

Polymer Science 2025/26

Exercise 8 – Solution

1. Let us better understand the simplest phenomenological mechanical models for viscoelasticity under different loading conditions. Schematically draw the evolution of strain or stress over time for the Maxwell and Voigt models in the following two experiments:

i) stress relaxation under tension (constant strain: $\epsilon = \epsilon_0, \dot{\epsilon} = d\epsilon/dt = 0$).

Hint 1: for the Maxwell model, see Slide 263;

ii) creep experiment under tension (constant stress: $\sigma = \sigma_0, d\sigma/dt = 0$),

Hint 2: for the Maxwell model, use the condition $\epsilon_{\text{dashpot}}(t = 0) = 0$ to find an expression for ϵ that is independent of ϵ_0 .

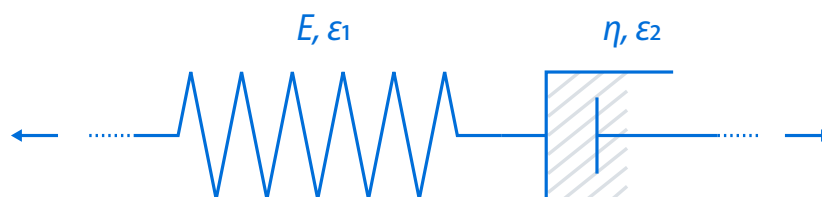
Hint 3: The first-order differential equation $y'(x) + \frac{a}{b}y(x) - \frac{c}{b} = 0$ has the solution

$$y = \frac{c}{a} \left[1 - \exp\left(\frac{-ax}{b}\right) \right]$$

Interpret your results (compare with the schematic graphs on Slide 268):

- Does the model predict complete stress relaxation?
- Does it predict a realistic creep response (decreasing strain rate with time)?
- Which model provides a better qualitative description of real polymer behavior?

Hint 4: (i) write down the constitutive laws for the spring and the dashpot, (ii) combine them for the total strain or stress, (iii) derive the differential equation for $\sigma(t)$ or $\epsilon(t)$ and solve it, (iv) sketch and interpret the time evolution.



For the Maxwell model under stress relaxation, the total strain and stress are:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 = \varepsilon_0 = \text{constant}, \quad \sigma = \sigma_1 = \sigma_2$$

Since the strain is constant, expressing it by its constitutive relations (Hooke's law for the spring and Newton's law for the dashpot) gives:

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt} = \frac{d\sigma}{E dt} + \frac{\sigma}{\eta} = 0 \quad \rightarrow \quad \frac{d\sigma}{\sigma} = -\frac{E}{\eta} dt$$

Integrating and exponentiating both sides:

$$[\ln \sigma]_{\sigma_0}^{\sigma} = -\frac{E}{\eta} [t']_0^t \quad \rightarrow \quad \sigma = \sigma_0 e^{-\frac{t}{\tau}} \quad \text{with} \quad \tau = \frac{\eta}{E}$$

Hence, the stress exponentially decays with time. However, according to the Maxwell model, the stress completely relaxes at long times, which is not realistic for real polymers, where a residual stress typically remains.

For the Maxwell model under creep, the total strain and stress are:

$$\varepsilon = \varepsilon_1 + \varepsilon_2, \quad \sigma = \sigma_1 = \sigma_2$$

Using Hooke's law for the spring and Newton's law for the dashpot:

$$\frac{d\sigma}{dt} = E \frac{d\varepsilon_1}{dt}, \quad \sigma = \eta \frac{d\varepsilon_2}{dt}$$

Thus, for the total strain rate:

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

For a creep test ($\sigma = \sigma_0 = \text{constant}$):

$$\frac{d\sigma}{dt} = 0 \quad \rightarrow \quad \frac{d\varepsilon}{dt} = \frac{\sigma_0}{\eta}$$

Integrating gives:

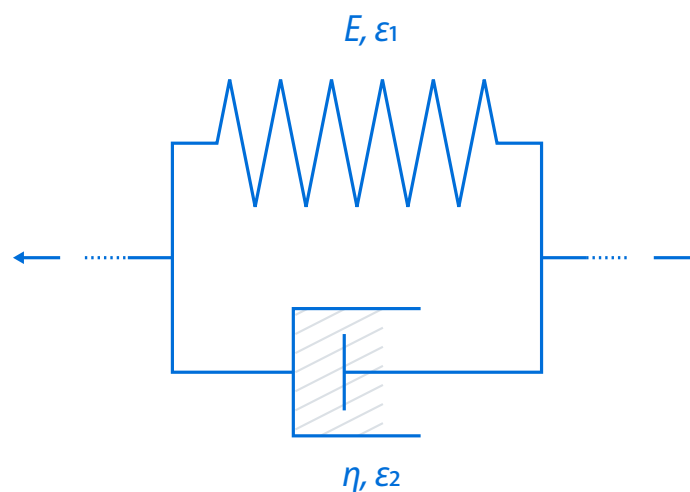
$$\varepsilon = \varepsilon_0 + \frac{\sigma_0}{\eta} t$$

With the initial condition $\varepsilon_2(t=0) = 0$, it follows that $\varepsilon(t=0) = \varepsilon_1(t=0)$. Therefore:

$$\varepsilon = \varepsilon_1 + \frac{\sigma_0}{\eta} t = \frac{\sigma_0}{E} + \frac{\sigma_0}{\eta} t$$

Hence, the Maxwell model predicts Newtonian flow: The strain increases linearly with time, while for real viscoelastic polymers, the strain rate $d\varepsilon/dt$ decreases with time. Note also the instantaneous elastic strain (σ_0/E) at $t = 0$.

Thus, the Maxwell model provides a reasonable description for stress relaxation, but a poor representation for creep, where it fails to capture the decreasing strain rate of real viscoelastic materials.



In the Voigt element, the total strain and stress are defined as

$$\varepsilon = \varepsilon_1 = \varepsilon_2, \quad \sigma = \sigma_1 + \sigma_2$$

The individual stresses in the spring and dashpot are given by Hooke's and Newton's law, respectively:

$$\sigma_1 = E\varepsilon, \quad \sigma_2 = \eta \frac{d\varepsilon}{dt}$$

Hence, the total stress becomes:

$$\sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt} \quad \rightarrow \quad \frac{d\varepsilon}{dt} = \frac{\sigma - E\varepsilon}{\eta}$$

For a creep test with a constant applied stress ($\sigma = \sigma_0$) and using Tip 3:

$$\frac{d\varepsilon}{dt} + \frac{E\varepsilon}{\eta} = \frac{\sigma_0}{\eta} \rightarrow \varepsilon = \frac{\sigma_0}{E} (1 - e^{-t/\tau})$$

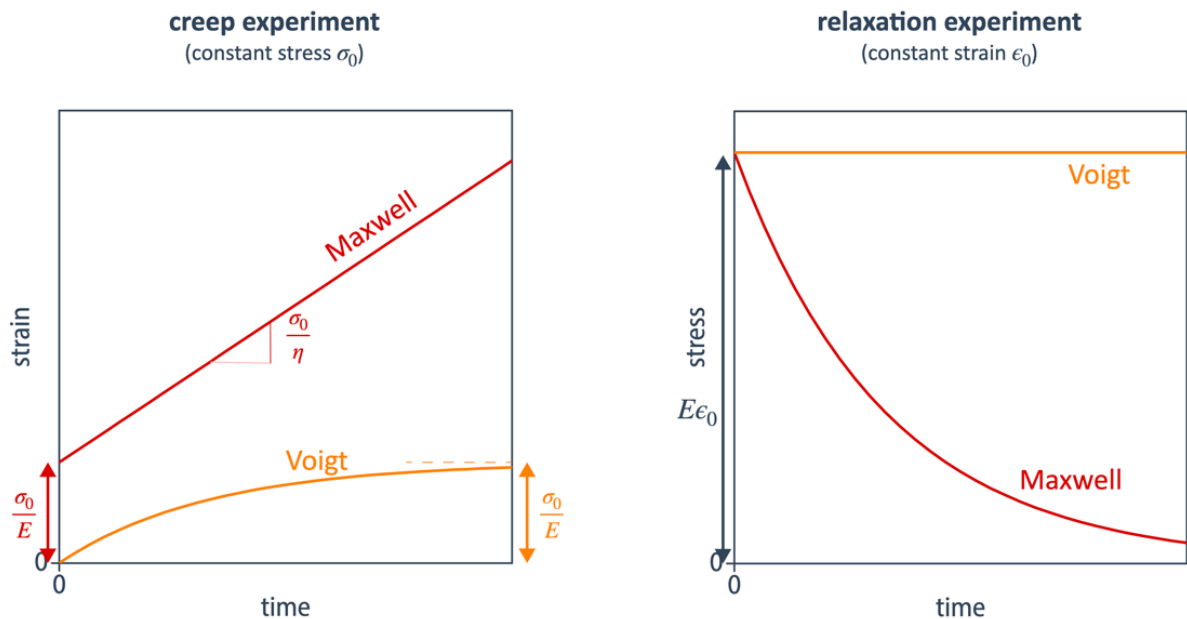
Thus, the strain increases asymptotically with time, approaching its equilibrium value $\varepsilon_\infty = \sigma_0/E$. The strain rate decreases with time, giving a realistic representation of creep behavior in viscoelastic materials.

For stress relaxation and a constant strain $\varepsilon = \varepsilon_0$ (i.e. $d\varepsilon/dt = 0$):

$$\sigma = E\varepsilon_0$$

Thus, the stress remains constant in time. The Voigt model does not predict stress relaxation.

Therefore, the Voigt model complements the Maxwell model: the two are often combined to form more accurate standard linear solid models.



2. According to the Voigt model for a viscoelastic solid, the creep compliance ($\sigma = \sigma_0 = \text{constant}$) is

$$D(t) = \frac{\varepsilon(t)}{\sigma} = \frac{1}{E} \left(1 - \exp\left(-\frac{t}{\tau}\right) \right)$$

where $\tau = \eta/E$ is the *relaxation time*, which characterizes the timescale over which the deformation develops (after τ , about 63% of the total strain has occurred).

Describe the behavior of the Voigt solid in a creep experiment in the following limits and explain what these limits represent for the material response:

- $t \ll \tau$;

$D(t) \rightarrow 0$, i.e. the instantaneous elastic response is zero (no jump in ϵ at $t = 0$) because the dashpot prevents an immediate displacement: an infinitely rigid solid.

- $t \gg \tau$?

$D(t) \rightarrow 1/E$, i.e. the dashpot has relaxed and the spring stores the load, the Voigt solid behaves as a purely elastic solid at long times with Young's modulus E and $\epsilon = \sigma_0/E$.

The relaxation time τ represents the transition time between these two states.

3. The shear storage compliance (J_1) vs $\log(\omega)$ curves of poly(octyl methacrylate) measured at different T are superimposable when shifted horizontally along the frequency axis. For a reference temperature $T_{\text{ref}} = 100$ °C, the corresponding horizontal shift factors α_T are listed in Table 1.

Show that the temperature dependence of the shift factor can be described by the empirical WLF-equation. Determine the constants C_1 and C_2 from the given data.

Discuss the physical meaning and range of validity of the WLF equation.

Assuming a thermally activated process, determine the apparent activation energy E_a from the Arrhenius relation. Why does the resulting plot deviate from perfect linearity?

Table 1: Shift factors.

T (°C)	$\log(\alpha(T))$	T (°C)	$\log(\alpha(T))$
129.5	-0.87	44.4	2.46
120.3	-0.62	38.8	2.80
109.4	-0.30	34.2	3.10
100	0.00	30	3.38
89.4	0.37	25.3	3.72
80.2	0.73	19.8	4.14
70.9	1.12	15.1	4.53
65.8	1.35	9.9	4.99
59.8	1.63	4.4	5.56
54.5	1.90	-0.1	5.98
50.2	2.13	-5	6.52

The WLF equation can be rearranged as:

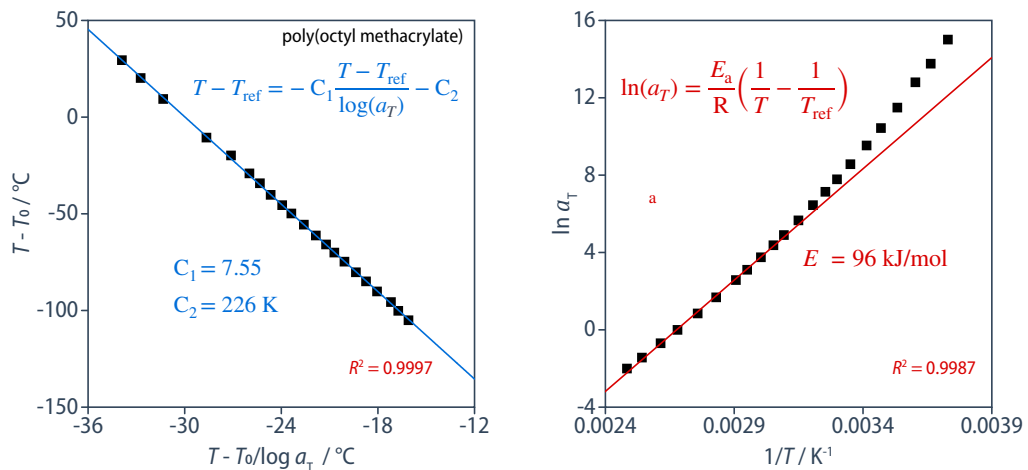
$$T - T_{\text{ref}} = -C_1 \frac{T - T_{\text{ref}}}{\log a_T} - C_2$$

If the data follows a straight line when plotting $(T - T_{\text{ref}})/\log(a_T)$ vs. $T - T_{\text{ref}}$, the WLF model is valid. Performing a linear regression of the provided data yields $C_1 = 7.55$ and $C_2 = 226$ K. Hence, the shift factors obey the WLF relation with these constants.

From the Arrhenius relation

$$\ln a_T = -\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right),$$

the activation energy E_a can be determined from the slope of the linear fit in a plot of $\ln a_T$ versus $1/T$. Using the provided data, we obtain $E_a \approx 96$ kJ/mol. At low temperatures (close to T_g), the plot deviates from ideal Arrhenius behavior. This deviation arises because free volume effects increasingly influence molecular mobility: as the polymer approaches T_g , molecular motion becomes strongly coupled to the expansion of free volume, and relaxation times no longer follow a simple thermally activated process.



The validity of the WLF equation indicates that polyoctyl methacrylate exhibits time-temperature superposition, meaning that its viscoelastic response at different temperatures can be represented by a single master curve using only horizontal (frequency or time) shifts.

The time-temperature superposition principle holds when all molecular relaxation processes share the same temperature dependence, i.e., they all

accelerate or slow down by the same factor a_T as T changes. In practice, this occurs only when one type of motion dominates the viscoelastic response.

Near the glass transition temperature, this dominant motion is the of segmental character, corresponding to cooperative rearrangements of short chain segments. Therefore, successful WLF-type superposition implies the dominance of a single characteristic relaxation time and is typically valid in the range from T_g to about $T_g + 50-100$ K.

4. The WLF equation can be used to estimate how the melt viscosity of a polymer changes with temperature. Suppose a polymer has a glass transition temperature of 0 °C. At 40 °C, its melt viscosity is $\eta_1 = 2.5 \cdot 10^4$ Pa s. What will its viscosity be at 50 °C?

The melt viscosity is proportional to the relaxation time (see Slide 152), and thus follows the WLF relation:

$$\log\left(\frac{\eta_1}{\eta_g}\right) = -\frac{17.44 \cdot (T_1 - T_g)}{51.6 + (T_1 - T_g)}$$

where η_g is the viscosity at T_g . For $T_1 = 40$ °C = 313 K:

$$\log \eta_g = \log(2.5 \cdot 10^4) + \frac{17.44 \cdot (313 - 273)}{51.6 + (313 - 273)} \approx 12.014$$

Polymers often have a melt viscosity near 10^{12} Pa s at their glass transition temperature (see the definition on Slide 136). For $T_2 = 50$ °C = 323 K:

$$\log \eta_2 = 12.014 - \frac{17.44 \cdot (323 - 273)}{51.6 + (323 - 273)} \approx 3.431$$

$$\eta_2 \approx 2.7 \cdot 10^3 \text{ Pa s}$$

A temperature increase of only 10 °C decreases the melt viscosity by approximately one order of magnitude, illustrating the strong temperature sensitivity of polymer flow near the glass transition region.

Reading suggestion:

- Reader on WLF Equation.

(You can download this document from the Moodle-folder 'Reading Recommendation'.)