Pressure Effects in the Capillary Flow of Amorphous Polymers

INTRODUCTION

Recently, Takahashi et al. have reported their work on high shear rate capillary rheometry using several homopolymers, including polystyrene and polycarbonate,[1] and on blends of SAN and polycarbonate.[2,3] A concern exists about the manner in which their data have been interpreted. Earlier work by Penwell and Porter discussed the effects of pressure on the capillary flow of amorphous polymers, most notably polystyrene and polycarbonate.[4-6] It was clearly demonstrated that anomalous viscosity behavior could be attributed to small volume changes and subsequent shifts in the glass transition temperature at sufficiently high pressures.[4-6] The effect of a shift in the glass transition temperature is a corresponding rise in the apparent viscosity. This appears to have been ignored in their work. Additionally, the acknowledged temperature rise[1] and lack of steady state flow further complicate the analysis of Takahashi et al.

A brief discussion regarding these comments follows, with the idea of stimulating further thought on their earlier and more recently reported work.

DISCUSSION

The following observations for polystyrene are made with respect to Figure 4 of Ref. 1. The original data were not tabulated and the data points used here were estimated from Figure 4. Begin with

$$\tau_w = \eta_a \dot{\gamma}_a \tag{1}$$

where τ_w, η_a, and $\dot{\gamma}_a$ are the shear stress at the capillary wall, apparent viscosity, and apparent shear rate, respectively. From Ref. 1, Figure 4, at $\eta_a = 2.5$ Pa s and $\dot{\gamma}_a = 2 \times 10^6$ s^{-1}, the shear stress is equivalent to 725 psi. Consider the next basic relation,

$$\Delta P = \frac{2L\tau_w}{R} \tag{2}$$

where ΔP is the pressure drop along the capillary and L and R are its length and radius, respectively. With $L = 10$ mm and $R = 0.25$ mm,[1] $\Delta P = 4000$ bars.

Using the well-established relation between the glass transition of polystyrene and pressure,[7]

$$T_g = T_{g0} + 0.028P \tag{3}$$

where T_{g0} ($\sim 100°C$) is the glass transition at atmospheric pressure, P is the pressure in bars, and T_g is the glass transition at the increased pressure, a resultant T_g of 212°C is obtained. Referencing the work of Penwell and Porter,[4-6] such a large increase in T_g could contribute to the viscosity changes implied in the work of Takahashi et al.[1]

An estimate of the average residence time of the material in the capillary can be obtained using

$$\dot{\gamma}_a = 4Q/\pi R^3 \tag{4}$$

where Q is the flow rate and R the radius of the capillary. With substitutions and an appropriate rearrangement of eq. (4), the average residence time t_r is given by

$$t_r = L_c / V_c = 4L / R \dot{\gamma}_a \qquad (5)$$

Inserting values used in eq. (2) to estimate ΔP, t_r is found to be on the order of 8×10^{-3} s. It is questionable whether steady state flow is ever achieved in this situation.

Takahashi et al. acknowledge the change and magnitude of the temperature rise in their work.[1] This further complicates their analysis, and when combined with the likelihood of pressure effects on the flow and lack of steady state conditions, casts doubt on their interpretation of their data.

A similar situation as that just described for polystyrene exists for their work on polycarbonate. If data are abstracted from Ref. 1, Figure 8, and utilized in calculations in the work done by Penwell and Porter for polycarbonate,[8] resultant increases in the glass transition and hence apparent viscosity are predicted in the areas where Takahashi et al. report anomalous behavior.

In summary, the likelihood of pressure effects on viscosity in the work of Takahashi et al., changing temperatures within the capillaries, and the appearance of nonsteady flow conditions suggest that further thought be given to the interpretation of their referenced work.[1-3]

References

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