School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Polymer Science 2025/26

Exercise 8

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: $\varepsilon = \varepsilon_0$, $\dot{\varepsilon} = \mathrm{d}\varepsilon/\mathrm{d}t = 0$).
   Hint 1: for the Maxwell model, see Slide 263;

   ii) creep experiment under tension (constant stress: $\sigma = \sigma_0$, $\mathrm{d}\sigma/\mathrm{d}t = 0$),
   Hint 2: for the Maxwell model, use the condition $\varepsilon_{\mathrm{dashpot}}(t = 0) = 0$ 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 $\varepsilon(t)$ and solve it, (iv) sketch and interpret the time evolution.

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

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

   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).

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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:

- $t << \tau$;
- $t >> \tau$?

3. The shear storage compliance (J_1) vs log (ω) curves of poly(octyl methacrylate) measured at different T are superimposable when shifted horizontally along the frequency axis. For a reference temperature T_{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(*α*(*T*))**	***T*** **(°C)**	**log(*α*(*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

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?

Reading suggestion:

- Reader on WLF Equation.

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

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