HW solution for Lecture 17

10.74
Assuming only one sulfur atom is involved in each cross-linking bond with butadiene, we know there is a one-to-one correspondence between the number of moles of sulfur and the number of moles of butadiene in the reaction. We are therefore able to assess the amount of sulfur required for 100% cross-linking.

\[
\text{mass of } S_{100\%} = MW_S \times (\text{No. of moles of } S) = MW_S \times (\text{No. of moles of butadiene})
\]

\[
= MW_S \left( \frac{\text{mass of butadiene}}{MW_{\text{butadiene (mer)}}} \right)
\]

The average molecular weight of the butadiene mer is:

\[
MW_{\text{polybutadiene}} = 6 \text{ H atoms } \times 1 \text{ g/mol } + 4 \text{ C atoms } \times 12 \text{ g/mol } = 54 \text{ g/mol}
\]

Substituting,

\[
\text{mass of } S_{100\%} = (32 \text{ g/mol}) \left( \frac{70 \text{ g}}{54 \text{ g/mol}} \right) = 41.48 \text{ g S}
\]

Thus for only 3 percent cross-linking,

\[
\text{mass of } S_{3\%} = 0.03 \times 41.48 \text{ g S} = 1.24 \text{ g S}
\]

Polybutadiene

10.78
Assuming one sulfur atom is involved in cross-linking each butadiene mer, the fraction of cross-link sites is simply the ratio of the moles of sulfur to the moles of butadiene.

\[
\text{No. of moles of } S = \frac{3000 \text{ g}}{32 \text{ g/mol}} = 93.75 \text{ mol S}
\]

\[
\text{No. of moles of butadiene} = \frac{300,000 \text{ g}}{54 \text{ g/mol}} = 5555.56 \text{ mol butadiene}
\]

The fraction of cross-link sites is thus,

\[
\text{Fraction of cross-link sites} = \frac{93.75}{5555.56} \times 100\% = 1.69\%
\]
Since the copolymer has 1 mole of styrene for every 7 moles of polybutadiene, we have

\[
7 \text{ moles polybutadiene} \times 54 \text{ g/mol} = 378 \text{ g}
\]
\[
1 \text{ mole polystyrene} \times 105 \text{ g/mol} = 105 \text{ g}
\]

Copolymer total mass = 483 g

However, in this reaction, only the butadiene can participate in the cross-linking with sulfur. We thus need the mass fraction of butadiene: \(378 \text{ g} / 483 \text{ g} = 0.783\). Using a basis of 100 g of copolymer, the number of moles of butadiene is,

\[
\text{moles butadiene} = \frac{\text{mass of butadiene}}{\text{MW(mer)}} = \frac{100 \text{ g} \times 0.783}{54 \text{ g/mol}} = 1.45 \text{ mol}
\]

The mass of sulfur required for 20 percent cross-linking is therefore,

\[
\text{mass of S}_{20\%} = (0.20)(1.45 \text{ mol})(32 \text{ g/mol}) = 9.28 \text{ g}
\]

And the weight percent of sulfur required for this reaction is

\[
\text{Weight percent S} = \frac{9.28 \text{ g}}{100 \text{ g} + 9.28 \text{ g}} \times 100\% = 8.49\%
\]

(a) The decrease in stress is given by \(\sigma = \sigma_0 e^{-t/\tau}\). Thus,

\[
\tau = \frac{-t}{\ln(\sigma / \sigma_0)} = \frac{-25 \text{ days}}{\ln(6 \text{ MPa} / 9 \text{ MPa})} = 61.7 \text{ days}
\]
(b) For a relaxation time constant of 61.7 days, the stress after 50 days will be,

\[ \sigma = (9.0 \text{ MPa}) e^{-\left(\frac{50 \text{ days}}{61.7 \text{ days}}\right)} = 4.0 \text{ MPa} \]

10.85
First, the relaxation time must be calculated for each set of conditions:

\[ \tau_1 = \frac{-t}{\ln(\sigma / \sigma_0)} = \frac{-25 \text{ days}}{\ln(750 \text{ psi} / 1000 \text{ psi})} = 86.90 \text{ days} \]

\[ \tau_2 = \frac{-t}{\ln(\sigma / \sigma_0)} = \frac{-30 \text{ days}}{\ln(400 \text{ psi} / 1100 \text{ psi})} = 29.66 \text{ days} \]

Since the Arrhenius-type equation uses absolute temperature, we must next convert the temperatures to Kelvin: \( T_1 = 27^\circ + 273^\circ = 300 \text{ K} \); \( T_2 = 50^\circ + 273^\circ = 323 \text{ K} \). Applying the Arrhenius-type rate equation, \( 1/\tau = C e^{-Q/RT} \), we obtain two equations in two unknowns.

\[ \frac{1}{\tau_1} = C e^{-Q/RT_1} \quad \text{and} \quad \frac{1}{\tau_2} = C e^{-Q/RT_2} \]

Dividing these equations, we obtain a single equation with one unknown – \( Q \)

\[ \frac{\tau_2}{\tau_1} = \exp \left[ \frac{-Q}{R \left( \frac{1}{T_1} - \frac{1}{T_2} \right)} \right] \]

Substituting the values provided and the calculated time constants,

\[ \frac{29.66}{86.90} = \exp \left[ \frac{-Q}{8.314 \text{ J/mol} \cdot \text{K} \left( \frac{1}{300 \text{ K}} - \frac{1}{323 \text{ K}} \right)} \right] \]

\[ Q = \left( \frac{-8.314 \text{ J/mol} \cdot \text{K}}{2.3736 \times 10^{-4} \text{ /K}} \right) \ln \left( \frac{29.66}{86.90} \right) = 37,653 \text{ J/mol} = 37.65 \text{ kJ/mol} \]
10.87

(a) The decrease in stress is given by \( \sigma = \sigma_0 e^{-t/\tau} \). Thus,

\[
t = -\tau \left[ \ln(\sigma / \sigma_0) \right] = -(100 \text{ days}) \left[ \ln(4.2 \text{ MPa} / 6 \text{ MPa}) \right] = 35.7 \text{ days}
\]

(b) By applying the Arrhenius-type rate equation, \( \frac{1}{\tau} = Ce^{-Q/RT} \), for two sets of general conditions and dividing the resulting equations, we obtain

\[
\frac{\tau_2}{\tau_1} = \exp \left[ \frac{-Q}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right]
\]

Substituting the values provided and the \( \tau_1 \) calculated above,

\[
\frac{\tau_2}{100} = \exp \left[ -\frac{25,000 \text{ J}}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{300 \text{ K}} - \frac{1}{313 \text{ K}} \right) \right]
\]

\( \tau_2 = 65.95 \text{ days} \)