Problem Set #5 Solutions
Chemical Engineering 160/260

Problem 8.4
We're given T_g as $10^{\circ}C$ and given the viscosity at $25^{\circ}C$, and asked to find the viscosity at $40^{\circ}C$. We can use equation 8.48 (WLF equation). Assume in this equation that log is log base 10. We solve for η_g and use this value to determine $\eta(40)$.

Base 10
$\eta_g = \eta(T) \exp(40.157(T-T_g)/(51.6+T-T_g)) = 5.083\ E^{12}$ Poises, with $T=25^{\circ}$, $T_g=10^{\circ}C$,
   $\eta(25)=6E^8$ Poises
$\eta(40^{\circ}C) = \eta_g \exp(40.157(T_g-T)/(-51.6-T+T_g)) = \mathbf{1.97\ E^6\ Poises}$, using $T=40^{\circ}C$, $T_g=10^{\circ}C$,
   η_g from above.

As expected viscosity decreases with increasing temperature.

Problem 8.12
The copolymerization of divinyl benzene (structure on page 100 in sperling) could be viewed in two manners. First, copolymerization in itself can act to elevate the glass transition temperature. Second, the divinyl benzene is difunctional and can act as a cross-linker. The relative magnitudes of the two shifts in T_g can be calculated using the formulas of sections 8.8.1 and 8.6.3.2, respectively.

Copolymerization:
We use the Fox equation. This makes several assumptions, including assumed miscibility and that the product of the $\Delta c_{pi}T_i$ = constant for both the components; according to Sperling, this latter condition is applicable for random copolymers.

The mass fractions of divinyl benzene and vinyl acetate are
$M_1=(130)(0.05)/((0.05*130)+0.95*86))=0.0737$, and $M_2=1-M_1=0.9263$, respectively. We are given $T_2=(29+273^{\circ}K)=302^{\circ}K$. We are not given any information on the glass transition temperature of poly(divinyl benzene). To first approximation, we can treat it as being very high molecular weight polystyrene, since we know that both molecular weight and cross-linking increase T_g. But we'd expect T_g to be even higher since polymerization of a difunctional monomer will likely lead to a very highly crosslinked, perhaps even fully gelled polymer. From Table 8.8, a T_g for polystyrene is $368^{\circ}C$. From Figure 8.25, very high molecular weight PS has $T_g\sim378^{\circ}C$. Let's assume a T_g of $400^{\circ}K$, and see what kind of effect this has on the copolymer T_g.

$T = (0.0737/400 + 0.9263/302)^{-1}= 307.6^{\circ}K$, or a shift in T_g of close to $\mathbf{5.6^o}$. Remember this is considering a fairly high T_g for the divinyl benzene component.

Crosslinking:
Equation 8.62 is the pertinent equation. K is given in Table 8.9 as roughly $1.3E^{-23}$. M is the mer molecular weight. We use a molar average of the two components: eg M = $(0.05*130+0.95*86) = 88.2$ g/mol. χ' is the number of crosslinkers by gram. Assume

that each divinyl benzene act as a crosslinker, and consider a 100 mol sample. The total number of crosslinkers (divinyl benzene molecules) in the sample is 5 mol * 6.022 E^{23} molecules/mol. The total weight of this sample is 5 mol * 130 g/mol + 95 mol * 86 g/mol = 8820g. Then χ'=5 * 6.022 E^{23} / 8820 = 3.4138 E^{20} g^{-1}.

γ is the number of flexible bonds per mer, backbone, and side chain. Table 8.9 gives values of 2 and 4 for polystyrene and PMMA respectively. This variable is somewhat cryptic; a first guess would be that all single bonds are "flexible" bonds; styrene then has two noting that the vinyl double bond becomes a single bond on polymerization. By the same treatment, however, methyl methacrylate would have γ=5 but its real value is 4. The exact value will not change the shift in T_g immensely, so taking styrene and methyl methacrylate as analogous to divinyl benzene and vinyl acetate, respectively, gives γ = 4 and γ = 3, respectively. A molar average of these values gives γ = 3.05 which is what we use.

Then we have:

$$KM\chi'/\gamma = (1.3E^{-23})(88.2)(3.4138\ E^{20}) \div 3.05 = 0.12834$$

$$\Delta T_g = (302)*(\ 0.12834\ /\ (1\text{-}0.12834)\ ) = \mathbf{44.5^oK}$$

This is a much larger value than that obtained by the copolymerization method. Thus we see that crosslinking in this case plays a much larger role in increasing the glass transition temperature. Combining the two results, we might expect the new T_g to be **75-80°C**.

Problem 9.2
We have a rectangular prism of an elastomer which is crosslinked with a tetrafunctional molecule. We are given the stress at 25°C in this material for an elongation of α=25/10 = 2.5.

a) The appropriate equation is 9.70, and for a tetrafunctional crosslinker the front factor is ½. We assume that there is no swelling so $r_i =r_o$. Solving for n,

$$n = 2\sigma/kT\ (\alpha - 1/\alpha^2)^{-1}$$

Note: 10 dynes/cm^2 = N/m^2. Substituting in values k=1.38E^{-23} J/K, T=298°K, α=2.5, and σ = 1.5E^6 N/m^2 yield **n = 517.5 mol m^{-3} = 5.175 E^8 mol cm^{-3}**. Multiplying by advogodro's number yields **3.116 E^{32} chains/cm^3**.

b) Using the results of part a) and changing α = 1.5 gives σ = **6.77 E^6 dyne/cm^2**.

c) Here we just change the temperature so T=373°C, and α = 2.5 again. We get **σ =1.878E^7 dyne/cm^2.**

Problem 9.13
We consider only the final state. A drawing of this state is shown below:
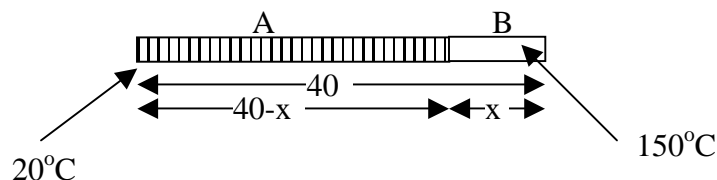
We make the assertion that any cross section is subject to the same amount of force*. If it were not, then rearrangement would occur (ie the line between the two pieces or rubber band would shift). Hence we can write two equations, one each for the force in each of the rubber bands, and equate the two. This approach allows for a change in the cross sectional area in each rubber band but assumes an infinitely fast jump in dimensions at the interface. We also assume ideal elastomers, in which poisson's ratio is ½, and volume is conserved during deformation. Hence if the original cross sectional area of the bands was A, then the area at any deformation is given by A/α.

Define: $\alpha_A = (40-x)/10$
            $\alpha_B = (x)/10$

In Rubber Band A:
$F = A/\alpha_A \ RTn(\alpha_A - 1/\alpha_A^2)$

In B:
$F = A/\alpha_B \ RTn(\alpha_B - 1/\alpha_B^2)$

Now we simply equate the two forces and solve for x with eg maple. (Maple did a poor job solving analytically, so I just plotted the two functions to solve for x).

We come up with an answer of **x = 14.22 cm.**

* Why force and not stress? My thought is the following. The condition for equilibrium from eg Newton's laws is really summation forces = 0. If we consider a particle or mass and draw a free body diagram for it, we consider all the forces on it, not the stresses. In this case the stresses will not be the same because the cross sectional areas of each rubber band are different. During the derivations in class however, we assumed uniform cross sectional areas, so the forces and stresses were both equal across elements in series.

```
> amm:=1/aA*TA*(aA - 1/aA^2);
> bmm:=1/aB*TB*(aB - 1/aB^2);
```

$$amm := \frac{TA\left(aA - \dfrac{1}{aA^2}\right)}{aA}$$

$$bmm := \frac{TB\left(aB - \dfrac{1}{aB^2}\right)}{aB}$$

```
> aA:=(40-x)/10;
```

$$aA := 4 - \frac{1}{10}x$$
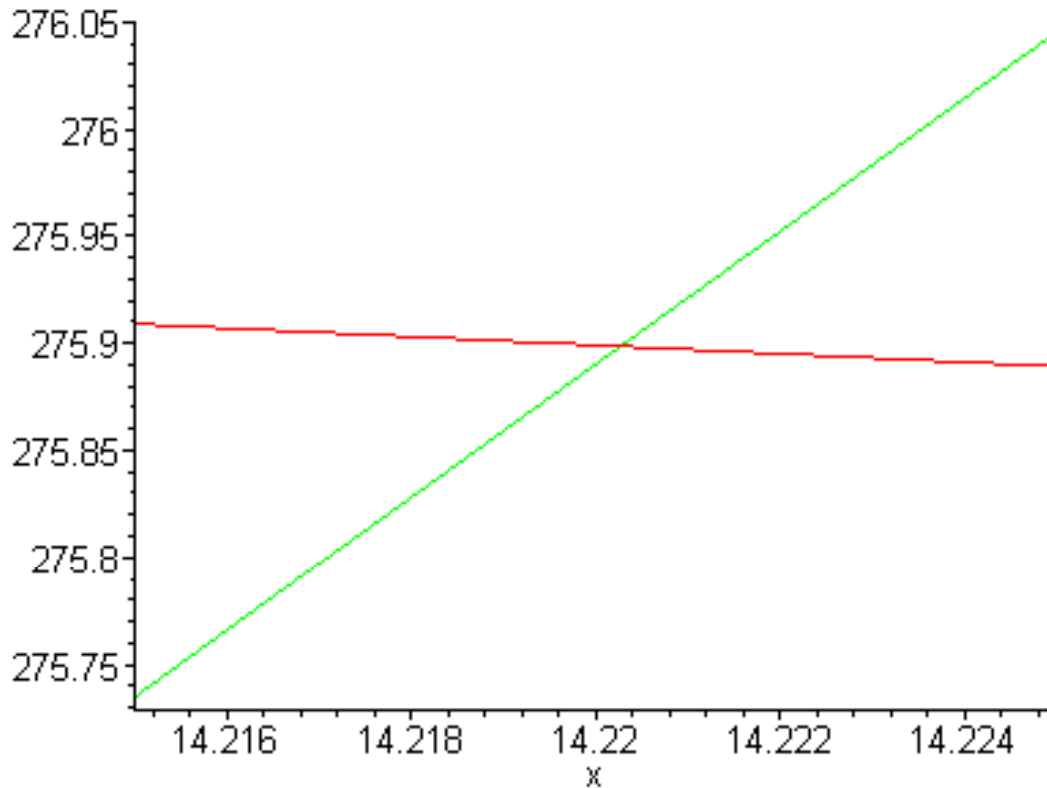
```
> aB:=x/10;
```

$$aB := \frac{1}{10}x$$

```
> TA:=20+273;
```

$$TA := 293$$

```
> TB:=150+273;
```

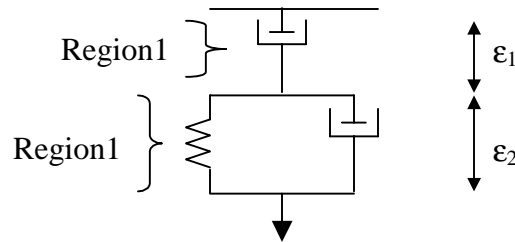$$TB := 423$$

```
> plot({amm,bmm}, x=14.215..14.225);
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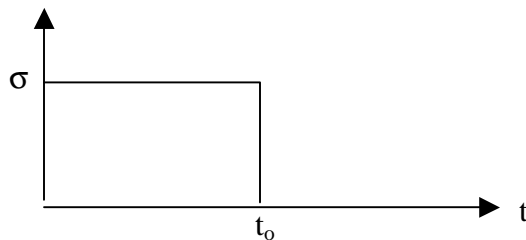


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>
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The total strain in the system can be determined as the sum of the strains in the upper dashpot and in the lower spring/dashpot system, that is:

$$\varepsilon = \varepsilon_1 + \varepsilon_2$$

Region1
Region1

ε_1
ε_2

The stress which is applied is a function of t as shown below:

σ

t_o

t

a) Derive the strain (length) for $0 < t < t_o$

We can consider regions 1 and 2 separately, each having a stress σ applied to it. This assertion can be proven just by taking a free body diagram at the node between 1 and 2.

For the strain ε_1, we can write

$$d\varepsilon_1 / dt = \sigma / \eta_1 \, ,$$

so integrating with initial condition $\varepsilon_2 \, (t=0) = 0$ yields:

$$\varepsilon_1 = \sigma / \eta_1 \, t \, ,$$

so this portion of the model extends linearly with time.

For the strain ε_2, we must consider that the strain in both arms must be the same, and that the total stress supported by both arms is equal to the sum of the stresses in each arm. If the stress across the spring is σ_s and the stress across the dashpot is σ_d then we know that

$$\sigma = \sigma_d + \sigma_s$$

$$d\varepsilon_2 / dt = \sigma_d / \eta_2$$

$$\varepsilon_2 = \sigma_s / E_2$$

Solving for the stresses in the last two equations and plugging them back into the first equation gives

$$\sigma = \eta_2 \frac{d\varepsilon_2}{dt} + E_2 \varepsilon_2 \qquad\qquad \text{Equation *}$$

Solving this equation by use of an integrating factor or other means yields

$$\varepsilon_2 = \frac{\sigma}{E_2}\left(1 - \exp(-\frac{E_2 t}{\eta_2})\right)$$

So this region begins with zero strain (the dashpot prevents instantaneous deformation) and increases exponentially to the limiting value dictated by the spring.

Therefore the total strain in of the system in the region $0 < t < t_o$ is

$$\boxed{\varepsilon = \varepsilon_1 + \varepsilon_2 = \frac{\sigma}{\eta_1}t + \frac{\sigma}{E_2}\left(1 - \exp(-\frac{E_2 t}{\eta_2})\right)}$$

A plot of this strain is shown below schematically.
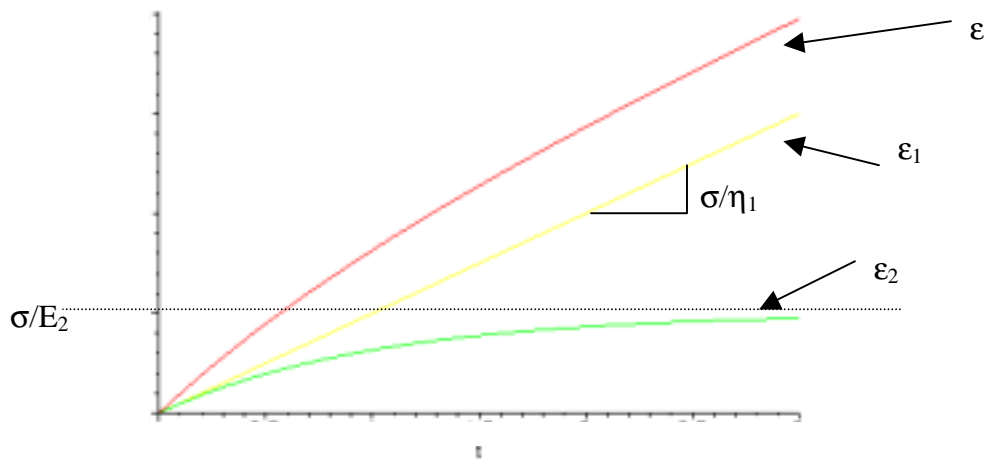
b) For this portion we want the strain for $t > t_o$. The stress is removed and the system allowed to relax. Again the strain is that for the two regions added. The dashpot at the top of the system cannot relax without a restoring force to cause it to contract. Since there is no such storing force (the applied stress is zero, not compressive), it remains strained to a value

$\varepsilon_1 = \frac{\sigma}{\eta_1}t_o$ for all $t > t_o$. The second region can relax however. The spring portion asserts

a restoring force because it is stretched. This causes a decrease in the strain toward zero, but again the rate is limited by the dashpot. Qualitatively we expect an exponential decrease in strain from the value at t_o to zero with infinite time. This can be shown by considering equation * (which still applies) and setting $\sigma = 0$.

$\eta_2 \, {d\varepsilon_2} / {dt} = -E_2\varepsilon_2$, or rearranging $-\dfrac{\eta_2}{E_2}\dfrac{d\varepsilon_2}{\varepsilon_2} = dt$. Integrating from times t_o to t with the

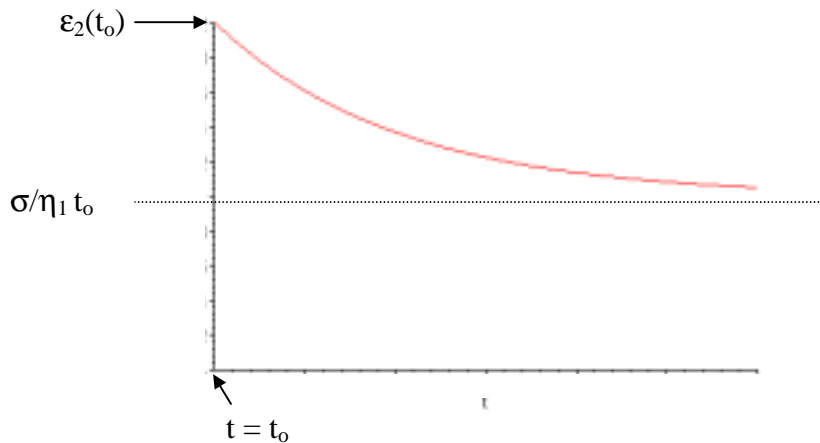initial condition that $\varepsilon_2(t_o) = {\sigma} / {E_2}\left(1-\exp(-{E_2 t_0} / {\eta_2})\right)$ yields

$$\varepsilon_2(t) = {\sigma} / {E_2}\left(1-\exp(-{E_2 t_0} / {\eta_2})\right)\exp({E_2} / {\eta_2}(t_o - t))$$

As predicted, this starts at $\varepsilon_2(t_o)$ at t=t$_o$ and decays to zero with time.
Again combining the strains yields total strain as a function of time t>t$_o$.

$$\varepsilon_2(t) = {\sigma} / {\eta_1}t_o + {\sigma} / {E_2}\left(1-\exp(-{E_2 t_0} / {\eta_2})\right)\exp({E_2} / {\eta_2}(t_o - t))$$

A schematic plot is shown below.

$\varepsilon_2(t_o)$

$\sigma/\eta_1 t_o$

$t = t_o$

Problem 10-14
Given Data:
$T_g = 5°C$
$T = 30°C$
$n = 1E^{-4}$ mol/cm^3
$\eta_g = 1E^{13}$ poises
$\sigma = 1E^7$ dynes/cm^2
We are told that E obeys rubber elasticity theory and viscosity obeys the WLF equation.
We are working with a polymer following the Kelvin model (spring and dashpot in
parallel).

a) The governing equation for a creep experiment within the Kelvin model was already

derived in the previous homework problem as $\varepsilon = {\sigma} / {E}\left(1-\exp(-{Et} / {\eta})\right)$. Note that this

derivation assumes that E is independent of strain. In actuality this is only true for small strains, as discussed in Sperling. For small strains, E~3nRT; for larger strains $E = \sigma/\varepsilon = nRT(\alpha - 1/\alpha^2) \div (\alpha - 1)$**, since $\varepsilon = (l - l_o)/l_o = l/l_o - 1 = \alpha - 1$. We will assume only small strains apply to simplify the problem.

$E = 3nRT = 3$ $(1E^{-4}$ mol/cm$^3)(10^6$ cm^3/m$^3)(273+30^\circ K)(8.314$ J/molK$) = 7.557E^5$ N/m^2 or $7.557E^6$ dynes/cm^2.

Viscosity obeys the WLF equation. We use the universal form of this equation $\log(\eta/\eta_g) = -17.44(T - T_g)/(51.66 + T - T_g)$. With $T - T_g = 25^\circ K$ and η_g as given in the problem, $\eta = 2.0328E^7$ Poises.

One poise is a g/cms $= 10^{-1}$Ns/m^2. So since $\sigma/E = 1E^7 / 7.557E^6 = 1.323$, and $E/\eta = 7.557E^6/2.0328E^7$ s$^{-1} = 0.3718$ s^{-1}, then

$\varepsilon = 1.323$ (1 – exp(-0.3718 t)) with t being in seconds, ε is unitless. The required plot is shown below.
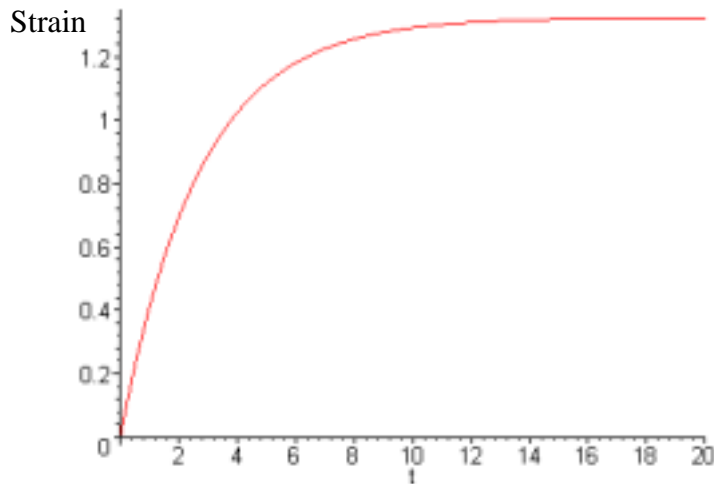
Two points are worth making. First, the limiting value dictated by the spring portion of the model is reached within a few seconds. Second, the strains predicted by our treatment are reality small, so the treatment with E = 3nRT is self consistent.

FYI: To solve the problem exactly for larger strains one can use the exact form of the young's modulus to arrive at a non-linear first order ODE for strain as a function of time. We use the same approach taken in the previous problem, arriving at equation *,

$\sigma = \eta \dfrac{d\varepsilon}{dt} + E\varepsilon$ Rather than having E as a constant, we assume it is a function of strain.

From Sperling eqn 9.36 $E = nRT(2\alpha^2 + 1/\alpha)$.** Since $\alpha = \varepsilon + 1$, this becomes

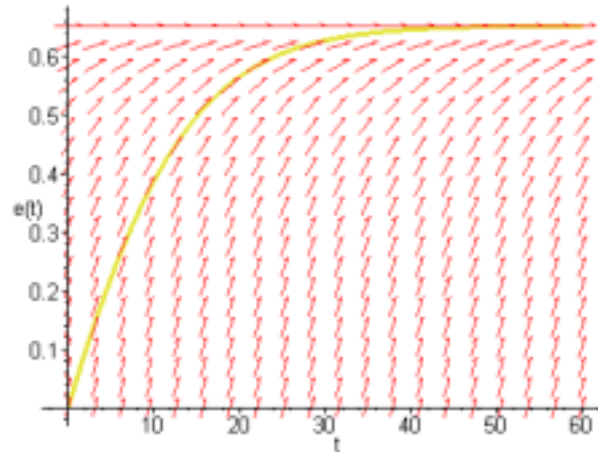$$E = nRT\left[2(\varepsilon + 1)^2 + \frac{1}{\varepsilon + 1}\right].$$

Dividing both sides by nRT gives the ODE as

$$\frac{\sigma}{nRT} = \frac{\eta}{nRT}\frac{\partial \varepsilon}{\partial t} + \varepsilon \left[2(\varepsilon+1)^2 + \frac{1}{\varepsilon+1} \right].$$

Evaluating the constants gives: $\dfrac{\sigma}{nRT} = 3.97$ and $\dfrac{\eta}{nRT} = 80.699$.

Using maple's DEplot numerical plotting method gives strain as a function of time shown below:

This approach does make a difference in both the rate of creep (faster) and the limiting strain (lower) compared to the case where E is independent of strain.

b) The rate of creep is the slope of the strain versus time plot. Obviously it might be of interest to slow this down to retain part dimensions, etc. Taking dε/dt we find that this rate is given by

$$\frac{d\varepsilon}{dt} = \frac{\sigma}{\eta}\exp(-Et/\eta)$$

Note that this equation gives the largest values (fastest rates of creep) at low times. This is obvious from the graph above.

So we have three variables to change to slow down this rate. A decrease in the applied stress with decrease the rate of creep for all times. Sometimes though this is not an option as the part is required to be used in certain dictated working conditions. An increase in young's modulus will also decrease the creep rate for all times greater than t=0.

A change in viscosity is a bit more complicated, as viscosity appears twice in the equation with competing trends. Plotting several values of viscosity shows that for low times, the rate decreases with increasing viscosity, while above a certain value of time, the creep rate increases with increasing viscosity. However the total creep experienced (proportional to the area under the curves from t=0 to infinity) is the same in all cases, provided the other variables are held constant. Since in service we would mostly be

concerned with the initial creep rate, then an increase in viscosity would be advantageous. Note that increasing the crosslinking density can increase both young's modulus (# active chain segments increases) and viscosity (leads to increase in T_g) making this advantageous for creep control.
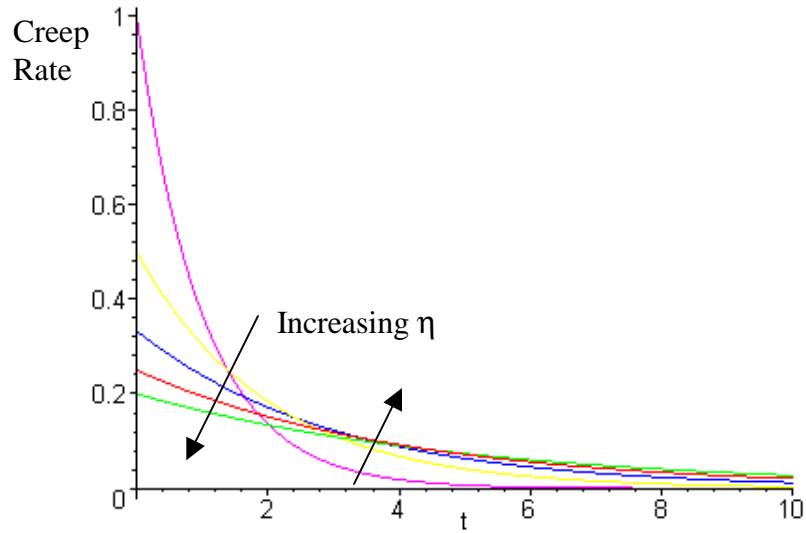
** Note: if you just use $E = \sigma / \varepsilon$ vs. Sperling 9.36 you get a different equation for E. I'm not sure why this discrepancy comes about. The results are similar.