Time-Temperature Superposition of Rheological Data

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Rheological data are a function of:
- rate (frequency or deformation rate),
- temperature, and
- material identity.

For a given material, the temperature- and rate-dependencies are related.

Figure 6.43, p. 202 Dannhauser et al.; P-OctylMethacrylate
Rheological differences among materials are observed to be divided into two classes:

- Material differences that are temperature-dependent
- Material differences that are independent of temperature

We seek a way to look at rheological data that separates out the temperature effects from the rest of the material effects.

For polymers, it has become customary to think of material behavior as arising from:

- Relaxation moduli, $g_i$
- Relaxation times, $\lambda_i$

Both are temperature-dependent.

$$G' = G'(\omega, \lambda_i, g_i)$$

$$G'' = G''(\omega, \lambda_i, g_i)$$
Exploring Temperature/Rate Relationship in Rheological Data

- Material differences that are temperature dependent
- Material differences that are independent of temperature

• Relaxation moduli, \( g_i \)
• Relaxation times, \( \lambda_i \)

Both are temperature dependent.

\[
G' = G' (\omega, \lambda_i, g_i) \\
G'' = G'' (\omega, \lambda_i, g_i)
\]

For the moduli, we can use experience with cross-linked rubbers (no \( \omega \)-dependence) to determine how the \( g_i \) vary with \( T \).
Exploring Temperature/Rate Relationship in Rheological Data

- Material differences that are temperature-dependent
- Material differences that are independent of temperature

- Relaxation moduli, $g_i$
- Relaxation times, $\lambda_i$

Both are temperature-dependent.

$$G' = G'\left(\omega, \lambda_i, g_i\right)$$
$$G'' = G''\left(\omega, \lambda_i, g_i\right)$$

The $T$-dependence of $\lambda_i$ is coupled with frequency; we discuss this first.

For the moduli, we can use experience with cross-linked rubbers (no $\omega$-dependence) to determine how the $g_i$ vary with $T$.

Exploring Temperature/Rate Relationship in Rheological Data

$$G' = G'\left(\omega, \lambda_i, g_i\right)$$
$$G'' = G''\left(\omega, \lambda_i, g_i\right)$$

- **Relaxation time** enters into the physics of polymers in conjunction with rate:

  $$\left(\frac{1}{\text{time}}\right)$$

- The relaxation time of a molecular or other material process is the characteristic time-constant of the process.

- Depending on the rate of excitation or perturbation, different processes are responsive in a material.

- Rate and time appear together in rheological response:

  $$\omega \lambda$$
Example: plot a simple function: \( f(\omega, \lambda) = \sin(\omega \lambda) + \omega \lambda \)

When plotted versus \( \omega \), we obtain a family of curves. When plotted versus the combined variable, we obtain a master curve.

Exploring Temperature/Rate Relationship in Rheological Data

Consider the temperature-dependence of \( \lambda \).

As it affects a rheological material function:

\[
G' = G'(\omega, \lambda_i, g_i)
\]

In general:

\[
G' = G'(\omega \lambda_{1}, \omega \lambda_{2}, \omega \lambda_{3}, \ldots, g_i)
\]

Suppose that the temperature-dependence of \( \lambda_i \) could be factored out.

Ignore for now
Suppose that the temperature-dependence of $\lambda_i$ could be factored out.

Let $a_T$ be the temperature-dependence of $\lambda_i$.

\[ \lambda_i (T) \equiv a_T (T) \tilde{\lambda}_i \]

not a function of temperature

**Empirical observation:** for many materials, all the relaxation times have the same functional dependence on temperature.

$a_T$ is the temperature-dependence of all the $\lambda_i$.

\[ \lambda_i (T) \equiv a_T (T) \tilde{\lambda}_i \]

not a function of temperature

In general:

\[ G' = G' (\omega \lambda_{1}, \omega \lambda_{2}, \omega \lambda_{3}, \ldots \lambda_i) \]

Not temperature dependent

Now, we can associate the temperature-dependence function with the frequency.

\[ G' = G' (\omega a_T \lambda_{1}, \omega a_T \lambda_{2}, \omega a_T \lambda_{3}, \ldots \lambda_i) \]

\[ G' = G' (\omega a_T \tilde{\lambda}_{1}, \omega a_T \tilde{\lambda}_{2}, \omega a_T \tilde{\lambda}_{3}, \ldots \lambda_i) \]

\[ G' = G' (\omega a_T \tilde{\lambda}_{1}, \tilde{\lambda}_{2}, \tilde{\lambda}_{3}, \ldots \tilde{\lambda}_{n}, \lambda_i) \]

\[ G' = G' (\omega a_T \tilde{\lambda}_{i}, \lambda_i) \]
Now, we can associate the temperature-dependence function with the frequency.

\[ G' = G' (\omega \lambda_1, \omega \lambda_2, \omega \lambda_3, ... g_i) \]

\[ G' = G' (\omega a_T \bar{\lambda}_1, \omega a_T \bar{\lambda}_2, \omega a_T \bar{\lambda}_3, ... g_i) \]

\[ G' = G' \left( (\omega a_T) \bar{\lambda}_1, (\omega a_T) \bar{\lambda}_2, (\omega a_T) \bar{\lambda}_3, ... g_i \right) \]

\[ G' = G' (\omega a_T, \bar{\lambda}_1, \bar{\lambda}_2, \bar{\lambda}_3, ... \bar{\lambda}_n, g_i) \]

Now, what is temperature dependence of the \( g_i \)?

\[ G' = G' (\omega a_T, \bar{\lambda}_i, g_i) \]

What is temperature dependence of the \( g_i \)?

• In cross linked rubber, modulus is proportional to absolute temperature and density

\[ g_i(T) = g_i \left( T \tilde{g}_i \rho \right) \]

Temperature dependence of all moduli is given by \( T \rho \)

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\[ g_i(T) = g_i(T\tilde{g}_i\rho) \]

**Theoretical result:** the \( g_i \) enter into the functions for \( G', G'' \) such that \( T\rho \) can be factored out of the function.

\[
g'_T = \frac{G'}{T\rho} = f\left(a_T\omega, \tilde{\lambda}_i, \tilde{g}_i\right)\]
\[
g''_T = \frac{G''}{T\rho} = \tilde{f}\left(a_T\omega, \tilde{\lambda}_i, \tilde{g}_i\right)\]

Therefore if we plot reduced variables, we can suppress all of the temperature dependence of the moduli.

\[
G'_T \equiv \frac{G'(T)T_{\text{ref}}\rho_{\text{ref}}}{T\rho} = f\left(a_T\omega, \tilde{\lambda}_i, \tilde{g}_i\right)T_{\text{ref}}\rho_{\text{ref}} = G'(T_{\text{ref}})\]
\[
G''_T \equiv \frac{G''(T)T_{\text{ref}}\rho_{\text{ref}}}{T\rho} = \tilde{f}\left(a_T\omega, \tilde{\lambda}_i, \tilde{g}_i\right)T_{\text{ref}}\rho_{\text{ref}} = G'(T_{\text{ref}})\]

Plots of \( G'_T, G''_T \) versus \( a_T\omega \) will therefore be independent of temperature. 

(\text{will still depend on the material through the } \tilde{\lambda}_i, \tilde{g}_i)
Shift Factors

Arrhenius equation

\[ a_T = \exp \left[ -\frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \]

found to be valid for \( T > T_g + 100^\circ C \)

Williams-Landel-Ferry (WLF) equation

\[ \log a_T = \frac{-c_0(T - T_{ref})}{c_2 + (T - T_{ref})} \]

found to be valid within 100°C of \( T_g \)

Shifting other Material Functions

Other linear viscoelastic material functions:

\[ \eta' = \frac{G''(T)}{\omega} \]
\[ \eta^* = \frac{G'(T)}{\omega} \]
\[ \tan \delta = \frac{G^*}{G'} \]
\[ J' = \frac{1/G'}{1 + \tan^2 \delta} \]
\[ J^* = \frac{1/G^*}{1 + (\tan^2 \delta)^{1/2}} \]

Independent of temperature

\[ G'_r = \frac{G'(T)T_{ref}P_{ref}}{T \rho} = f(a, \omega, \tilde{\lambda})T_{ref}P_{ref} = G'(T_{ref}) \]
\[ G^*_r = \frac{G^*(T)T_{ref}P_{ref}}{T \rho} = h(a, \omega, \tilde{\lambda})T_{ref}P_{ref} = G^*(T_{ref}) \]
Shifting other Material Functions

**linear viscoelastic**

\[
\eta'_r = \frac{G'(T) T_{ref} \rho_{ref}}{a_r \omega T \rho} = \frac{\eta' T_{ref} \rho_{ref}}{a_r T \rho}
\]

\[
\eta''_r = \frac{G''(T) T_{ref} \rho_{ref}}{a_r \omega T \rho} = \frac{\eta'' T_{ref} \rho_{ref}}{a_r T \rho}
\]

\[
J'_r = \frac{J'(T) T \rho}{T_{ref} \rho_{ref}}
\]

\[
J''_r = \frac{J''(T) T \rho}{T_{ref} \rho_{ref}}
\]

**steady shear**

\[
\eta_r(\alpha_T \dot{\gamma}) = \eta(T) T_{ref} \rho_{ref} \frac{a_r T \rho}{a_T T \rho}
\]

\[
\tan \delta = \frac{G''}{G'} = \text{independent of temperature when plotted versus reduced frequency}
\]

Steady shear viscosity - Temperature dependence

**Figure 6.46, p. 204 Gruver and Kraus; PB melt**
Another consequence of $\lambda_i(T) = \tilde{\lambda}_i a_T(T)$ is the similarity between $\log G'(\omega)$ and $\log G'(T)$.

Take data for $G'$, $G''$ at a fixed $\omega$ for a variety of $T$.

$$G'_r(T) = \frac{G'(T)T_{\text{ref}} \rho_{\text{ref}}}{T \rho} = f(a_T, \omega, \tilde{\lambda}_i)$$

$$G''_r(T) = \frac{G''(T)T_{\text{ref}} \rho_{\text{ref}}}{T \rho} = h(a_T, \omega, \tilde{\lambda}_i)$$

But since $\log a_T$ is approximately a linear function of $T$,

Curves of $\log G'$ versus $T$ (not $\log T$) at constant $\omega$ resemble slightly skewed plots of $\log G'$ versus $\log a_T \omega$.

(mirror image)
Application of SAOS

Using $G'(T)$ in research on pressure-sensitive adhesives

Figure 6.48, p. 207 Kim et al.; SIS block copolymer with tackifier

Instructions for Time-Temperature Shifting of Rheological Data using Microsoft Excel

www.chem.mtu.edu/~fmorriso/cm4655/TimeTempSuperpositionWithExcel.pdf

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Done!