Experimental Data (continued)

Next

Unsteady shear flow

- Small strain - SAOS, step strain **1**
  - *linear polymers, material effects,*
  - **2** *temperature effects*
- Large strain - start-up, cessation, creep, large-amplitude step strain

Time-temperature superposition

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later . ..

Steady elongation

Unsteady elongation

Small-Amplitude Oscillatory Shear - temperature dependence

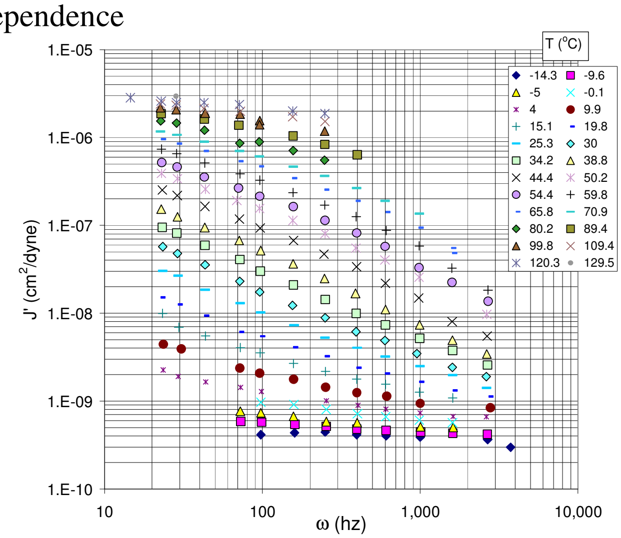


Figure 6.43, p. 202 Dannhauser et al.; P-OctylMethacrylate

Time-Temperature Superposition

Material functions depend on g_i, λ_i

relaxation times

relaxation moduli

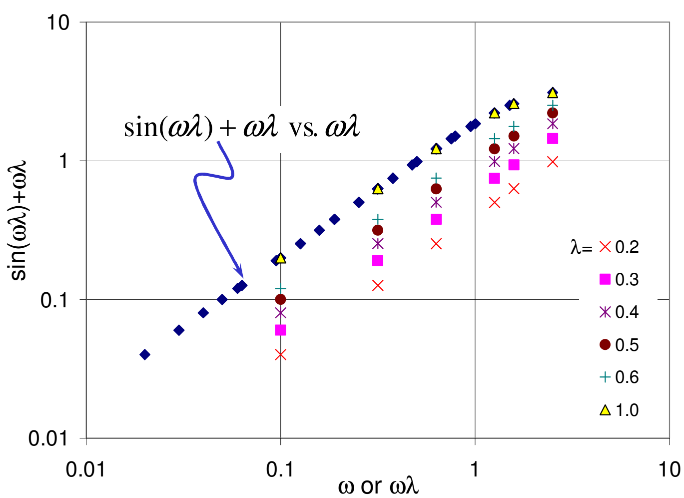
$$G' = G'(\omega, \lambda_i, g_i)$$
$$G'' = G''(\omega, \lambda_i, g_i)$$

g_i, λ_i are in turn functions of temperature and material properties

> *Theoretical result*: in the linear-viscoelastic regime, material functions are a function of $\omega\lambda_i$ rather than of ω and λ_i individually.

Example: plot a simple function

$$f(\omega, \lambda) = \sin(\omega\lambda) + \omega\lambda$$



In general,

$$G' = G'(\omega\lambda_1(T),\ \omega\lambda_2(T),\ \omega\lambda_3(T),\ \ldots\quad)$$

Suppose that the temperature-dependence of λ_i could be factored out. Let $a_{Ti}(T)$ be the temperature-dependence of λ_i.

$$\lambda_i(T) = a_{Ti}(T)\tilde{\lambda}_i$$

not a function of temperature

Then we could group the temperature-dependence function with the frequency.

$$G' = G'(a_{T1}\omega\tilde{\lambda}_1,\ a_{T2}\omega\tilde{\lambda}_2,\ a_{T3}\omega\tilde{\lambda}_3,\ \ldots\quad)$$

Time-Temperature Superposition

- Relaxation times decrease strongly as temperature increases
- Moduli associated with relaxations are proportional to absolute temperature; depend on density

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

$$\lambda_i(T) = \tilde{\lambda}_i a_T(T)$$

temperature dependence of all relaxation times

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

temperature dependence of all moduli

Second theoretical result: the g_i enter into the functions for G', G'' such that $T\rho$ can be factored out of the function

$$\frac{G'}{T\rho} = \tilde{f}(a_T\omega, \tilde{\lambda}_i)$$

$$\frac{G''}{T\rho} = \tilde{h}(a_T\omega, \tilde{\lambda}_i)$$

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

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

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

Plots of G'_r, G''_r versus $a_T\omega$ will therefore be independent of temperature.

(will still depend on the material through the $\tilde{\lambda}_i$)

Shifting other Material Functions

linear viscoelastic

$$\eta'_r \equiv \frac{G''(T)T_{ref}\rho_{ref}}{a_T\omega T\rho} = \frac{\eta' T_{ref}\rho_{ref}}{a_T T\rho}$$

$$\eta''_r \equiv \frac{G'(T)T_{ref}\rho_{ref}}{a_T\omega T\rho} = \frac{\eta'' T_{ref}\rho_{ref}}{a_T T\rho}$$

$$J'_r \equiv \frac{J'(T)T\rho}{T_{ref}\rho_{ref}}$$

$$J''_r \equiv \frac{J''(T)T\rho}{T_{ref}\rho_{ref}}$$

steady shear

$$\eta_r(a_T\dot{\gamma}) = \frac{\eta(T)T_{ref}\rho_{ref}}{a_T T\rho}$$

Small-Amplitude Oscillatory Shear - temperature dependence

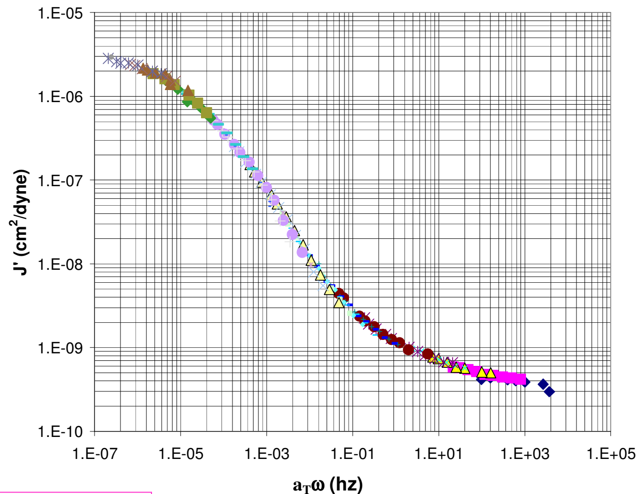


Figure 6.44, p. 202 Dannhauser et al.; P-OctylMethacrylate

Small-Amplitude Oscillatory Shear - temperature dependence

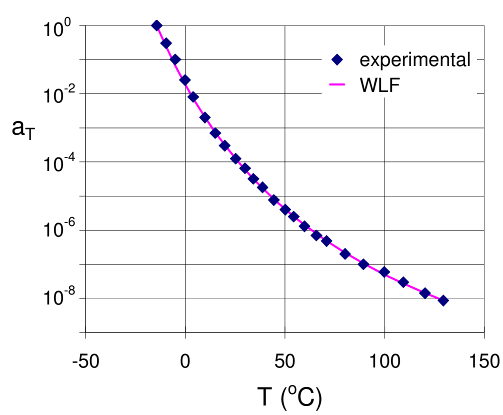


Figure 6.45, p. 203 Dannhauser et al.; P-OctylMethacrylate

Shift Factors

Arrhenius equation

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

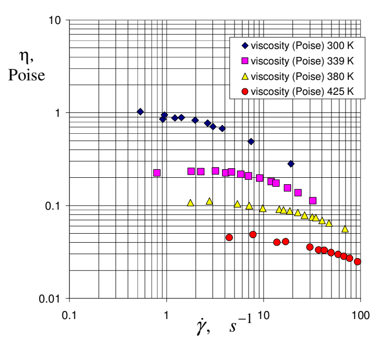
found to be valid for $T > T_g + 100°C$

Williams-Landel-Ferry (WLF) equation

$$\log a_T = \frac{-c_1^0 (T - T_{ref})}{c_2^0 + (T - T_{ref})}$$

found to be valid *w/in* 100°C of T_g

Steady shear viscosity - Temperature dependence



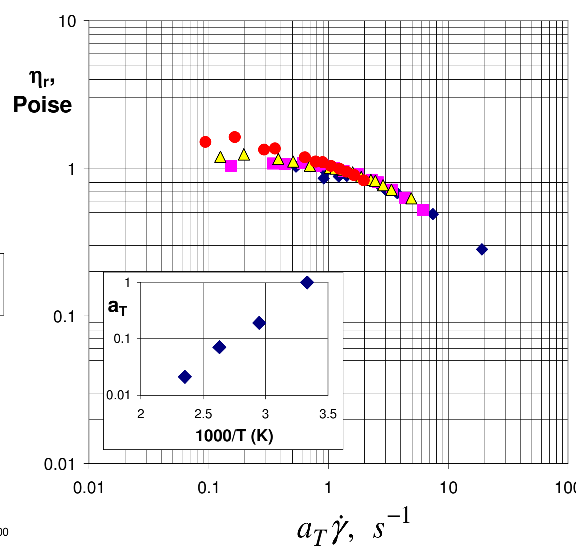
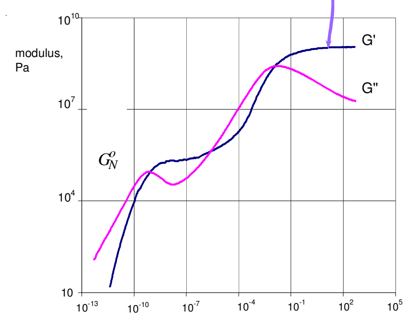


Figure 6.46, p. 204 Gruver and Kraus; PB melt

Another consequence of $\lambda_i(T) = \tilde{\lambda}_i a_T(T)$ is the similarity between log $G'(\omega)$ and log $G'(T)$.



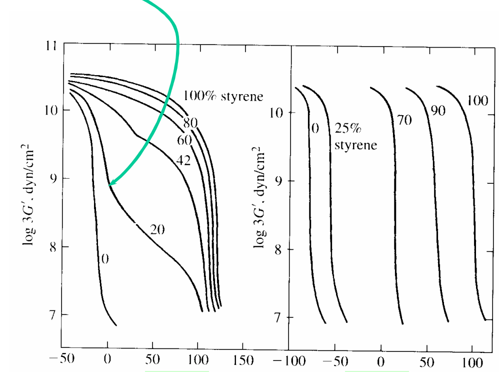


Figure 6.30, p. 192 Plazek and O'Rourke; PS

Figure 6.39, p. 198 Cooper and Tobolsky; SIS block and SBS random

Take data for G', G'' at a fixed ω for a variety of T.

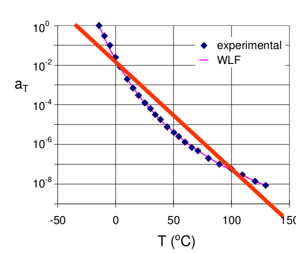
$$G_r' \equiv \frac{G'(T)T_{ref}\rho_{ref}}{T\rho} = f(a_T\omega, \tilde{\lambda}_i)$$

but, what is $a_T(T)$?

We do not know.

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

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



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

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

Height of plateau modulus and temperature of glass transition are key performance factors for PSAs.

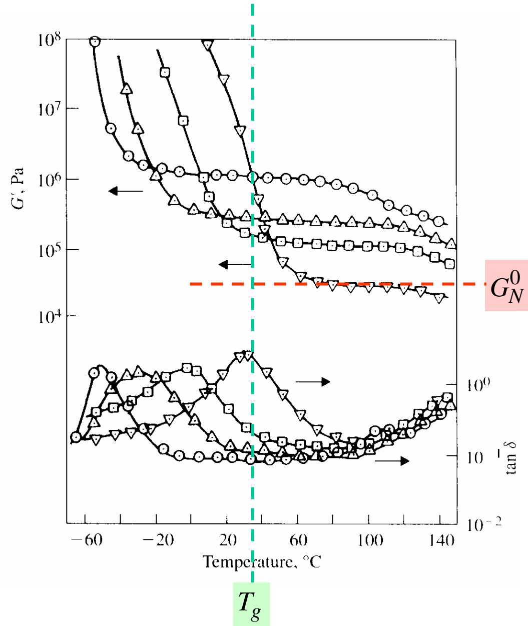


Figure 6.48, p. 207 Kim et al.; SIS block copolymer with tackifier