Notes

New Linearized Relation for the Universal Viscosity−Temperature Behavior of Polymer Melts

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The temperature dependence of zero-shear viscosity (η) or terminal flow relaxation time (τ) is one of the most fundamental properties of polymer melts.[1] Generally, the viscosity−temperature behavior is divided in two regions, although Ngai and Plazek[2] have proposed four groups of relaxation mechanisms above the glass transition temperature T_g in the coupling model. Each region is described by semiempirical functions involving two or three adjustable parameters (whose physical significance is not always clear). The first region is located at temperatures well above T_g, i.e., $T_g + 100\ °C$ or $\sim 1.3 T_g$, and follows a simple Arrhenius equation:

$$\eta(T) = A \exp\left(\frac{E_a}{RT}\right) \qquad (1)$$

where R is the gas constant and T is the absolute temperature. The preexponential factor A is related to the polymer chemical composition (more specifically to the monomeric friction coefficient) as well as the molecular weight (MW) and its distribution. The parameter E_a is called the flow activation energy. It depends on chemical composition and architecture but is independent of MW or distribution.[3]

At lower temperatures, in the range from T_g to $T_g + 100\ °C$, the WLF equation[4] has to be used instead:

$$\log \alpha_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \qquad (2)$$

Here C_1 and C_2 are adjustable parameters. The shift factor α_T is defined as $\eta(T)T_r\rho_r/\eta(T_r)T\rho$,[1] where ρ is the density and the subscript r refers to properties of a reference state. Because of the relatively small temperature dependence of $T_r\rho_r/T\rho$, α_T is nearly the same as $\eta(T)/\eta(T_r)$. The WLF equation is strictly equivalent to the Vogel−Fulcher−Tammann (VFT) expression:[5]

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$$\eta(T) = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \qquad (3\text{-}1)$$

or

$$\tau(T) = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \qquad (3\text{-}2)$$

where η_0, τ_0, B, and T_0 are material constants. The WLF and VTF parameters are of course related:[6]

$$C_2 = T_r - T_0 \qquad (4)$$

$$2.303 C_1 C_2 = B \qquad (5)$$

The parameters identified by fitting eq 2 or eq 3 to experimental data are quite variable depending on chemical composition and the experimentally accessible temperature range. Typically, for the VFT form, $\tau_0 \sim 10^{-12}$–10^{-20} s, $B \sim 500$–2500 K, and $T_g - T_0 \sim 30$–80 K.[7] It is therefore logical that no master curve can be constructed for the viscosity of different polymers vs $T - T_g$.[8,9] Similarly, the so-called "universal" $C_1^g = 17.44$ and $C_2^g = 51.6$ WLF constants (for $T_r = T_g$) only work in limited cases.[1] It is worth noting that Plazek and Ngai[10] normalized the local segmental relaxation based on the temperature ratio $(T - T_g)/T_g$ and the coupling constant (or the stretched exponent) n.

In this well-known context, Ding and Sokolov[11] have very recently made a rather surprising observation, i.e., that the temperature dependence of the terminal relaxation time of six polymers could be reduced to a master curve by a T_g-scaled Arrhenius plot. The authors indicate that observed T_g/T scaling reflects the energetic scaling of the friction coefficient and state that "it would be important to verify whether this universality will hold also for chain relaxation in other polymeric systems". Moreover, the results reported by Ding and Sokolov only cover a narrow T_g/T range from 0.825 to 1 (equivalent to T/T_g from 1 to 1.2) and are located entirely in the non-Arrhenius (WLF) region. It would also be of interest to check whether the universality extends in the "Arrhenius" region.

The objective of the present note is to verify and expand the validity of the T_g/T universal scaling by analyzing a large set of dynamic moduli data in a broad temperature range. We have compiled experimental results for 14 widely different amorphous polymers or copolymers,[12−16] with T_g ranging from −100 to 177 °C. The data span an extended T/T_g range from 1 to 2. The results are shown in Figure 1, where a vertical shift (factor A') is needed to superpose the data of other polymers on the PBD curve. A universal dependence of α_T vs T_g/T is indeed observed for all the polymers in both the non-Arrhenius and Arrhenius regions. Moreover, our observations are entirely coherent with those reported in ref 11 since a set of data[16] for atactic polypropylene (aPP) included in both papers is consistent with all others.
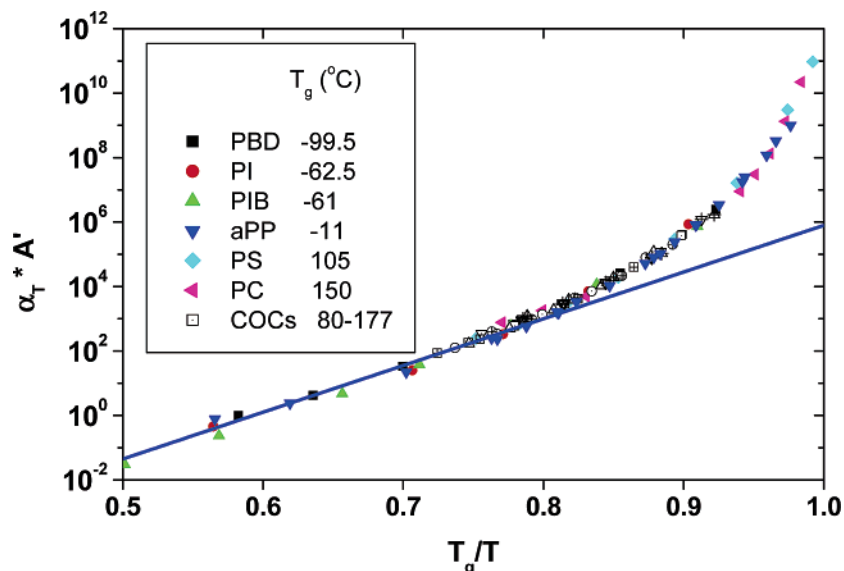
In the Arrhenius region ($T_g/T < 0.75$ or $T/T_g > 1.3$), the T_g-scaled Arrhenius plot is linear (see bold line in Figure 1).

Figure 1. T_g-scaled Arrhenius plots of shift factors (dynamic measurements) for different polymers: polycarbonate (PC),[12] cyclic olefin copolymers (COCs): four ethylene−norbornene copolymers and four ethylene−tetracyclododecene copolymers with T_g from 80 to 177 °C,[13] polyisobutylene (PIB),[14] polybutadiene (PBD),[15] polyisoprene (PI),[15] polystyrene (PS),[15] atactic polypropylene (aPP).[16] The errors in the shift factors are typically within a factor 2. Vertical shift (factor A') was applied for superposition. The bold line represents a linear relation for log α_T vs T_g/T at $T > 1.3T_g$.

Therefore, the flow activation energy, E_a, can be directly correlated with the glass transition temperature:

$$E_a = CRT_g \tag{6}$$

with C a universal constant.

On the basis of free volume concepts, Wang and Porter[3] have proposed a semiempirical equation for E_a in the Arrhenius region (for temperatures above $T_g + 150$ °C):

$$E_a = \frac{RT_g(T_g + 150)^2}{0.164(0.23T_g + 150)^2} \tag{7}$$

The Wang−Porter relation has been validated for a large set of polymers as shown in Figure 2 (reproduced from Figure 4 of ref 3). However, a linear T_g dependence following eq 6 can roughly capture the trend (bold line in Figure 2).

The Wang−Porter equation is based on two assumptions. The first one is the Simha−Boyer relation,[17] which expresses that free volume at T_g is a constant:

$$\alpha_l T_g = 0.164 \tag{8}$$

where α_l is the volume expansion coefficient above T_g. Although the Simha−Boyer equation does not work for all polymers, it is obeyed in many cases.[17] Therefore, the parameter B in the VFT equation is directly and universally related to T_g.[3] The second assumption for the Wang−Porter equation is the Adams−Gibbs relation:[9]

$$T_0 = 0.77T_g \tag{9}$$

Equation 9 is based on the Gibbs−DiMarzio lattice model[18] and relates T_g to the temperature T_0 at which the equilibrium conformational entropy becomes zero. This relationship is consistent with an observation made by Ding and Sokolov[11] about the "fragility" parameter (m) describing the steepness of the temperature dependence of the relaxation time:

$$m = \frac{d \log \tau}{d(T_g/T)}\Big|_{T=T_g} \tag{10}$$
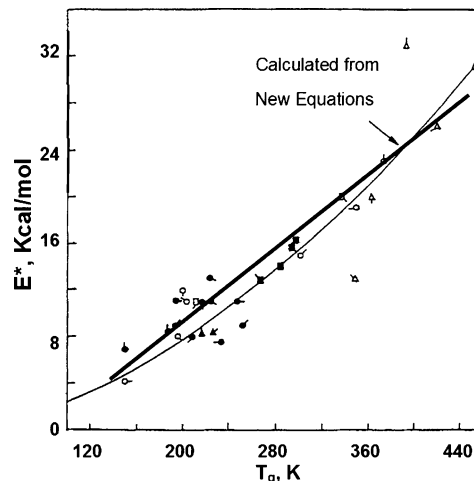
Figure 2. Flow activation energy E_a of polymers as a function of T_g. The curve represents the Wang−Porter relation (eq 7). The bold line represents a linear correlation between E_a and T_g according to eq 6. Reprinted with permission from ref 3. Copyright 1995 Springer Verlag.

The ratio T_0/T_g is related to m as[11]

$$T_0/T_g \approx 1 - \frac{17}{m} \tag{11}$$

Combining eqs 9 and 11 gives a value for m close to 50, which is precisely what Ding and Sokolov have observed for the chain relaxation time.[11]

The universal scaling illustrated by Figure 1 can further be linearized by using a suitable function of the rescaled temperature $T^* = T/T_g$. With the help of eqs 8 and 9, the VFT equation (eq 3-1) can be simplified as follows:[3]

$$\log\left(\frac{\eta(T)}{\eta_0}\right) = \log K + \log(\alpha_T A') = \frac{B/2.303}{T - T_0} \cong \frac{C_g T_g}{T - 0.77T_g} = \frac{C_g}{T^* - 0.77} \tag{12}$$

where η_0 is related to the polymer chemical composition and MW, the constant $K = \eta(T_r)/\eta_0$ for PBD, A' is a vertical shift
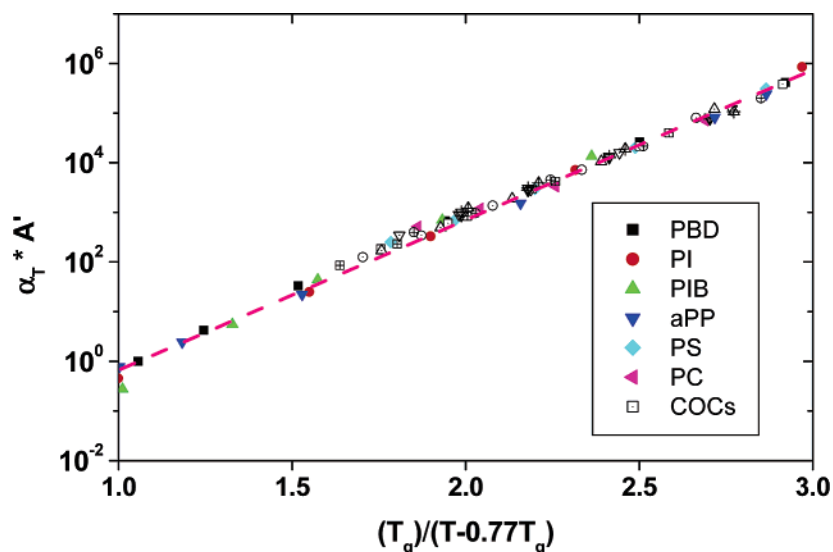
Figure 3. Data of Figure 1 replotted as log $\alpha_T A'$ vs $T_g/(T - 0.77T_g)$. The dashed line corresponds a slope of 3. Note: $1/(T^* - 0.77)$ range from 1 to 3 corresponds to T/T_g ranging from 1.1 to 1.77.

factor (same as in Figure 1) for superposing the data of other polymers on the PBD data, and C_g is a constant. When all data in Figure 1 are replotted as $\log(\alpha_T A')$ vs $(T^* - 0.77)^{-1}$ in Figure 3, a universal *linear* relation is found for all tested polymers in the non-Arrhenius as well as the Arrhenius regions. C_g is a *universal* constant with a value close to 3 (dashed line in Figure 3). To our knowledge, this universal *linear* relationship has not been shown before. Van Krevelen and Hoftyzer[19] have previously proposed a universal relation for viscosity with a rescaled T/T_g temperature. However, they use an additional *empirical* parameter to arbitrarily compress or extend the vertical axis. The additional parameter, although it appears to be close to 1 for many polymers,[19] could be important for accurate predictions in the Arrhenius region, as evidenced by the residual scatter of the flow activation energies shown in Figure 2. The universality in the Arrhenius region therefore has to be confirmed by more tests. On the other hand, our observations are quite consistent with eq 12 (without the need of an additional parameter) in the non-Arrhenius region ($T^* < 1.4$) for all 14 polymers tested. Equation 12 shows that B is proportional to T_g. This is a direct consequence of the Simha–Boyer equation. Comparing eq 3 with eq 12, we find $B \approx 6.9T_g$, and $T_g - T_0 \approx 0.23T_g$ (equivalent to eq 9), which is consistent with the observed range of experimental values ($B \sim 500-2500$ K and $T_g - T_0 \sim 30-80$ K).[7]

Magill and Li[20] have previously proposed a universal relation for viscosity as an empirical equation:

$$\log(\eta/\eta_s) = A[\exp(BT_g/T) - \exp(B/(1 + \phi))] \quad (13)$$

This equation is also based on the temperature ratio T/T_g. Hence, it should have a similar physical meaning as the finding of Ding and Sokolov, confirmed by us. Magill and Li show the original WLF is less satisfactory to fit the data. Indeed, the universality based on the temperature ratio T/T_g is different from the WLF equation. However, they cannot linearize the viscosity–temperature relation and need three empirical parameters.

In summary, we confirm the universal "T_g scaling" of the temperature dependence of η or τ for a wide variety of amorphous polymers over an extended temperature range encompassing both the Arrhenius and non-Arrhenius regions (Figure 1). We have further linearized the master curve by combining the VFT and Simha–Boyer and Adam–Gibbs equations (Figure 3).

The universal relationships can also be used for practical purposes. If the preexponential factors A or η_0 in eq 1 or 3 are known from single point measurements on a given polymer, the viscosity can be estimated for all molecular weights in a broad range of temperatures ($T/T_g \sim 1.1-1.8$ in Figure 3) by combining the universal temperature dependence with the well-known 3.4 power law dependence for molecular weight.

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