

Comments on "Viscosity of Polystyrene Near the Glass Transition"

In their paper on "Viscosity of Polystyrene Near the Glass Transition" [*J. Appl. Polym. Sci.*, **13**, 2427 (1969)], R. C. Penwell and R. S. Porter have used what they claim to be the W.L.F. equation, together with the experimental frequency dependence of T_g from oscillatory measurements, to predict that the viscosity of polystyrene increases with frequency (or shear rate). Not surprisingly, they find no experimental evidence of this from steady shear measurements on the melt at atmospheric pressure.

The W.L.F. equation,¹

$$\log a_T = \frac{C_1(T - T_0)}{C_2 + T - T_0},$$

describes the frequency shift factor a_T necessary to superimpose the modulus or compliance data versus log angular frequency ω measured at different temperatures T ; C_1 , C_2 , and T_0 are assumed to be disposable frequency-independent constants when fitting the experimentally observed a_T versus T relation. A similar equation,

$$\log \eta = \log A + B/(T - T_0),$$

called the Tamman-Hesse equation by the authors, can be used to fit experimental data of steady shear Newtonian viscosity η versus temperature. Although the reference temperature T_0 is found to be roughly 50°C below T_g , the exact difference will depend on the frequency at which T_g was measured. Therefore, it is not possible to replace T_0 with the frequency-dependent quantity ($T_g - \text{constant}$) in the W.L.F. or Tamman-Hesse equations and then use the modified equation to predict a viscosity dependent on the frequency of measurement.

References

1. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, p. 212.

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Received April 11, 1970