

Time-Temperature Superposition WHICH VARIABLES ARE TEMPERATURE DEPENDENT IN THE ROUSE AND REPTATION MODELS?

Rouse Relaxation Modulus:

$$G(t) = \frac{\rho(T)RT}{M} \sum_{p=1}^N e^{-tp^2/\lambda_R}$$

Rouse Relaxation Time:

$$\lambda_R = \frac{a^2 N^2 \zeta(T)}{6\pi^2 kT}$$

Reptation Relaxation Modulus:

$$G(t) = \frac{8}{\pi^2} \frac{\rho(T)RT}{M_e} \sum_{p \text{ odd}}^N \frac{1}{p^2} e^{-p^2 t/\lambda_d}$$

Reptation Relaxation Time:

$$\lambda_d = \frac{a^2 N^2 \zeta(T)}{\pi^2 kT} \frac{M}{M_e}$$

Both models have the same temperature dependence. This is hardly surprising, since reptation is just Rouse motion confined in a tube.

$$\text{Modulus Scale} \quad G \sim \rho(T)T$$

$$\text{Time Scale} \quad \lambda \sim \frac{\zeta(T)}{T} \sim \lambda_N$$

Since the friction factor is related to the shortest Rouse mode λ_N .

$$\lambda_N = \frac{a^2 \zeta(T)}{6\pi^2 kT}$$

Time-Temperature Superposition METHOD OF REDUCED VARIABLES

All relaxation modes scale in the same way with temperature.

$$\lambda_i(T) = a_T \lambda_i(T_0) \quad (2-116)$$

a_T is a time scale shift factor

T_0 is a reference temperature ($a_T \equiv 1$ at $T = T_0$).

$$G_i(T) = \frac{G_i(T_0) T \rho}{T_0 \rho_0} \quad (2-117)$$

Recall the Generalized Maxwell Model

$$G(t) = \sum_{i=1}^N G_i \exp(-t/\lambda_i) \quad (2-25)$$

with full temperature dependences of the Rouse (and Reptation) Model

$$G(t, T) = \frac{T \rho}{T_0 \rho_0} \sum_{i=1}^N G_i(T_0) \exp\{-t/[\lambda_i(T_0) a_T]\} \quad (2-118)$$

We simplify this by defining **reduced variables** that are independent of temperature.

$$G_r(t) \equiv G(t, T) \frac{T_0 \rho_0}{T \rho} \quad (2-119)$$

$$t_r \equiv \frac{t}{a_T} \quad (2-120)$$

$$G_r(t_r) = \sum_{i=1}^N G_i(T_0) \exp[-t_r/\lambda_i(T_0)] \quad (2-118)$$

Plot of G_r as a function of t_r is a **universal curve** independent of temperature.

Time-Temperature Superposition EMPIRICAL MASTER CURVE

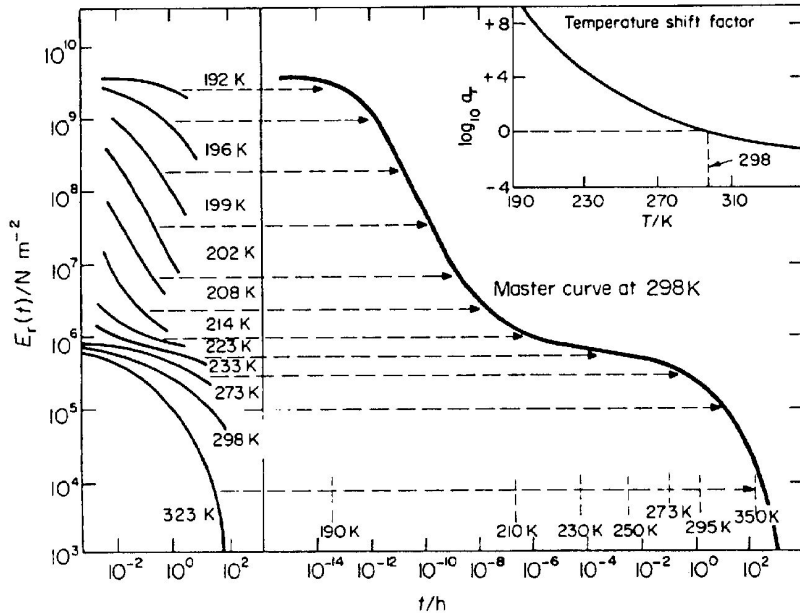


Figure 1: Reduced Variables Generates a Master Curve from the Stress Relaxation Modulus Data for a Polymer Melt.

Can now estimate the relaxation modulus at any temperature in the range $192\text{K} < T < 350\text{K}$, covering EIGHTEEN ORDERS OF MAGNITUDE IN TIME!

Time-Temperature Superposition

TEMPERATURE DEPENDENCE OF VISCOSITY (P. 1)

Recall

$$\eta_0 = \int_0^{\infty} G(t)dt \quad (2-19)$$

$$G_r(t) \equiv G(t, T) \frac{T_0 \rho_0}{T \rho} \quad (2-119)$$

Substitute for $G(t)$.

$$\eta_0(T) = \frac{T \rho}{T_0 \rho_0} \int_0^{\infty} G_r(t)dt$$

Change integration variable to $t_r \equiv t/a_T$, so $dt = a_T dt_r$.

$$\eta_0(T) = \frac{a_T T \rho}{T_0 \rho_0} \int_0^{\infty} G_r(t_r)dt_r \quad (2-122)$$

Since $G_r(t_r)$ refers to the reference temperature T_0

$$\eta_0(T_0) = \int_0^{\infty} G(t, T_0)dt = \int_0^{\infty} G_r(t_r)dt_r \quad (2-123)$$

we can rewrite (2-122)

$$\eta_0(T) = \frac{a_T T \rho}{T_0 \rho_0} \eta_0(T_0) \quad (2-125)$$

Solve for a_T

$$a_T = \frac{\eta_0(T) T_0 \rho_0}{\eta_0(T_0) T \rho} \quad (2-126)$$

Since viscosity is far more temperature dependent than $T \rho$

$$a_T \cong \frac{\eta_0(T)}{\eta_0(T_0)} \quad (2-127)$$

Time-Temperature Superposition

TEMPERATURE DEPENDENCE OF VISCOSITY (P. 2)

Arrhenius equation — Viscosity is thermally activated (first applied to viscosity by Andrade)

$$\eta_0 \sim \exp \left[\frac{E_a}{RT} \right] \quad T > T_g + 100\text{K}$$

E_a is the activation energy for flow

$$\frac{\eta_0(T)}{\eta_0(T_0)} = \exp \left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad T > T_g + 100\text{K} \quad (2-128)$$

Doolittle equation — Viscosity is determined by free volume v_f

$$\eta_0 \sim \exp \left[\frac{B(v - v_f)}{v_f} \right]$$

$$\ln \eta = \ln A + \frac{B(v - v_f)}{v_f} \quad (10-11)$$

If one assumes free volume v_f is proportional to temperature

$$v_f = v_f(T_g) + \alpha_f(T - T_g) \quad (10-12)$$

one gets the WLF (Williams-Landel-Ferry) EQUATION

$$\log \eta_0(T) = \log \eta_0(T_g) - \frac{(B/2.3f_g)(T - T_g)}{(f_g/\alpha_f) + T - T_g} \quad (10-13)$$

$f_g = v_f(T_g) / [v_f(T_g) + v_o(T_g)]$ is the fractional free volume at T_g

WLF EQUATION for an arbitrary reference temperature T_0

$$\log(a_T) = \frac{-C_1^0(T - T_0)}{[C_2^0 + T - T_0]} \quad (2-129)$$

At high temperatures WLF approaches Arrhenius behavior with an activation energy

$$E_a = 2.303RC_1^0C_2^0 \cong 4 \text{ kcal/mole}$$

Time-Temperature Superposition SUMMARY

The modulus scale shift factor is really more complicated than

$$G_r(t) \equiv G(t, T) \frac{T_0 \rho_0}{T \rho} \quad (2-119)$$

because the entanglement molecular weight can depend weakly on temperature. Thus we generally write

$$G_r(t) \equiv \frac{G(t, T)}{b_T}$$

The Rouse Model has

$$b_T = \frac{T \rho}{T_0 \rho_0}$$

but most polymers do not obey this equation, so b_T is treated as an empirical modulus scale shift (analogous to a_T for the time scale shift, but b_T is much smaller).

$$t_r \equiv \frac{t}{a_T} \quad (2-120)$$

$$G(t, T) = b_T G\left(\frac{t}{a_T}, T_0\right)$$

$$G'(\omega, T) = b_T G'(\omega a_T, T_0)$$

$$G''(\omega, T) = b_T G''(\omega a_T, T_0)$$

$$J(t, T) = \frac{J\left(\frac{t}{a_T}, T_0\right)}{b_T}$$

Time-Temperature Superposition EXAMPLE

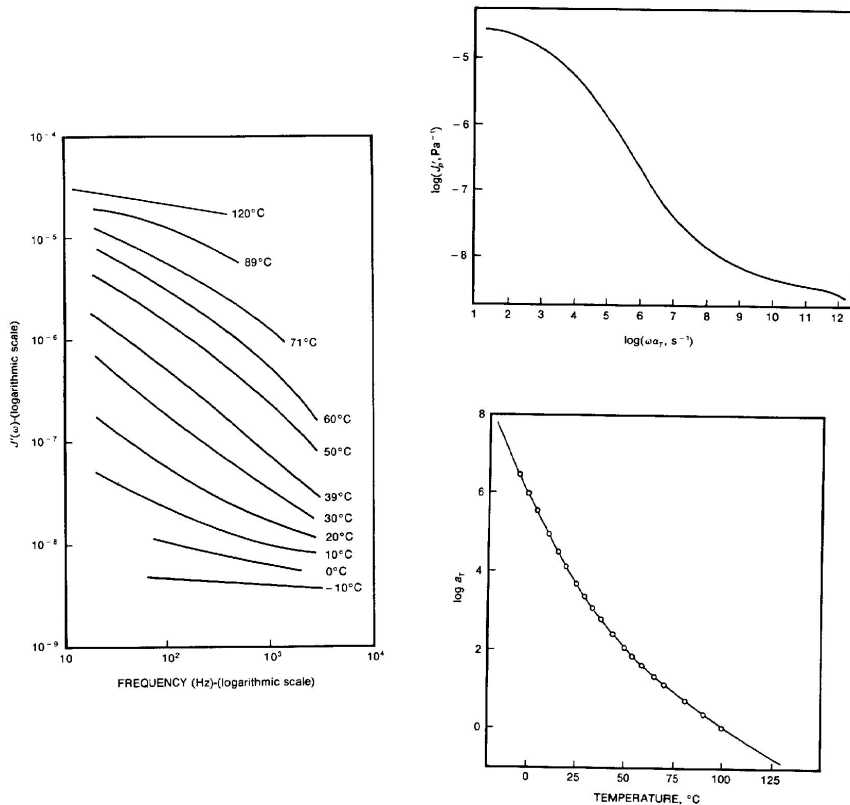
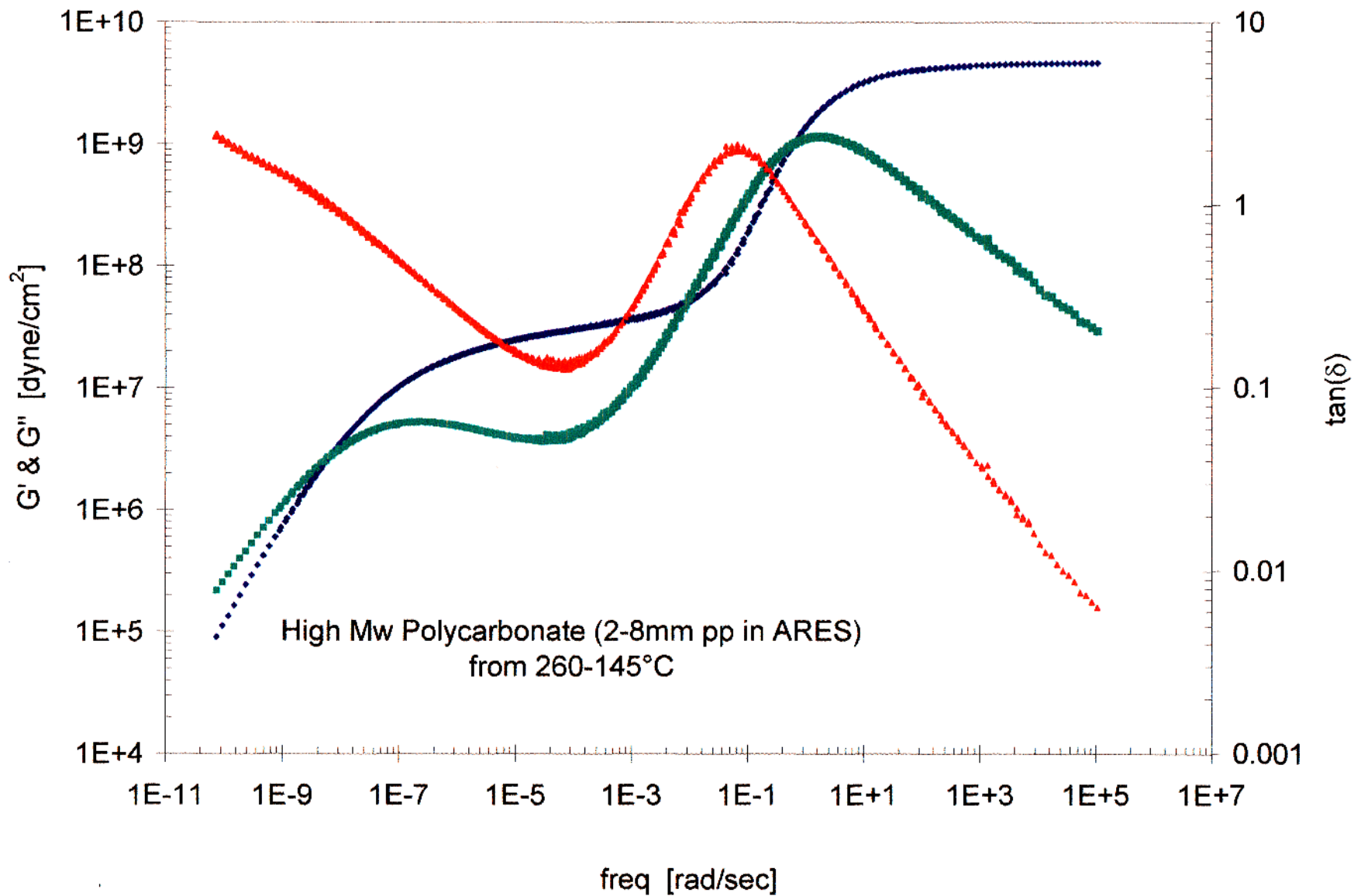
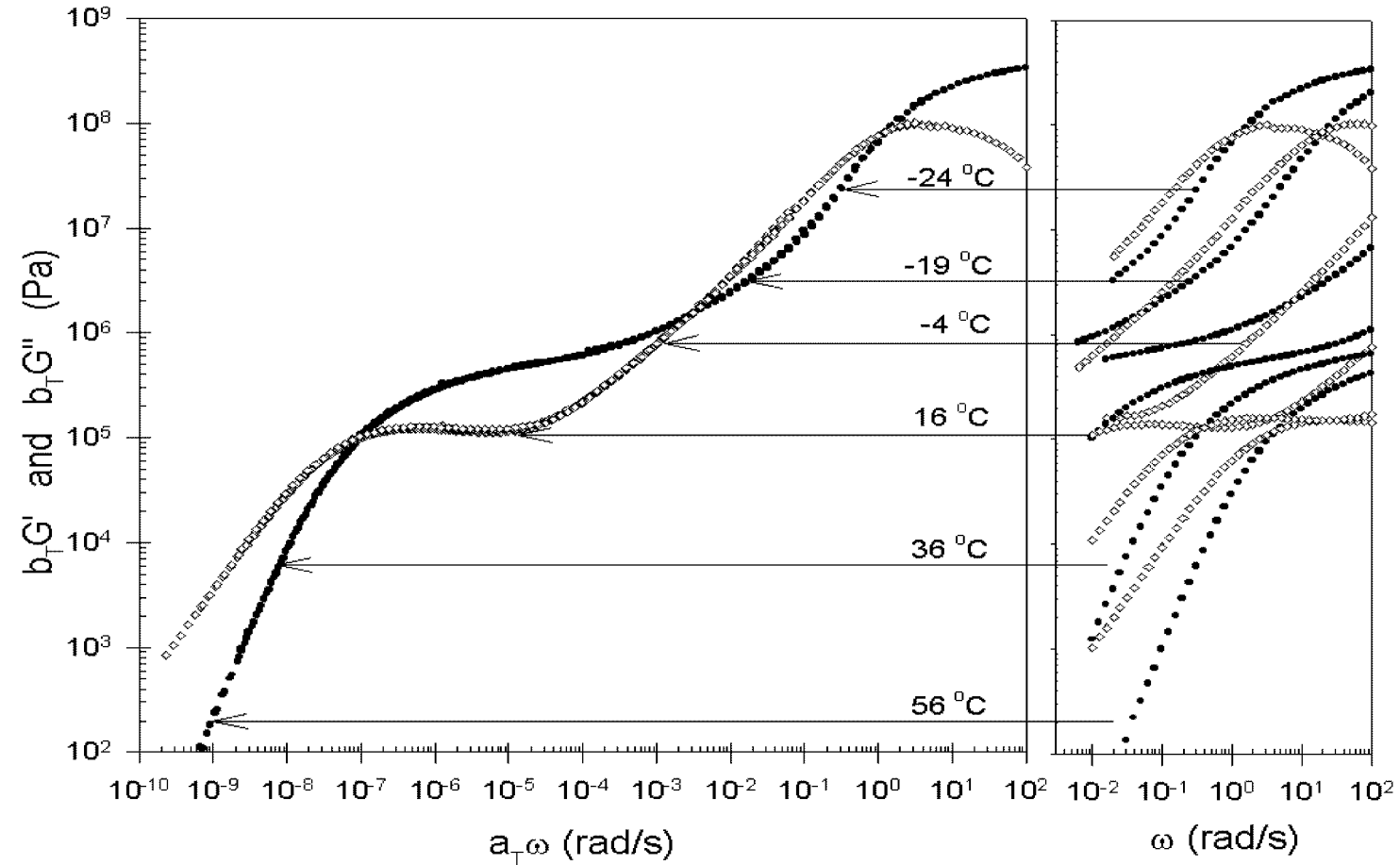


Figure 2: Time-Temperature Superposition for Storage Compliance of Poly(N-octyl methacrylate) with $T_0 = 100^\circ\text{C}$.





Time-Temperature Superposition COUNTER-EXAMPLE

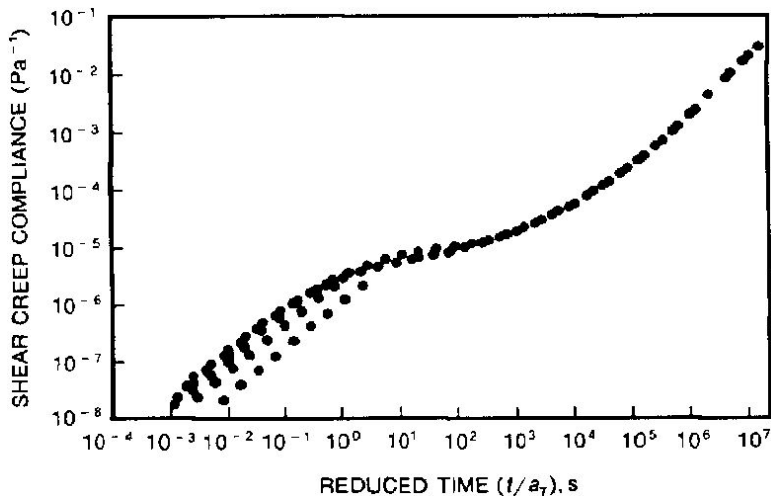


Figure 3: Failure of Time-Temperature Superposition in the Glass Transition Zone of Polystyrene with $T_0 = 126.7^\circ\text{C}$.

Time-Temperature Superposition does not always work!!!