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

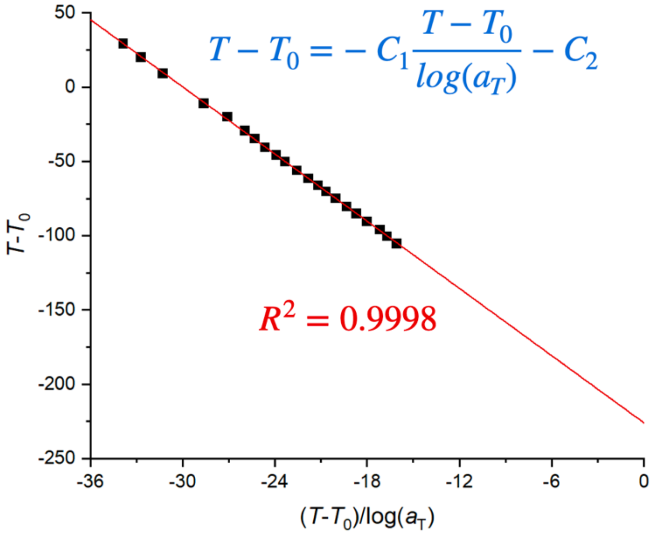
Polymer Science 2024/25

Exercise 8 - Solution

1. The shear storage compliance (J_1) vs log (ω) curves of polyoctyl methacrylate at different T are superimposable. For a reference temperature T_0 = 100 °C, the horizontal displacements, α_T, necessary to carry out such a superposition are given in Table 1.

   Show that this data can be described by the empirical WLF-equation. What are the values of C_1 and C_2?

   The formula is valid, if (for example) (T - T_0)/log (α_T) vs. T - T_0 is a straight line. From the slope obtained after linear regression of the given data, we can deduce C_1 = 7.55 and from the interception with the y-axis, C_2 = 226 K.



Note that the WLF implicitly assumes that the polymer's response to stress (or strain) depends on a single dominant relaxation time across the entire frequency range, at least within the relevant temperature range for the experiment. In reality, polymers may exhibit multiple relaxation processes (such as local motions, segmental motions, and chain motions), each associated with different relaxation times. However, above the glass transition temperature and in the rubbery plateau region, the polymer's viscoelastic

behavior is often dominated by a single characteristic relaxation time, making the WLF equation an effective model for time-temperature superposition.

If the polymer's behavior depends on several relaxation times that have the same temperature dependence, the time-temperature superposition remains valid, and the shifts applied to the curves for different temperatures will align. However, if this is not the case, the shape of the transitions (e.g. modulus or compliance curves) will change with temperature, and the superposition will no longer work as expected. This breakdown occurs because different relaxation processes will shift differently, distorting the superposition. In practice, the time-temperature superposition using the WLF equation is typically valid for temperature between T_g and $T_g + 50$ K, where the polymer exhibits primarily one dominant relaxation process. Outside this temperature range, particularly at lower temperature near or below T_g, the behavior may become more complex, and the WLF equation may not adequately describe the material's dynamics.

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

The melt viscosity is proportional to the relaxation time (see Slide 137). Hence:

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

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

Polymer often have a melt viscosity near 10^{12} Pa s at their glass transition temperature (see the definition on Slide 121). The viscosity at 50 °C is calculated accordingly:

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

$$\log \eta_2 \approx 2.70 \cdot 10^3 \text{ Pa s}$$

Thus, a 10 °C increase in temperature has decreased the melt viscosity by approximately one order of magnitude.

3. In a relaxation test, a constant strain is applied and we look at the evolution of the stress as a function of time. In shear and for an applied strain, γ_0, for example, we can write

$$\sigma = G(t)\gamma_0$$

where $G(t)$ is the relaxation modulus. According to the phenomenological models (springs and dashpot) generalized for a linear viscoelastic material

$$G(t) = G_\infty + \textstyle\sum_1^n G_i e^{-t/\tau_i} \qquad (1)$$

where the parameters G_∞ and G_i are adjustable (within the limit of an infinite number of elements, the G_i can be replaced by a continuous function, the relaxation time spectrum, and the sum by an integral).

In Rouse's model for a dilute solution of N_m chains per unit volume, each containing n bonds, the expression for $G(t)$ becomes

$$G(t) = N_m kT \sum_{p=1}^{m} e^{-t/\tau_p} \qquad \tau_p \approx \frac{\xi m^2 r_s^2}{6\pi^2 p^2 kT} = C\frac{n^2}{p^2}, \qquad p = 1,2,\ldots$$

and C is a constant, provided that $m >> p$, and $m >> 1$.

i) What do m, p, ξ and r_s^2 mean? Why is the effective value of G_∞ equal to 0 in this case?

Rouse's model consists of a chain of n bonds of length l divided into m - 1 segments per m "beads" (including two at each end of the chain) which interact with the solvent, so that the force on the i^{th} ball at the position $\vec{r}$ is given by

$$f = \xi\frac{d\vec{r}_i}{dt}$$

where ξ is a friction coefficient. So, each segment contains $n/(m$ - 1) bonds and r_s^2, the mean square distance of such a chain segment, is

$$r_s^2 = \frac{n}{m-1}l^2 \approx \frac{n}{m}l^2$$

assuming that $m >> 1$ and that it is a freely jointed chain. Finally, p defines the chain length characteristic of each relaxation mode, that is, the number of segments involved in the p mode is therefore equal to n/p. $p = 1$ denotes

the relaxation mode involving the whole chain, $p = 2$ half chain lengths, $p = 3$ a third of the chain, etc.

In the long-time limit (as $t \to \infty$), each term in the sum approaches zero because the exponential decay becomes negligibly small for large t. This means that the stress response eventually vanishes as the system reaches equilibrium. Thus, in the long-time limit, the relaxation modulus G_∞, which represents the final steady-state stress after which all relaxation processes have occurred is zero.

ii) If the monomeric friction coefficient $\xi_o = n\xi/m$, show that

$$\tau_p \approx \frac{\xi_o n^2 l^2}{6\pi^2 p^2 kT}, \qquad for \quad m \gg 1, p$$

and therefore, that the maximum relaxation time, the "Rouse relaxation time", is proportional to M^2.

$$\tau_p \approx \frac{\xi m^2 r_s^2}{6\pi^2 p^2 kT} = \frac{m^2}{6\pi^2 p^2 kT}\left(\frac{n\xi_o}{m}\right)\left(\frac{nl^2}{m}\right) = \frac{\xi_o n^2 l^2}{6\pi^2 p^2 kT}$$

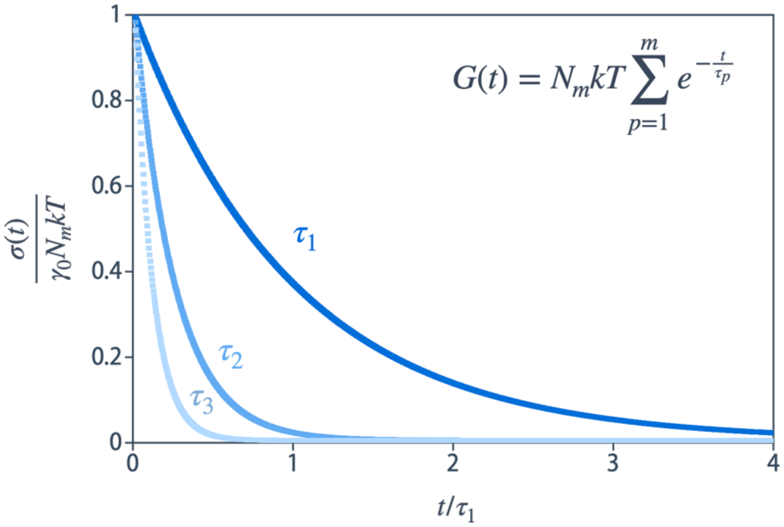
The mass of the chain is equal to nM_b and the Rouse relaxation time which corresponds to $p = 1$ is given by $\tau_R \propto M^2$, therefore.

iii) Draw schematically the evolution of $\sigma/N_m kT$ as a function of t/τ_1 for the component of $G(t)$ which corresponds to $p = 1$ (this is the slowest mode of relaxation). Add the contributions that correspond to $p = 2$ and 3 to the same diagram. In general, what can we say about the contribution to the stress of fast relaxation modes, when $t \geq \tau_1$?

According to the expression for G(t),

$$\frac{\sigma(t)}{\gamma_0 N_m kT} = \sum_{p=1}^{m} e^{-t/\tau_p}$$

and we must therefore plot $\sigma(t)/\gamma_0 N_m kT$ as a function of t/τ_1, which is a simple exponential decrease.



The contributions of the terms corresponding to comparably fast relaxation modes decrease relatively quickly, so the contribution to the stress of the fast relaxation modes becomes negligible when $t \geq \tau_1$

iv) These expressions are valid for relatively long times (if we ignore the hydrodynamic effects related to the solvent), but one meets problems with very short times, where one must take the contributions of modes corresponding to high p into account. Indeed, the choice of m, which defines the maximum value of p, is arbitrary, but does the model remain reasonable when m approaches n?

We see that we can ignore the contributions of high p terms if $t >> \tau_p$. In other words, if we want to model the response to short t, it is necessary to include terms corresponding to sufficiently high p so that the condition $t >> \tau_p$ is always respected. But if p and therefore m are too high, we reduce the number of bonds in each segment too much, so that we cannot apply the theory on rubber elasticity (which admits long chains). Indeed, if m tends to n, we end up having subchains containing $n/(m\text{-}1) \approx 1$ bond! So, this model does not work for too short times.

v) Suppose that $\tau_1 = \infty$ and that $\tau_p = 0$ for $p > 1$. Write the resulting expression for $G(t)$. What do you notice? Interpret this result.

$$G(t) = N_m kT e^{-t/\infty} + N_m kT \sum_{p=2}^{m} e^{-t/\tau_p} = N_m kT + N_m kT \sum_{p=2}^{m} e^{-t/\tau_p}$$

For $t > 0$, the contributions from the higher Rouse modes ($p > 1$) decay instantaneously to zero because their relaxation times are $\tau_p = 0$. Consequently, these modes do not contribute to the shear modulus. Meanwhile, the longest relaxation time, $\tau_1 = \infty$, implies that the material does

not relax in response to stress in the first mode, which corresponds to the overall motion of the polymer chain (e.g., the movement of the two ends of the chain). Therefore, only the first mode contributes to the shear modulus, and the system behaves as if it has a constant, time-independent modulus $G = N_m kT$.

This result is reminiscent of elastomers, where crosslinks between polymer chains prevent full relaxation. For elastomers, the shear modulus G is expressed as $G = N$kT, where N is the number of crosslinks per unit volume. In the present model, we simulate a system where all polymer chains are crosslinked at their ends, which prevents the relaxation of the overall chain motion (mode $p = 1$).

By eliminating the contributions from modes with $p > 1$, we assume the chain can change its conformation freely and instantaneously, except for the overall motion (mode p = 1) which is blocked. This is a key feature of elastomeric behavior, where the material's elasticity arises from the connectivity (crosslinking) between polymer chains, not from the intrinsic relaxation properties of the individual chains. Note that the absence of intermolecular forces is one of the assumptions underlying elastomeric behavior.

This model here is particularly valid for an amorphous polymer with $M < 2M_e$ at $T >> T_g$.