

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
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3.22 MECHANICAL PROPERTIES OF MATERIALS
PROBLEM SET 5 SOLUTIONS

1. (Hertzberg 6.2) If it takes 300 seconds for the relaxation modulus to decay to a particular value at T_g , to what temperature must the material have been raised to effect the same decay in 10 seconds?

Using the time-temperature equivalence relationship for amorphous polymers,

$$\log\left(\frac{t_T}{t_{T_g}}\right) = \frac{-17.44(T - T_g)}{51.6 + T - T_g}$$
$$\log\left(\frac{10}{300}\right) = \frac{-17.44(T - T_g)}{51.6 + T - T_g}$$
$$\Rightarrow \boxed{T = T_g + 4.77 \text{ K}}$$

2. (Hertzberg 6.3) Calculate the relaxation time for glass and comment on its propensity for stress relaxation at room temperature. $E \approx 70 \text{ GPa}$ and $\eta \approx 1 \times 10^{12} \text{ GPa}\cdot\text{s}$.

Relaxation time is defined as the ratio of viscosity to modulus.

$$\tau = \frac{\eta}{E} = \frac{10^{12} \text{ GPa}\cdot\text{s}}{70 \text{ GPa}} = 1.4 \times 10^{10} \text{ sec}$$

The relaxation time is a measure of the time it takes for viscous behavior to play a significant role in deformation. The relaxation time calculated for glass is over 400 years, indicating that there is limited stress relaxation. Thus, glass behaves essentially completely elastically.

3. Your Irish post doc asked you to determine the time for the relaxation modulus to decay to a particular value at 75°C by testing the polymer at its glass transition temperature, 0°C . She said a simple calculation using the empirical time-temperature relationship for amorphous polymers would give you the desired result. You find experimentally that the relaxation time is 217.2 seconds for the relaxation modulus to decay to the particular value. However, the refrigeration unit that was supposed to keep the temperature at 0°C (glass transition temperature) was not functioning and the test was carried out at 20°C , the ambient temperature in the laboratory. Can you use the data from this test to determine the relaxation time to decay to the specified value at 75°C ? If so, what is the value?

It is possible to determine the relaxation time to decay at 75°C . The relaxation time is $\boxed{0.0007527 \text{ sec}}$. To find the relaxation time at some arbitrary temperature, we need to find the relaxation time at the glass transition temperature or the glass transition temperature plus 50 K. We are given the glass transition temperature, $T_g = 0 \text{ K}$. We find the time to the particular relaxation modulus at T_g by the empirical time-temperature relation for amorphous polymers.

$$\log\left(\frac{t_T}{t_{T_g}}\right) = \frac{-17.44(T - T_g)}{51.6 + T - T_g}$$

$$\log\left(\frac{217.2 \text{ sec}}{t_{T_g}}\right) = \frac{-17.44(20^\circ\text{C} - 0^\circ\text{C})}{51.6 + 20^\circ\text{C} - 0^\circ\text{C}}$$

$$\Rightarrow t_{T_g} = 1.616 \times 10^7 \text{ sec}$$

Now we can use the time to the relaxation modulus at T_g to compute the time to a particular relaxation modulus at a given temperature. We do this at 75°C .

$$\log\left(\frac{t_T}{t_{T_g}}\right) = \frac{-17.44(T - T_g)}{51.6 + T - T_g}$$

$$\log\left(\frac{t_T}{1.616 \times 10^7 \text{ sec}}\right) = \frac{-17.44(75^\circ\text{C} - 0^\circ\text{C})}{51.6 + 75^\circ\text{C} - 0^\circ\text{C}}$$

$$\Rightarrow t_{T_g} = \boxed{7.528 \times 10^{-4} \text{ sec}}$$

4. (Hertzberg 6.5) The deformation response of a certain polymer can be described by the Voigt model. If $E = 400 \text{ MPa}$ and $\eta = 2 \times 10^{12} \text{ MPa-s}$, compute the relaxation time. Compute $\varepsilon(t)$ for times to 5τ when the steady state stress is 10 MPa . How much creep strain takes place when $t = \tau$ and when $t = \infty$?

The relaxation time can be calculated by

$$\tau = \eta/E = 2 \times 10^{12} \text{ MPa-s} / 400 \text{ MPa} = 5 \times 10^9 \text{ sec}.$$

The strain experienced by a Voigt element can be expressed by the expression

$$\varepsilon = \frac{\sigma}{E} \left(1 - e^{-t/\tau}\right).$$

The strain at the indicated times is

$$\varepsilon(t = \tau) = 1.58 \times 10^{-2}$$

$$\varepsilon(t = 5\tau) = 2.48 \times 10^{-2}.$$

$$\varepsilon(t = \infty) = 2.5 \times 10^{-2}$$

(Hertzberg 6.6) Compare the fractional amount of the total deformation that would occur if $t = \tau$ when $\eta = 2 \times 10^{12} \text{ MPa-s}$ and $\eta = 8 \times 10^{12} \text{ MPa-s}$, respectively.

The relaxation time, τ , by definition is the time to reach a particular strain. Therefore, for each material, at $t = \tau$, the strains will be the same.

However, if one uses a time of $5 \times 10^9 \text{ sec}$ for the $\eta = 8 \times 10^{12} \text{ MPa-s}$ material, we can calculate the strain.

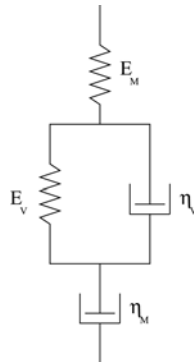
$$\tau = \eta/E = 8 \times 10^{12} \text{ MPa-s} / 400 \text{ MPa} = 2 \times 10^9 \text{ sec}$$

$$t/\tau = 0.25$$

$$\varepsilon(t = 5 \times 10^9 \text{ sec}) = 5.53 \times 10^{-3}$$

This makes intuitive sense, as the strain at a given time for a more viscous material is lower than the low viscosity material.

5. To improve the description of polymer behavior, Maxwell and Voigt models can be combined in series. For the four-element viscoelastic model shown below, derive an expression for the strain as a function of time for a given applied stress. Discuss the advantages of the four-element viscoelastic model over the Maxwell and Voigt models.



To find the total strain as a function of time, we can sum the elastic, viscoelastic, and viscous strain components.

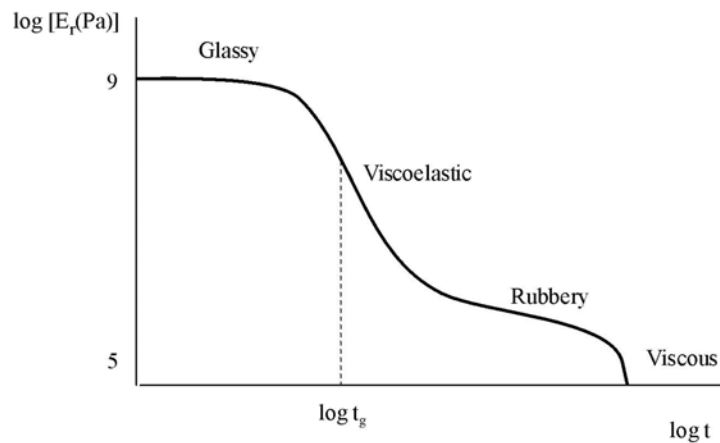
$$\varepsilon(t) = \varepsilon(t)_{spring} + \varepsilon(t)_{Voigt} + \varepsilon(t)_{dashpot}$$

$$\varepsilon(t) = \frac{\sigma}{E_M} + \frac{\sigma}{E_V} (1 - e^{-t/\tau}) + \frac{\sigma}{\eta_M} t$$

$\tau \equiv \eta_V / E_V$ is defined as the relaxation time for the Voigt element.

The four-element viscoelastic model accounts for instantaneous strain and creep strain. Upon unloading, the Voigt element accounts for creep recovery and the single dashpot accounts for permanent deformation that is irrecoverable. Thus, this simplistic model is much more accurate than the Maxwell or Voigt elements alone. The Maxwell element is unable to account for creep recovery and the Voigt element does not account for instantaneous strain or permanent deformation.

6. Sketch a log-log plot of relaxation modulus versus temperature for an amorphous polymer with cross-links.
- Identify the various regions and characteristic relaxation modulus values on the plot.



CORRECTION: There is no viscous portion in a cross-linked polymer. The rubbery regime should extend to the right.

- b. Explain the trends in relaxation modulus in the various regions in terms of the bonding in polymers.

For low temperatures times, the relaxation approaches a maximum limiting value where the material exhibits glassy behavior associated with negligible molecule segmental motions. In this region, the primary carbon-carbon bonds are stretched. At intermediate temperatures, the material transitions to a region of leathery behavior associated with short-range molecule segmental motion. At this elevated temperature, enough thermal energy is present to break weak secondary bonds between the polymer chains that permits segmental motion. At still higher temperatures, thermal energy is great enough to permit complete molecule movements in the rubbery region. Note that as the temperature is increased into the rubbery region, the modulus *increases* due to entropic effects.

- c. How would each regime change if the polymer had no cross-linking?

A polymer without cross-linking would have a limited rubbery region and experience visous flow as a liquid. Physical entanglement of polymer chains causes networks to form and restrict molecular flow. The restriction is responsible for rubbers (heavily cross-linked) having a stable rubbery region. See sketch in part (a).

7. Creep compliance values for polyethylene are given.

T (hours)	$J(t)$ ($\text{psi}^{-1} \times 10^{-4}$)
0	0.600
100	0.700
200	0.720
300	0.730
400	0.740
500	0.770

Consider a sample of polyethylene (cross-section 0.5 in. \times 0.1 in.) for the given load history at the same test conditions as the data above.

Load (lbs.)	Duration (hours)
20	100
5	200
50	100
0	100

- a. Calculate the strain at 200 and 500 hours.

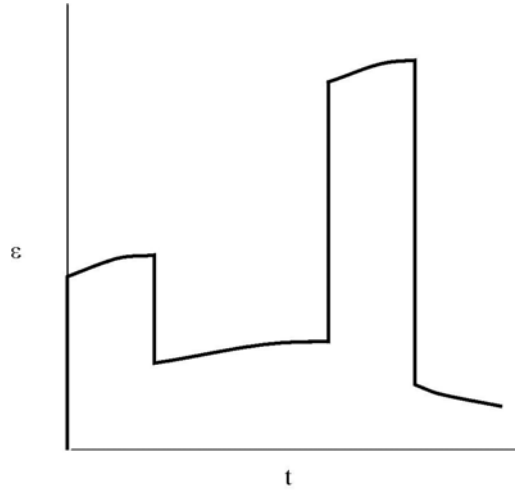
$$\begin{aligned}\Delta\sigma(0 \text{ hours}) &= \frac{20 \text{ lbs}}{0.5 \text{ in} \cdot 0.1 \text{ in}} = 400 \text{ psi} \\ \Delta\sigma(100 \text{ hours}) &= \frac{-15 \text{ lbs}}{0.5 \text{ in} \cdot 0.1 \text{ in}} = -300 \text{ psi} \\ \Delta\sigma(300 \text{ hours}) &= \frac{45 \text{ lbs}}{0.5 \text{ in} \cdot 0.1 \text{ in}} = 900 \text{ psi} \\ \Delta\sigma(400 \text{ hours}) &= \frac{-50 \text{ lbs}}{0.5 \text{ in} \cdot 0.1 \text{ in}} = -1000 \text{ psi}\end{aligned}$$

Using the Boltzmann superposition principle, we calculate the strains.

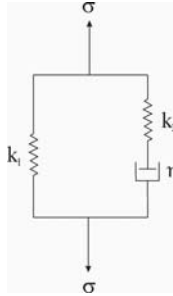
$$\begin{aligned}\varepsilon(t = 200 \text{ hours}) &= \Delta\sigma(0 \text{ hours}) \cdot J(t - 0 \text{ hours}) + \Delta\sigma(100 \text{ hours}) \cdot J(t - 100 \text{ hours}) \\ \varepsilon(t = 200 \text{ hours}) &= \Delta\sigma(0 \text{ hours}) \cdot J(200 \text{ hours}) + \Delta\sigma(100 \text{ hours}) \cdot J(100 \text{ hours}) \\ \varepsilon(t = 200 \text{ hours}) &= (400 \text{ psi})(0.72 \times 10^{-4} \text{ psi}^{-1}) + (-300 \text{ psi})(0.70 \times 10^{-4} \text{ psi}^{-1}) \\ \varepsilon(t = 200 \text{ hours}) &= \boxed{0.0078}\end{aligned}$$

$$\begin{aligned}
\varepsilon(t = 500 \text{ hours}) &= \Delta\sigma(0 \text{ hours}) \cdot J(t - 0 \text{ hours}) + \Delta\sigma(100 \text{ hours}) \cdot J(t - 100 \text{ hours}) + \dots \\
&\quad \dots \Delta\sigma(300 \text{ hours}) \cdot J(t - 300 \text{ hours}) + \Delta\sigma(400 \text{ hours}) \cdot J(t - 400 \text{ hours}) \\
\varepsilon(t = 500 \text{ hours}) &= \Delta\sigma(0 \text{ hours}) \cdot J(500 \text{ hours}) + \Delta\sigma(100 \text{ hours}) \cdot J(400 \text{ hours}) + \dots \\
&\quad \dots \Delta\sigma(300 \text{ hours}) \cdot J(200 \text{ hours}) + \Delta\sigma(400 \text{ hours}) \cdot J(100 \text{ hours}) \\
\varepsilon(t = 500 \text{ hours}) &= (400 \text{ psi})(0.77 \times 10^{-4} \text{ psi}^{-1}) + (-300 \text{ psi})(0.74 \times 10^{-4} \text{ psi}^{-1}) + \dots \\
&\quad \dots (900 \text{ psi})(0.72 \times 10^{-4} \text{ psi}^{-1}) + (-1000 \text{ psi})(0.70 \times 10^{-4} \text{ psi}^{-1}) \\
\varepsilon(t = 500 \text{ hours}) &= \boxed{0.0034}
\end{aligned}$$

b. Sketch a qualitative strain-time plot.



8. Derive the constitutive relation for the viscoelastic model shown below.



Based on the configuration, we know that the strain in the spring k_1 is equal to the combined strain in the spring k_2 and the dashpot η , and that the total stress is equal to the sum of the stress in the spring k_1 and the spring k_2 . Because the spring k_2 is in series with the dashpot η , they bear the same stress.

$$\varepsilon = \varepsilon_{k1} = \varepsilon_{k2} + \varepsilon_{\eta}$$

$$\sigma = \sigma_{k1} + \sigma_{k2} = \sigma_{k1} + \sigma_{\eta}$$

Looking at the elastic response of the spring k_1 gives

$$\sigma_{k1} = k_1 \varepsilon_{k1} = k_1 \varepsilon \rightarrow \sigma = k_1 \varepsilon + \sigma_{k2} \text{ or } \sigma_{k2} = \sigma - k_1 \varepsilon.$$

Taking the time derivative of the first equation yields

$$\dot{\varepsilon} = \dot{\varepsilon}_{k2} + \dot{\varepsilon}_{\eta} = \dot{\sigma}_{k2}/k_2 + \sigma_{k2}/\eta.$$

Combining the last two equations leads to the desired result.

$$\dot{\varepsilon} = \dot{\sigma}_{k2}/k_2 + \sigma_{k2}/\eta$$

$$\dot{\varepsilon} = (\dot{\sigma} - k_1 \dot{\varepsilon}) / k_2 + (\sigma - k_1 \varepsilon) / \eta$$

$$\frac{d\varepsilon}{dt} = \frac{1}{k_2} \frac{d\sigma}{dt} - \frac{k_1}{k_2} \frac{d\varepsilon}{dt} + \frac{\sigma}{\eta} - \frac{k_1}{\eta} \varepsilon$$

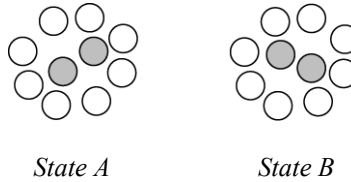
$$\boxed{\frac{\sigma}{\eta} + \frac{1}{k_2} \frac{d\sigma}{dt} = \frac{k_1}{\eta} \varepsilon + \left(1 + \frac{k_1}{k_2}\right) \frac{d\varepsilon}{dt}}$$

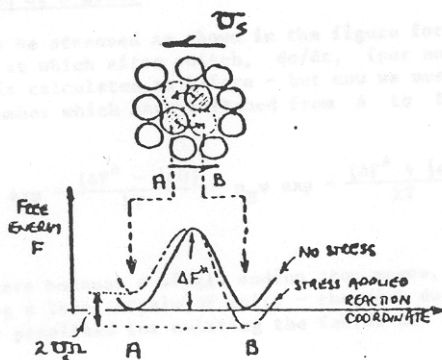
9. Evaluate the viscosity of the simple glass shown below by the following approximate procedure. Assume that half of the atoms pairs in the glass are in a position permitting an activated shear to the left (state A) and that the remaining half of the atom pairs are in the complementary position (state B). In the absence of a stress, states A and B have the same energy, F , and are separated by an activation energy of magnitude, ΔF^* . The stress σ_s raises the energy of atoms in state A, and lowers that of atoms in state B. The difference in energy between the two states is

$$\Delta F = 2\sigma_s \gamma \Omega,$$

where γ is the shear strain that occurs when an atom pair stretch from A to B, (which you may take to be unity) and 2Ω is the volume of two atoms. The vibration frequency (attempt frequency) of atom pairs is ν . Calculate the rate of shear, $\dot{\gamma}$, of the unit volume of the liquid, subjected to a shear stress, σ_s , by calculating the number of atom pairs jumping, per second, from A to B and from B to A.

Assume that $\sigma_s \Omega \ll kT$ (this means that $\exp(\sigma_s \Omega / kT) \approx 1 + \sigma_s \Omega / kT$) where k , is Boltzmann's constant and T is the absolute temperature and derive an equation for the viscosity of the liquid. (You may assume that a switching event, although it converts a pair of atoms in the state A into a pair in state B, also creates with the atoms surrounding it new pairs in state A, so that the fraction of atoms in state A remains constant and equal to one half.)





The stress lowers the activation energy for jumps from A to B from:

$$\Delta F^* \text{ to } \Delta F^* - \alpha\Omega, \quad (A \rightarrow B)$$

and raises that for jumps from B to A from:

$$\Delta F^* \text{ to } \Delta F^* + \alpha\Omega, \quad (B \rightarrow A)$$

The net rate of jumping from A to B is then:

$$\begin{aligned} \dot{N} \text{ atom pairs per unit volume per second} &= n_A v \exp - \frac{(\Delta F^* - \alpha\Omega)}{kT} \\ &- n_B v \exp - \frac{(\Delta F^* + \alpha\Omega)}{kT} \end{aligned}$$

where n_A is the number of pairs per unit volume in State A and n_B the number in State B. The number of atoms per unit volume is $1/\Omega$ where Ω is the atomic volume, so that:

$$n_A = n_B = \frac{1}{2\Omega}$$

Now if \dot{N} atom pairs jump per second, then the liquid suffers a shear $\gamma = 1$ when all atom pairs have jumped once, that is, in a time:

$$\frac{1}{2\Omega} \cdot \frac{1}{\dot{N}}$$

The strain rate $\dot{\gamma}$ is therefore:

$$\dot{\gamma} = 2\Omega\dot{N}$$

(check the dimensions of this equation). Hence:

$$\begin{aligned} \dot{\gamma} &= v \left(\exp \frac{(\Delta F^* - \alpha\Omega)}{kT} - \exp - \frac{(\Delta F^* + \alpha\Omega)}{kT} \right) \\ &= v \exp \left(- \frac{\Delta F^*}{kT} \right) \left(\exp \frac{\alpha\Omega}{kT} - \exp - \frac{\alpha\Omega}{kT} \right) \end{aligned}$$

If $q\Omega \ll kT$, we have:

$$\dot{\gamma} = \frac{2\nu q\Omega}{kT} \exp - \frac{\Delta F^*}{kT} \quad \text{NEWTONIAN-VISCOUS FLOW}$$

and the viscosity η , is defined by:

$$\eta = \frac{\sigma_s}{\dot{\gamma}}$$

Hence:

$$\eta = \frac{kT}{2\nu q\Omega} \exp \frac{\Delta F^*}{kT}$$

The viscosity falls rapidly as temperature rises:

