### 3.11 Mechanics of Materials Recitation #10

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### **Rubber Elasticity**

- An extra sample problem
  - Just a little review of what we've just covered
  - Problem #1
    - If a single polymer chain has a Helmholtz free energy of 1.543\*10^-18 J when its end-to-end distance is 2.25um, what is the chain stiffness k? In that configuration, what is the restoring force?
    - At what end-to-end distance can a single polymer chain have no restoring force acting on it?

a)  

$$A(r = 2.25 * 10^{-6} m) = \left[\frac{3k_BT}{2*n*a^2}\right] (2.25 * 10^{-6} m)^2 = 1.543 * 10^{-18} J$$

$$\left[\frac{3k_BT}{2*n*a^2}\right] = \frac{1.543 * 10^{-18} J}{(2.25 * 10^{-6} m)^2} = 3.048 * 10^{-7} N_m$$

$$k = -\frac{3k_BT}{n*a^2} = -2*\left[\frac{3k_BT}{2*n*a^2}\right] = -2*3.048 * 10^{-7} N_m$$

$$k = -6.1*10^{-7} N_m$$

$$f_{rest}(r) = -\frac{3k_BT}{n*a^2}r = -6.1*10^{-7} N_m * 2.25*10^{-6} m$$

= 
$$-1.37 * 10^{-12} N$$
  
=  $-1.37 pN$ 

b)

Since  $f_{rest}(r) = -\frac{3k_BT}{n^*a^2}r$ ,  $f_{rest}(r)$  can only be zero when  $\mathbf{r} = \mathbf{0}$  m.

### Viscoelasticity

- Time dependent behavior can be modeled by spring-dashpot models
- A linear-viscoelastic (applications:polymers, biomatls)
  - Behavior between that of elastic solid and viscous fluid
  - Time and temperature dependent behaviour
  - Linear:  $\sigma$  &  $\epsilon$  are linearly related at a given time and temperature
    - Elastic Solid:  $\sigma = E \epsilon$  (Hooke's law)
    - Fluid (viscous):  $\tau = \mu dv/dy$  (Newtonian)
      - Viscosity,  $\mu = \mu oexp$  (Q/RT) Temperature dependence
      - Velocity gradient, dv/dy is related to a strain rate gamma dot = gamma/t = (δ/l)/t

# Two common tests used to characterize viscoelasticity 1<sup>st</sup>: CREEP TEST

- Apply constant stress, measure strain as a function of time
- If material is linear viscoelastic, then strain at any time is proportional to the stress.
  - i.e. double stress, then double strain at a given time



### Two common tests used to characterize viscoelasticity

- 2<sup>nd</sup>: RELAXATION TEST
  - Apply constant strain, measure stress as a func. of time
  - Keep in mind this is occuring at a constant temperature.



### Temp. effect on amorphous polymers

- Consider the relaxation modulus at a given time, as a function of temperature
  - At low temp.
    - Hard, brittle glassy behavior (high Er (modulus 10^9GPa)
    - Modulus depends on change in energy with straining associated with stretching or compressing bonds
  - As temp. increases
    - Expansion of material somewhat more open structure & segments of polymer chains can begin to slide voer one another
  - Tg, secondary bonds melt (middle of viscoelastic regime)
    - Much more open structure
  - Increase in temp  $\rightarrow$  rubbery regime
  - Modulus depends on entropic changes (rubbery regime depends on change in entropy with strain (E about 10^5GPa)
  - If no covalent x-links, get viscous fluid (initial physical entanglement of chains causes viscous flow to occur over some temperature range)

### Graph to demonstrate last slide



## Spring-dashpot models for viscoelasticity

Spring

-A spring is E =  $\sigma/\epsilon$ 

- Dashpot
  - $-\eta = \sigma/(d\epsilon/dt) \rightarrow d\epsilon/dt$  is the strain drain rate
    - $E = (d\sigma/d\epsilon)$
  - Like a piston (think that you are trying to close a door that has hinges acting against your force)

### Spring-dashpot Model #1

• Maxwell Model – In series

– 
$$\sigma_{\sf spring}$$
 =  $\sigma_{\sf dashpot}$  =  $\sigma_{\sf total}$ 

- $-\epsilon_{spring} + \epsilon_{dashpot} = \epsilon_{total}$
- Relaxation Response ε const.



- $-\sigma = E \epsilon \exp(-Et/\eta)$  exponential decay
- Physically not very realistic → most polymers require more than 1 relaxation term to describe relaxation & σ wouldn't decay to 0.
- Creep Response  $\sigma$  const.
  - $d\sigma/dt = 0$ ,  $\varepsilon = \sigma/E + (\sigma/\eta)t$  (elastic + dashpot)
  - Poor representation of real polymers because wouldn't recover strain from dashpot.

### Model #2

- Voigt or Kelvin Model (in parallel)
  - $-\sigma_{spring} + \sigma_{dashpot} = \sigma_{total}$
  - $-\varepsilon_{\text{spring}} = \varepsilon_{\text{dashpot}} = \varepsilon_{\text{total}}$
  - σ = Eε + η (dε/dt)
- Relaxation Response
   Not physically realistic
- Creep Response



- These are all very simplistic b/c doesn't give exponential response for creep and relaxation. To really model a polymer, you need multiple springs & dashpots to model the flow.
- To get exponential response for both, you need to sum voigt and maxwell models to get a better approximation of viscoelastic behavior

### **Viscoelastic Problems**

2. A material has a viscoelastic response that can be modeled by a Maxwell model, where the spring modulus is 50 MPa and the viscosity is 600 MPa-s.

a) Calculate the relaxation time of the material

b) If the material is initially stretched to a strain of 0.2, what will be the stress in the material after 6 seconds? How much time will it take for the stress to reach one tenth of its initial value?

3. In a stress relaxation test, a 10-cm long bar of material was stretched instantly until the stress reached 200 MPa. After 2 minutes, the stress measured in the bar had decreased to 160 MPa. Assume the material response can be modeled by a Maxwell model.

a) Calculate the relaxation time of the material.

b) If the initial stress was reached by extending the bar by 16 mm, what is the viscosity of the dashpot in the model?

c) Calculate the relaxation modulus of the material after 3 minutes, given the same conditions as in part (b).

### Answers to Problem 2

#### 2.

a) (1 pt)  $\tau_r = \eta/k = 600 \text{ MPa-s/50 MPa} = 12 \text{ s}$ 

b) (3pts, method:2, each answer:0.5)  $\varepsilon_0 = 0.2 \Rightarrow \sigma_0 = k^* \varepsilon_0 = 50 \text{ MPa}^* 0.2 = 10 \text{ MPa}$ 

$$\sigma(t) = \sigma_0 \exp(-t/\tau_r) = 10 \text{ MPa exp} (-t/12s)$$

After 6 seconds, the stress is  $\sigma(t=6s) = 10$  MPa exp (-6s/12s) = 6.07 MPa

The time needed to reach one tenth of the initial stress is found by  $\sigma(t) = 0.1 * 10 \text{ MPa} = 1 \text{ MPa} = 10 \text{ MPa} \exp(-t/12s)$ 

→ 
$$t = -12 * \ln(1MPa/10MPa) = 27.6 s$$

### **Solution Problem 3**

a) 
$$\sigma_0 = 200$$
 MPa. After 2 minutes, or 120 seconds,  
 $\sigma(t=120s) = 200$  MPa  $\exp(-120s/\tau_r) = 160$  MPa  
 $\Rightarrow \tau_r = -120s / \ln(160 \text{ MPa}/200 \text{ MPa})$   
 $\tau_r = 538 \text{ s}$ 

3.

b) 
$$\varepsilon_0 = \Delta L/L_0 = 16 \text{ mm} / 100 \text{ mm} = 0.16$$
  
 $\sigma_0 = k^* \varepsilon_0 \Rightarrow k = \sigma_0 / \varepsilon_0 = 200 \text{ MPa} / 0.16 = 1250 \text{ MPa}$   
 $\tau_r = 538 \text{ s} = \eta/k \Rightarrow \eta = \tau_r^* k = 1250 \text{ MPa}^* 538 \text{ s}$   
 $\eta = 672,500 \text{ MPa-s} = 672.5 \text{ GPa-s}$ 

c)  $\sigma(t=180s) = 200$  MPa exp(-180s/538s) = 143.1 MPa E<sub>R</sub>(t=180s) =  $\sigma(t=180s)/\epsilon_0 = 143.1$  MPa / 0.16 E<sub>R</sub>(t=180s) = **894.4** MPa