strain rate,  $d\varepsilon/dt = (d\sigma/dt)/E + \sigma/\eta$ .  
For creep test, where stress is constant ( $d\sigma/dt = 0$ ),  $d\varepsilon/dt = \sigma/\eta$ , which describes only the viscous behavior.
    - (b) Show that a Kelvin model cannot describe stress relaxation behavior correctly.

In the Kelvin (Voight) model, the spring and the dashpot are in parallel, and are subject to the same strain.  
Then the stress,  $\sigma = E \varepsilon + \eta (d\varepsilon/dt)$ .  
For stress relaxation test, where strain is constant ( $d\varepsilon/dt = 0$ ),  $\sigma = E \varepsilon$ , which describes only the elastic behavior.
    - (c) The problems of the models of (a) and (b) results from the fact that they have *single retardation* or *relaxation* time, which is unrealistic.
  
  2. In the construction of 'master curve' using the time-temperature superposition principle;
    - (a) Vertical shift can be ignored. Why?  
 $E = \rho R T / M \rightarrow E(T_1, t) / \rho(T_1) T_1 = E(T_2, t/a_T) / \rho(T_2) T_2$   
As temperature increases density decreases.  
The effect of change in temperature and density on modulus are about the same and cancel out each other.  $\rho(T_1) T_1 \sim \rho(T_2) T_2$ .
    - (b) For horizontal shift, does the result at a temperature higher than reference temperature shift to a shorter or longer time frame? Why?  
To a longer time.  
The effect of high temperature is equivalent to the effect of long time according to the time-temperature superposition principle
  
  3. (a) When a strip of rubber is stretched rapidly, it gets warm. Explain why.  
When a rubber is stretched there is a decrease in entropy without change in internal energy. In adiabatic condition (fast stretching), loss of entropy results in heating.
  - (b) Using Deborah number, show that every material is viscoelastic.  
In the viewpoint of Deborah number,  $De$ , which is the ratio of material (relaxation) time to experimental time, every material is viscoelastic. Solids show only elasticity due to their very large relaxation time and  $De$  at observable experimental time. Liquids show viscosity only due to their very small relaxation time. Polymers show viscoelasticity since the time for relaxation and experiments are within a similar scale.
  - (c) Why does the equation of state theory for rubber elasticity predict the behavior of rubber only to a certain extension ratio?  
EOS theory assumes rubber being incompressible and isotropic. Rubber becomes compressive, anisotropic, and strain-induced crystallize at high extension ratios.
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4. Suppose that you are a scientist working for a company. Your company need a plastic material that will be used at 150 °C. You are given a piece of plastic sample from a supplier, who claims that the polymer 'melts' at 200 °C.
  - (a) How would you know if it is made of an amorphous or a semicrystalline polymer? Suggest two methods to distinguish.

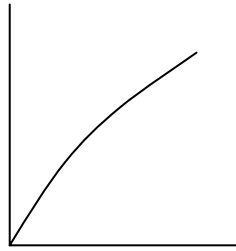
See if it is transparent (amorphous) or opaque (semicrystalline).  
See if it has melting transition (DSC, DMA etc).  
See if it has crystalline structure (X-ray, microscopy etc).

- (b) Your lab assistant reports that the polymer ‘softens’ at 100 °C, how would you know whether it is  $T_g$  or  $T_m$ ? Suggest two methods to distinguish.  
See if it is a slope change ( $T_g$ ) or a peak ( $T_m$ ) in DSC.  
See if volume changes continuously ( $T_g$ ) or discontinuously ( $T_m$ ).  
See if morphology changes (crystals disappear,  $T_m$ ) or not ( $T_g$ )

- (c) How would you explain the difference between  $T_g$  and  $T_m$  to the president of your company? Suppose that your president has never taken a college-level science or engineering course, and is a friend of the supplier.  
[Just a possible answer. Other good answers using only the everyday life terms earn points.]  
Polymers or plastics, not like metals, change their states in two steps. At a lower transition temperature polymers become rubber from solid. At a higher transition temperature polymers become liquid from rubber. The given plastic cannot be used as a solid, since it is a rubber at 150 °C.

5. How are (i) the stress-strain rate behavior of shear flow, (ii) normal stress difference upon shear flow, and (iii) the stress-strain rate behavior of elongational flow, respectively, of polymer fluids different from those of Newtonian fluids?
- (i) Newtonian; stress is linearly proportional to shear (strain) rate: Polymer fluid; the tangent slope, i.e., viscosity, decreases as shear rate increases (shear thinning).
  - (ii) Newtonian; normal stress difference is zero: Polymer fluid; positive in the direction of flow.
  - (iii) Newtonian; stress is linearly proportional to strain rate: Polymer fluid; the tangent slope, i.e., elongational viscosity, may increase (tension-thickening), decrease (tension-thinning), or remain the same (Troutonian) as strain rate increases.
6. When a polymer is said to be “hard,” its Rockwell hardness, R, or Shore hardness, S, is large. Using analogy, fill the blanks.
- (a) When a polymer is said to be “strong,” yield strength (stress),  $\sigma_y$ , or tensile strength,  $\sigma_u$ , is large.
  - (b) When a polymer is said to be “stiff,” Young’s (tensile) modulus, E, or shear modulus, G, is large.
  - (c) When a polymer is said to be “tough,” fracture energy (critical strain energy release rate),  $G_{Ic}$ , or fracture toughness (critical stress intensity factor),  $K_{Ic}$ , is large.
  - (d) When a polymer is said to be “incompressible,” bulk modulus, K (B), or Poisson’s ratio,  $\nu$ , is large.
  - (e) When a polymer is said to be “heat resistant,” glass transition temperature,  $T_g$ , heat distortion temperature, or Vicat softening temperature is large.
  - (f) When a polymer is said to be “ductile,” it is able to yield and to be cold-drawn (strain-softened and strain-hardened).
  - (g) When a polymer is said to be “tough,” it is able to resist to crack propagation.

7. Using the creep curve in the right (Note that the strain is given in %);  
(a) Construct the 1-day isochronous stress-strain curve.



- (b) Estimate the Young's modulus after 1 year ( $\sim 3 \times 10^7$  s) upon the stress of 20 MPa.

At 1 year,  $\varepsilon \sim 0.01$  for  $\sigma$  of 20 MPa.

$$E = \sigma / \varepsilon = 2000 \text{ MPa} = 2 \text{ GPa}$$

- (c) For the polymer rod with the dimensions of 10 mm x 10 mm x 100 mm, what would be the cross-sectional area after 1 year upon the stress of 20 MPa along the 100 mm direction. Use the Poisson's ratio of 0.4.

$$\varepsilon_x = 0.01$$

$$\varepsilon_y = \varepsilon_z = -\nu \varepsilon_x = -0.004$$

$$\text{Area} = 9.96 \times 9.96 = 99.2 \text{ mm}^2$$