Calculation of the Apparent Viscosity of Polystyrene Melts

Empirical relationships between the apparent viscosity of linear, amorphous polymers and molecular parameters or experimental conditions involved in the determination of viscosity have been presented in several recent publications.[1-3] This note shows that these separate relationships can be combined to permit calculation of the apparent viscosity, η, as a function of the molecular weight, temperature, and shear rate or shear stress. As a test of the procedure, calculated values of η are compared to experimental melt viscosity data for a polystyrene having a narrow distribution of molecular weights.

Synthesis of Empirical Expressions

According to Fox and Flory,[1] the zero shear viscosity, η_0, of polystyrene fractions depends on the 3.4 power of the molecular weight M, as indicated by the equation:

$$\log \eta_0 = 3.4 \log M + K \qquad M > 38{,}000 \quad (1)$$

K in eq. (1) is a constant at a particular temperature and has the value of -13.40 at 217°C. for polystyrenes.

Williams[2] has advanced a universal expression for the temperature dependence of viscosity for glass-forming systems:

$$\log a_T = \frac{-8.86(T - T_s)}{101.6 + T - T_s} \qquad T_g < T < (T_g + 100) \quad (2)$$

The parameter a_T appearing in eq. (2) is the Ferry temperature-shift factor, which is approximately equal to the ratio of the zero shear viscosity at temperature T to that at the reference temperature T_s. Williams, Landel, and Ferry[4] give 408°K. as the reference temperature for polystyrenes.

Equations (1) and (2) can be combined to yield:

$$\log \eta_0 = 3.4 \log M + [900.2/(T - 306.4)] - 18.38 \quad (3)$$

This description of the molecular weight and temperature dependence of the zero shear viscosity of undiluted polystyrenes is valid for the ranges of the independent variables indicated above for the component equations.

Recently, Bueche and Harding[3] published an empirical curve giving the ratio η/η_0 as a universal function of the product $D\tau$, where D is the rate of shear and τ is a molecular parameter. For the case of undiluted melts, this molecular parameter is evaluated as:

$$\tau = 12\eta_0 M/\pi^2 \rho R T \quad (4)$$

where ρ is density, R is the gas constant, and T is absolute temperature.

If the molecular weight is specified, η can be calculated over a range of shear rates (or shear stresses) at a particular temperature by the sequential application of these empirical expressions. Thus, η_0 can be computed from eq. (3) and inserted into eq. (4) to give τ. One can then read from the Bueche-Harding curve a series of (η/η_0) vs. $(D\tau)$ values. Knowing η_0 and τ, one can obtain the desired η vs. D relationship.

Results and Discussion

Experimental viscosity data obtained with a capillary extrusion rheometer[5] at 450°F. (505.4°K.) for a polystyrene ($\bar{M}_w/\bar{M}_n < 1.2$) are plotted against shear rate in Figure 1. Also shown is the calculated shear rate dependence of apparent viscosity obtained by the procedure outlined above. The agreement between the calculated and observed values seems quite satisfactory inasmuch as no adjustable parameters enter into the calculations.

While this example was worked out for the case of a monodisperse polystyrene melt, the calculational procedure should be generally applicable to linear amorphous polymers having "normal" polydispersity. Preliminary experiments with blends of polystyrene fractions indicate that the apparent viscosity varies with the weight-average molecular weight at low shear rates, but appears to vary with number-average molecular weight at high shear rates. In calculating η for polydisperse systems one must, therefore, use appropriate molecular weight averages to conform to this experimental observation.
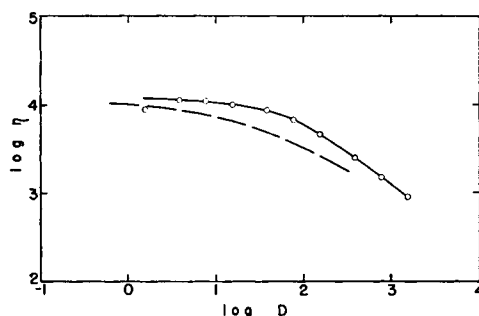

Fig. 1. Calculated (- -) and observed (--O--) shear rate dependence of polystyrene melt viscosity at 450°C.

Since the combination of empirical expressions allows one to compute η as a function of molecular weight, temperature, and shear rate or shear stress, the apparent energy of activation for viscous flow, ΔH, can be derived as well. The variation of ΔH, computed either at constant shear rate or constant shear stress, can be studied as a function of the several variables involved. A future publication will discuss these and other ramifications of the synthesis of empirical relationships to predict the rheological behavior of polymer melts.

References

1. Fox, T. G., Jr., and P. J. Flory, J. Polymer Sci., 14, 315 (1954).
2. Williams, M. L., J. Phys. Chem., 59, 95 (1955).
3. Bueche, F., and S. W. Harding, J. Polymer Sci., 32, 177 (1958).
4. Williams, M. L., R. F. Landel, and J. D. Ferry, J. Am. Chem. Soc., 77, 3701 (1955).
5. Merz, E. H., and R. E. Colwell, ASTM Bull., No. 232, 63 (1958).

W. P. Cox
R. L. Ballman

Monsanto Chemical Company
Plastics Division
Springfield 2, Massachusetts