

## Polymer Science 2024/5

### Exercise 7 - Solution

1. Let us try to better understand the simplest phenomenological mechanical models for viscoelasticity under different types of loading. Schematically draw the evolution of strain or stress over time for the Maxwell model and the Voigt model in case of

i) a stress relaxation experiment under tension ( $\varepsilon = \varepsilon_0, d\varepsilon/dt = 0$ ).

Tip 1: for the Maxwell model, see the Slide 249;

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

Tip 2: for the Maxwell model, use the condition  $\varepsilon_{dashpot}(t = 0) = 0$  to find an expression for  $\varepsilon$  that is independent of  $\varepsilon_0$ .

Tip 3: The 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 (graphically depicted on Slide 254)!

#### Maxwell model in the case of stress relaxation:



Hooke & Newton

$$\frac{d\epsilon}{dt} = \frac{d\epsilon_1}{dt} + \frac{d\epsilon_2}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

stress relaxation:  $\epsilon = \epsilon_1 + \epsilon_2 = \epsilon_0 = \text{constant}$

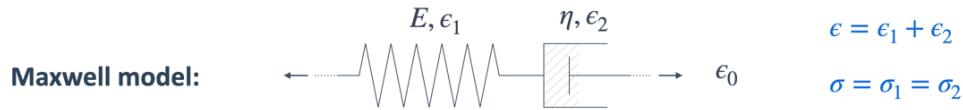
$$\frac{d\epsilon}{dt} = 0 \quad \longrightarrow \quad \frac{d\sigma}{\sigma} = -\frac{E}{\eta} dt$$

integration

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

The stress exponentially decays. However, according this model, the stress completely relaxes over a long time period which is usually not the case for a real polymer.

Maxwell model in the case of creep:



Hooke & Newton  $\longrightarrow$   $\frac{d\sigma}{dt} = E \frac{d\epsilon_1}{dt}$   $\sigma = \eta \frac{d\epsilon_2}{dt}$

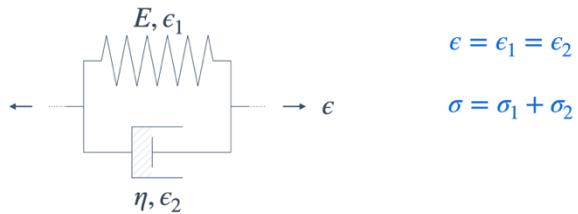
$$\frac{d\epsilon}{dt} = \frac{d\epsilon_1}{dt} + \frac{d\epsilon_2}{dt} \longrightarrow \frac{d\epsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

creep experiment:  $\sigma = \sigma_0$   $\frac{d\sigma}{dt} = 0$   $\longrightarrow$   $\frac{d\epsilon}{dt} = \frac{\sigma_0}{\eta}$   $\xrightarrow{\text{integration}}$   $\epsilon(t) = \epsilon_0 + \frac{\sigma_0}{\eta} t$

initial condition:  $\epsilon_2(t = 0) = 0$   $\longrightarrow$   $\epsilon(t = 0) = \epsilon_1(t = 0) = \frac{\sigma_0}{E}$   $\longrightarrow$   $\epsilon(t) = \frac{\sigma_0}{E} + \frac{\sigma_0}{\eta} t$

Thus, the Maxwell model predicts Newtonian flow: The strain is expected to increase linearly with time, while for a viscoelastic polymer  $d\epsilon/dt$  increases with time. Note also an initial instantaneous strain response ( $\sigma_0/E$ ) of the elastic spring at time  $t=0$ . The Maxwell model may hence provide a better representation of polymer behavior under relaxation (with limitations though!) than under creep.

Voigt (or Kelvin) model in the case of creep and stress relaxation:

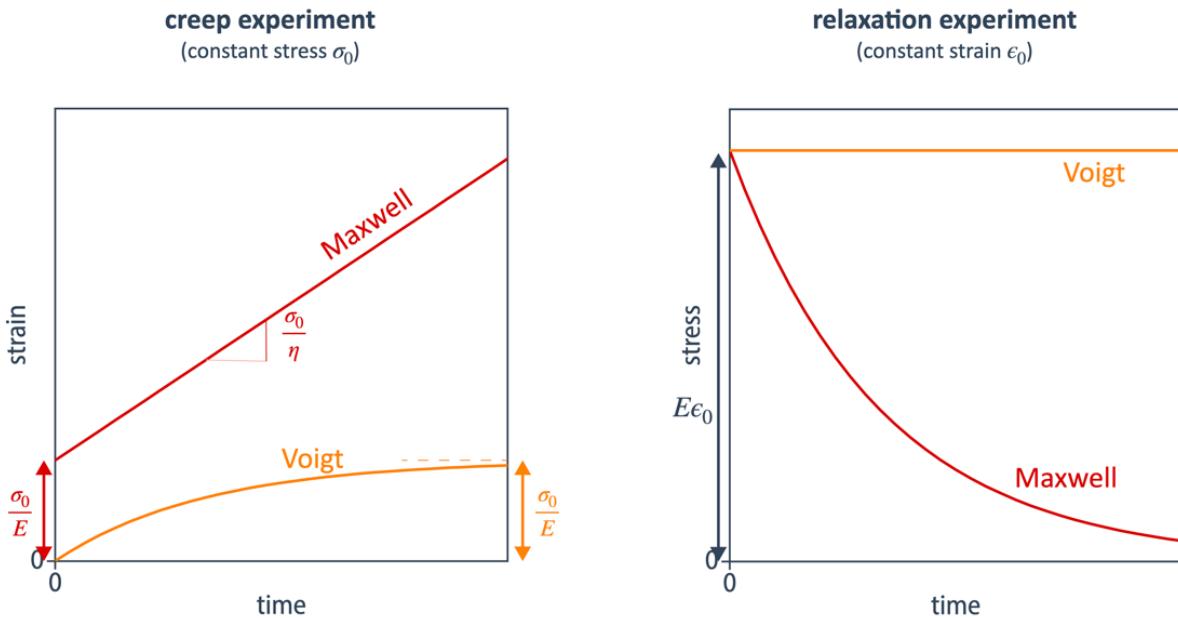


Hooke & Newton  $\longrightarrow$   $\sigma_1 = E\epsilon$   $\sigma_2 = \eta \frac{d\epsilon}{dt}$   $\longrightarrow$   $\frac{d\epsilon}{dt} = \frac{\sigma}{\eta} - \frac{E\epsilon}{\eta}$

creep experiment:  $\sigma = \sigma_0$   $\longrightarrow$   $\frac{d\epsilon}{dt} + \frac{E\epsilon}{\eta} = \frac{\sigma_0}{\eta}$   $\longrightarrow$   $\epsilon = \frac{\sigma_0}{E} \left(1 - e^{-\frac{\eta}{E}t}\right)$

stress relaxation:  $\frac{d\epsilon}{dt} = 0$   $\longrightarrow$   $\frac{\sigma}{\eta} = \frac{E\epsilon_0}{\eta}$   $\longrightarrow$   $\sigma = E\epsilon_0$

Correct creep representation in the sense of a strain rate decreasing with time. However, the Voigt model does not predict relaxation at all.



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

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

where  $\tau = \eta/E$  is the *relaxation time*. Equation 1 implies that most of the strain will occur when the time,  $t$ , is close to  $\tau$ .

What will be the behavior of the Voigt solid in creep within the limits

- $t \ll \tau$ ;
- $t \gg \tau$ ?

As one would expect, in the limit  $t \ll \tau$ ,  $D(t) \rightarrow 0$ , i.e. an infinitely rigid solid, and the strain,  $\varepsilon = 0$  when  $\sigma = \sigma_0 = \text{constant}$  (the dashpot does not allow the spring to respond instantaneously). In the limit  $t \gg \tau$ ,  $D(t) \rightarrow 1/E$ , i.e. elastic behavior with Young's modulus  $E$ , and  $\varepsilon = \sigma_0/E$ . The relaxation time,  $\tau$ , represents the transition time between these two states.

3. A viscoelastic polymer is deformed by a sinusoidal stress, oscillating at an angular frequency  $\omega$ . Assuming that the variation of the strain,  $\varepsilon$ , and the stress,  $\sigma$ , can be represented by the equations:

$$\begin{aligned}\varepsilon &= \varepsilon_0 \sin(\omega t) \\ \sigma &= \sigma_0 \sin(\omega t + \delta)\end{aligned}$$

where  $\delta$  is the phase shift between stress and strain, show that the energy dissipated per deformation cycle,  $\Delta U$ , is given by

$$\Delta U = \sigma_0 \varepsilon_0 \pi \sin(\delta)$$

Tips:  $\frac{\text{work}}{\text{unit volume}} = \Delta U = \int \sigma d\varepsilon \quad \cos^2 x = \frac{1+\cos 2x}{2}$

$$d\varepsilon = \varepsilon_0 \omega \cos(\omega t) dt \quad \text{and} \quad \Delta U = \int_0^T \omega \sigma_0 \varepsilon_0 \sin(\omega t + \delta) \cos(\omega t) dt,$$

where  $T = 2\pi/\omega$  is the periodicity of the cycle.

$$\begin{aligned}& \int_0^T \omega \sigma_0 \varepsilon_0 \sin(\omega t + \delta) \cos(\omega t) dt \\ &= \int_0^T \omega \sigma_0 \varepsilon_0 (\sin(\omega t) \cos(\delta) + \cos(\omega t) \sin(\delta) \cos(\omega t)) dt \\ & \int_0^T \sin(\omega t) \cos(\omega t) dt = 0 \quad \text{and} \quad \int_0^T \frac{1+\cos(2\omega t)}{2} dt = \frac{T}{2} \\ & \Delta U = \sigma_0 \varepsilon_0 \omega \frac{T}{2} \sin(\delta) = \sigma_0 \varepsilon_0 \pi \sin(\delta)\end{aligned}$$