Modification of a Model Relating Rheological Behavior of Polymer Melts to the Molecular Weight Distribution

A model has been proposed[1-3] by Bersted to predict the viscous and elastic rheological properties of molten polymers of high molecular weight in terms of their molecular weight distributions (MWD). Good agreement was reported between the predicted and experimental shear viscosity and first normal stress difference as a function of shear rate for relatively broad MWD polyethylene and polystyrene melts.

The model referred to above made the assumption that the effect of shear is to progressively truncate the relaxation spectrum, such that at any given shear rate $\dot{\gamma}$ the largest active relaxation time τ_c was assumed to be

$$\tau_c = \beta/\dot{\gamma} \tag{1}$$

where β is a constant. The specific connection to the MWD was made by empirically determining a relation between the molecular weight M_c whose largest relaxation time is equivalent to τ_c. The empirical relationship between M_c and $\dot{\gamma}$ was found[1] to be of the form

$$M_c = M_0(\dot{\gamma})^d \tag{2}$$

Recent publications[4,5] have shown serious discrepancies between the model's predictions and certain experimental data.

The empirically determined relationship given in eq. (2) has been shown to be an adequate description in high-density[1,2] and low-density[5] polyethylene and polystyrene[3] melts of varying MWDs. The applicability of eq. (2) will not be questioned here. Recently,[4] however, significant differences between calculated values for $G'(\omega)$, $G''(\omega)$, and the relaxation spectra for narrow MWD polystyrene samples have been reported. Additionally, application of the Bersted model to low-density polyethylene has led Ram and Pedersen[5] to conclude that the assumed relation in eq. (1) must be modified in order to give good agreement between predictions and experimental melt elasticity data in low-density polyethylene. Ram and Pederson modified the Bersted model by assuming that

$$\tau_c = \alpha(M_c)^a \tag{3}$$

where a is the exponent in the zero shear–MWD relation and α is a constant for a given polymer type and temperature. The relation in eq. (3) is in agreement with the form observed experimentally[6] for the long relaxation times of concentrated systems, in which the relaxation time is proportional to the zero shear viscosity $\eta_0(M)$ for a monodisperse sample of molecular weight M. The limiting viscosity at low shear rates, $\eta_0(M)$, has been found[7] to be related to molecular weight as

$$\eta_0 = K(\overline{M}_w)^a \tag{4}$$

where $\overline{M}_w$ is the weight-average molecular weight ($\overline{M}_w$ is replaced by M for a monodisperse sample of molecular weight equal to M), K is a constant which depends on polymer molecular structure and temperature, and a is a constant which has been found to be equal to 3.5 ± 0.2 for most polymeric melts and concentrated solutions; a has been found to be independent of temperature and is thought[6] to reflect increased (relative to dilute solutions or low molecular weights) frictional losses due to entanglement formation.

In order to see if the use of eq. (3) instead of eq. (1) could improve agreement between experimental and predicted values, the relaxation spectrum of a previously reported[3] narrow MWD polystyrene sample, having $\overline{M}_w$ = 411,000, was reexamined. The results are given in Figure 1, in which substantially better agreement is obtained using the assumption of eq. (3) in place of eq. (1). It is therefore concluded that, combining eqs. (1) and (3), the relation

$$\tau_c = \alpha(M_0)^a(\dot{\gamma})^{ad} \tag{5}$$

provides a better description of the shear rate dependence of τ_c than eq. (1). The refined constant α for polystyrene at 190°C is $\alpha = 2.73 \times 10^{-19}$.

The proposed modification does not significantly affect earlier reported[1,2] results on HDPE since $a \times d$ for HDPE is −1.008, and therefore eq. (4) is in substantial agreement with that previously assumed in eq. (1).
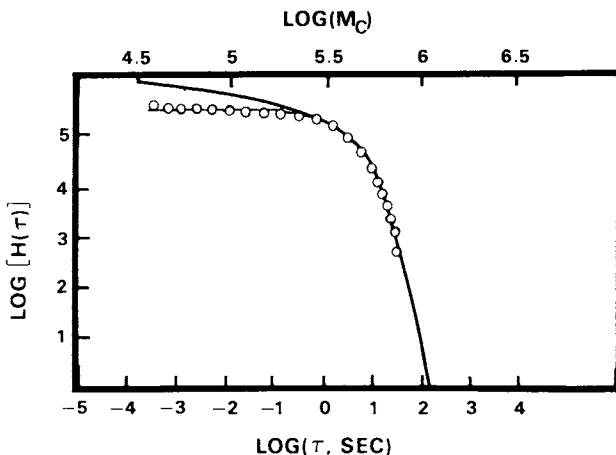
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Fig. 1. Relaxation spectrum for $\overline{M}_w = 411{,}000$ Pressure Chemical polystyrene standard of $\overline{M}_w/\overline{M}_n$ < 1.1. Heavy line is the calculated spectrum based on the original model's assumption that $\tau_c = \beta/\dot{\gamma}$. Narrow line is that calculated using the modification that $\tau_c = \alpha(M_c)^a$. Experimental data of Prest[8] at 192°C are given by circles.

Ease of applying the Bersted model for arbitrary temperatures could be effected if the temperature dependence of the model's parameters were predictable. It is shown in the appendix that, within the framework of the Bersted model, the constants in the model, M_0 and α, have only to be determined at a single temperature. They are shown to be related to the temperature dependence of the constant K in the zero shear relation

$$\eta_0 = K(\overline{M}_w)^a \tag{6}$$

as

$$M_0' = M_0(K/K')^{1/a} \tag{7}$$

and

$$\alpha' = \alpha(K'/K) \tag{8}$$

where the primed and unprimed quantities represent different temperatures. It is assumed that d is independent of temperature on the basis of previously reported data.[3,5]

Appendix

Temperature Dependence of Model Parameters

For a monodisperse sample of molecular weight M at a temperature T_0, the zero shear viscosity is related by

$$\eta_0(T_0) = K_{T_0}(M)^a \tag{1}$$

where a is temperature independent and K_T varies with temperature. At any other temperature T, the zero shear viscosity is related by

$$\eta_0(T) = K_T(M)^a \tag{2}$$

However, at T one can alternatively view the relation at T_0 to be valid, but the molecular weight M to act at T as though it were of molecular weight M'. Consequently,

$$\eta_0(T) = K_T(M)^a = K_{T_0}(M')^a \tag{3}$$

or

$$M' = M(K'/K)^{1/a} \tag{4}$$

where $K' = K_T$ and $K = K_{T_0}$. In other words, a sample of molecular weight M at T can be thought of as rheologically equivalent to a sample of molecular weight M' at T_0.

The shear rate for the onset of non-Newtonian behavior, $\dot{\gamma}_c$, is then

$$\dot{\gamma}_c(M,T) = \dot{\gamma}_c(M',T_0) \tag{5}$$

since it has been previously shown that $\dot{\gamma}_c$ can be related to molecular weight at a given temperature by

$$\dot{\gamma}_c = (M/M_0)^{1/d} \tag{6}$$

where d is a constant dependent only on molecular backbone structure ($d \times a$ is equal to the limiting power law exponent).

Combining eqs. (4), (5), and (6), we get

$$M_0' = M_0(K/K')^{1/a} \tag{7}$$

The relation given in eq. (7) gives the constant M_0 (at any temperature in terms of the zero shear constant K) in the relation between shear rate and the largest molecular weight species undergoing Newtonian flow, M_c, such that

$$M_c = M_0(\dot{\gamma})^d \tag{8}$$

where d is assumed temperature independent. Some support for this assumption has previously been given.[3,5]

It will be assumed that the model's relation between relaxation time τ and molecular weight at T_0 can be related by

$$\tau = \alpha M^a \tag{9}$$

and at T

$$\tau = \alpha'M^a = \alpha(M')^a \tag{10}$$

Using eqs. (4) and (10) we get

$$\alpha' = \alpha(K'/K)^1 \tag{11}$$

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