Effects of Mineral Oil on the Rheological Behavior of Polystyrene Melts

B. H. BERSTED, *Research and Development Department, Amoco Chemicals Corporation, Amoco Research Center, Naperville, Illinois 60566*

Synopsis

The effects of mineral oil on the small strain rheological functions of polystyrene are shown to be simply related to the oil content and the rheological behavior for the neat material. Reduced variables, which are analogous to the effects of temperature, are found to successfully reduce the data for all levels of oil. The use and form of these reduced variables are shown to be predicted by the model of Bersted, which relates the rheological functions directly to the molecular weight distribution. The effects of the oil are argued to suggest that the mineral oil acts as a plasticizer for polystyrene.

INTRODUCTION

A study of the steady shearing viscosity and first normal stress coefficient of high impact polystyrene (HIPS) containing mineral oil has been recently reported.[1,2] The results of Kruse and Southern[1] indicated a reduction of the viscosity with mineral oil content, with the Newtonian viscosity being adequately described by a logarithmic blending rule. However, no systematic description of the small strain rheological functions as a function of frequency and mineral oil content was reported. The objectives of this paper are to examine the effect of mineral oil on the dynamic small strain rheological behavior of a well-characterized polystyrene, to compare the dynamic results with those obtained by means of steady shear flow, and to demonstrate the prediction of the viscosity as a function of frequency and oil level from knowledge of either the molecular weight distribution (MWD) or from the rheological data on the base polymer.

EXPERIMENTAL

The atactic polystyrene sample used in this study originally contained no oil. The MWD data for this sample are given in Table I. The MWD data were obtained on a Model 200 Waters gel permeation chromatograph with THF as solvent. Calibration was effected using narrow MWD polystyrene standards. Oil was added to the sample in three ways: physically blending the polystyrene powder and mineral oil, extruder blending, and solution blending with subsequent freeze drying of the solution in benzene. The mineral oil content of compression-molded specimens were analyzed by means of liquid chromatography.

The dynamic rheological data were obtained using the Rheometrics mechanical spectrometer with a 5.0 cm cone (0.02 radian angle) and plate geometry and a 50-μm gap. A strain level of 15% was used, since this was established by varying the strain level to be well within the linear range.

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| | $\times\,10^{-3}$ | | |
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$
Polystyrene C-45C	77	257	489

The viscosity of the mineral oil was determined using a Cannon-Fenske viscometer.

The glass transition temperatures were determined on a DuPont 990 differential scanning calorimeter at a rate of 20°C/min.

The high shear rate steady shearing data were obtained using an Instron capillary rheometer with a die having an $L/D = 33{:}1$. Rabinowitsch corrections were applied to the data.

RESULTS AND DISCUSSION

Effect of Mineral Oil on the Newtonian Viscosity

The dynamic viscosity η' for various selected oil levels is given in Figure 1. Results for the Newtonian viscosity as a function of oil level are given in Figure 2. The results given in Figure 2 involve three different methods of oil blending and two modes (steady shearing and dynamic) of viscosity measurement. In view of the different methods of measurement and sample preparation, it would appear that a unique relationship between the percent mineral oil and the Newtonian viscosity exists. In view of the reasonable agreement between the dynamic and steady shearing data, which were obtained from substantially different flow geometries, it would also appear that the changes in the viscosity with the addition of oil reflect material, and not instrumental differences.

From Figure 2 a logarithmic blending law of the form

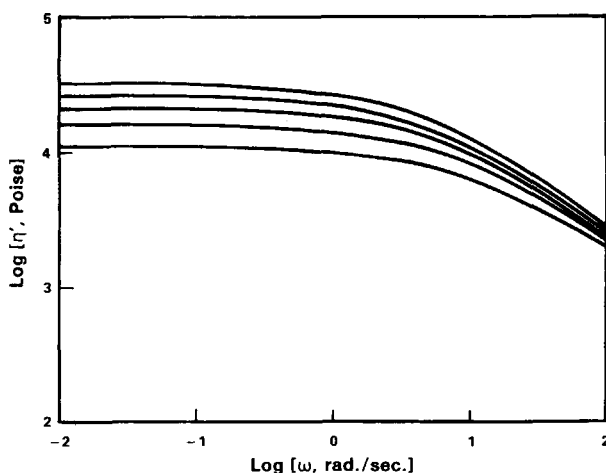$$\eta_B = (\eta_1)^{w_1} (\eta_2)^{w_2} \tag{1}$$

Fig. 1. The dynamic viscosity as a function of angular frequency for polystyrene samples containing 0%, 0.85%, 2.18%, 4.0%, and 5.5% mineral oil at 225°C.
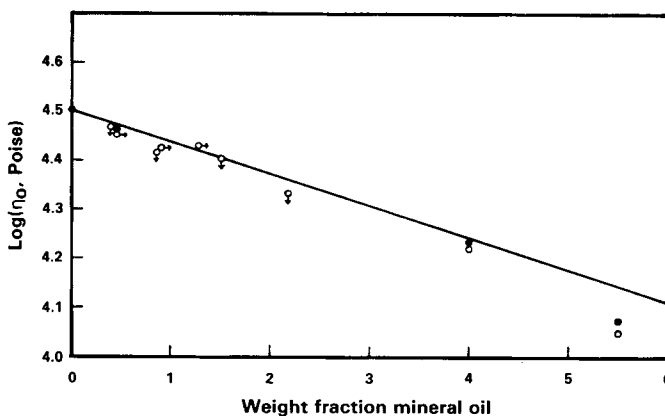
Fig. 2. The Newtonian viscosity at 225°C as a function of mineral oil content for various methods of incorporating the oil into the polystyrene matrix. ⊙'s represent freeze dried blends, ⊙→ extrusion blends, and ⊙ physical blends with the polystyrene powder. Open circles are dynamic data and solid are steady shearing data.

can be seen to adequately describe the variation of the Newtonian viscosity with oil level, where the viscosity of the oil was taken from Figure 3, the subscripts refer to the components of the blend, and w_1 and w_2 are the weight fractions of the components.

The results given in Figure 2 agree with those of Kruse and Southern[1] for the steady shearing viscosity. This uniqueness argues against the drop in viscosity with oil level being due to lubrication or slippage at the polymer interface. If any significant lubricating effect were present, the dependencies of the steady shearing and the small strain dynamic Newtonian viscosities on oil level would be expected to be different. The effect of the oil is unlikely to be just that of a diluent, as suggested by Kruse and Southern,[1] since only an approximately 20% drop in viscosity would be predicted from consideration of the $\eta_0 - \overline{M}_w$ relationship.
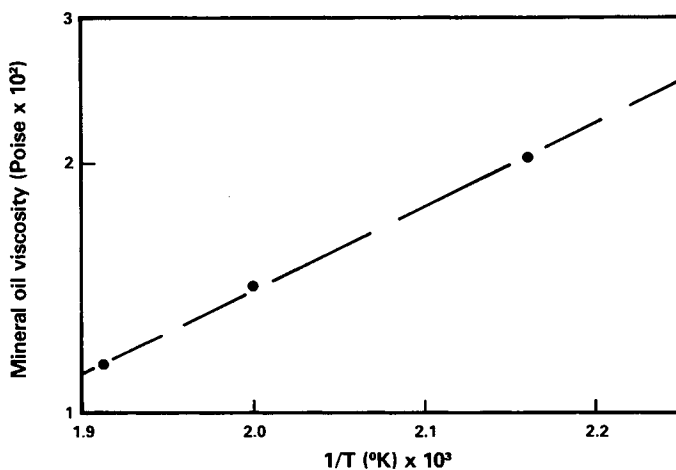

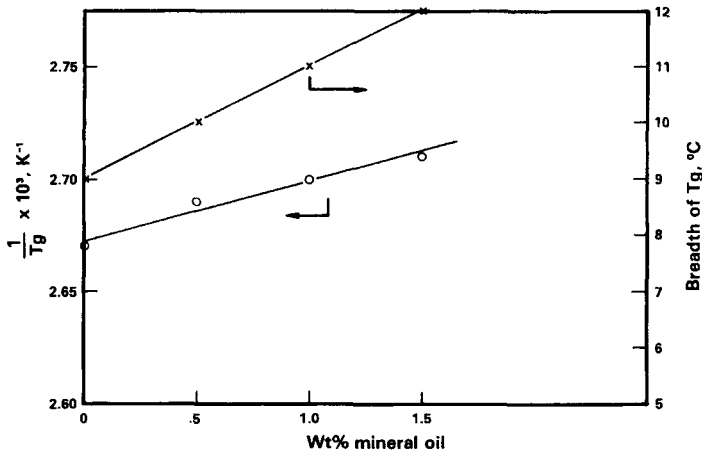Fig. 3. Measured mineral oil viscosity at various temperatures.

Fig. 4. The variation of the glass transition of polystyrene with mineral oil content.

The glass transition temperature as a function of oil level is given in Figure 4. This behavior is consistent with that of a plasticized system.[3]

Effects of Oil on the Dynamic Rheological Properties as a Function of Frequency

From the foregoing results the Newtonian viscosity has been shown to be predictable from the behavior of the neat polystyrene and knowledge of the mineral oil level. From a consideration of the data in Figure 1, it was found that the logarithmic blending law is increasingly in error at the higher frequencies. The dynamic modulus G' as a function of frequency is given in Figure 5. These
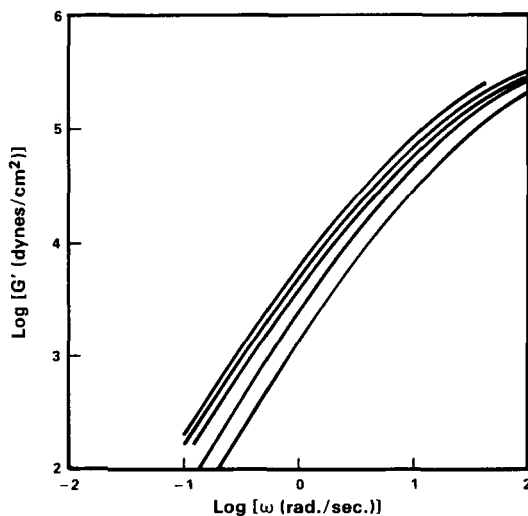

Fig. 5. The dynamic modulus as a function of angular frequency for polystyrene samples containing 0%, 0.85%, 2.18%, and 5.5% mineral oil at 225°C.
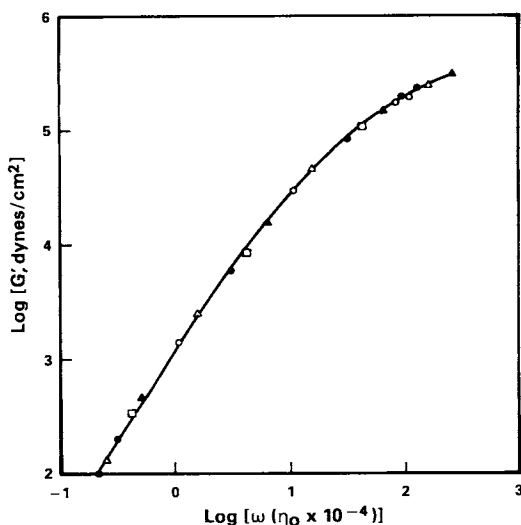
Fig. 6. The data in Figure 5 for the dynamic modulus plotted using the radical variables from the various oil levels (%): (●) 0; (▲) 0.85; (□) 2.18; (△) 4; (⊙) 5.5%.

data are also not capable of being described by a logarithmic blending law at the higher frequencies. A different approach was clearly necessary.

The approach, which I have chosen to describe the effects of oil on the dynamic behavior, will involve treating the effects of oil in a similar fashion to a change in temperature. As justification for this procedure we note that both raising the temperature and the addition of a plasticizing agent increase the mobility of individual relaxation mechanisms in a similar fashion. The effects of temperature for steady shearing flow has been described previously by Bersted[4] in terms of a model relating molecular weight distribution to rheological behavior. It will be within the framework of this model of Bersted's that the generalized description of the dynamic behavior for varying oil levels will be described.

First we will consider the effects of temperature (or oil) on the relaxation times and the relaxation spectrum. For a given molecular weight species, M_k, in our sample, its longest relaxation time, τ_k, can be expressed[4] as

$$\tau_k = \alpha(M_k)^{3.4} \tag{2}$$

where the constant α has the same temperature dependence as K in the Newtonian viscosity–MWD relationship [i.e., $\eta_0 = K(M_w)^{3.4}$]. In other words, for two different temperatures (or oil levels)

$$\alpha/\alpha' = K/K'$$

Additionally, the relaxation spectrum has been shown[5] to be capable of being expressed as

$$H(\tau_k) = \frac{K}{\alpha} \frac{(\overline{M}_w^*)^{2.4} \overline{A}_2}{(M_k)^{2.4}} \tag{3}$$

where $\overline{M}_w^* = \Sigma_{i=1}^{k} \overline{h}_i M_i + M_k \overline{A}_2$, $\overline{A}_2 = \Sigma_{i=k}^{\infty} \overline{h}_i$, and $\overline{h}_i$ are the weight percentages of each molecular species present in the sample. From eq. (3) we can see that $H(\tau_k)$ is independent of temperature, but τ_k changes in the same manner with temperature as does α.
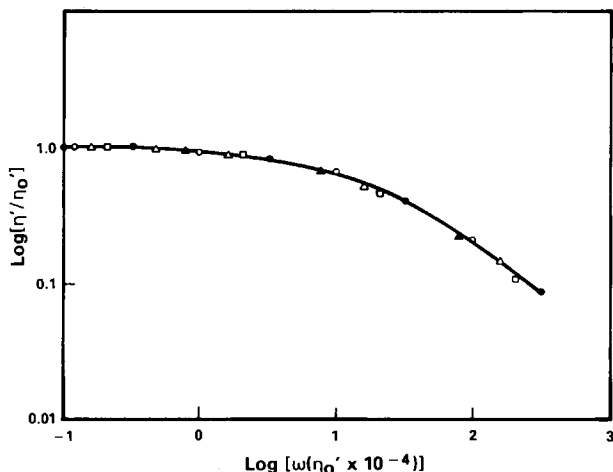
Fig. 7. The data in Figure 1 for the dynamic viscosity replotted using the reduced variables form for the various oil levels. The oil level designations are as given in Figure 6.

We will now consider the temperature dependence of the dynamic modulus, G', and viscosity η'. The equation relating G' to the relaxation spectrum is given[6] by

$$G' = \int_0^\infty \frac{H\omega^2 \tau_k \, d\tau_k}{1 + \omega^2\tau_k^2} \tag{4}$$

Since $H(\tau_k)$ is independent of oil level and τ_k varies only as α, or equivalently η_0, we see from eq. (3) that a plot of G' vs. $\omega\eta_0$ should give a single curve for all oil levels. As can be seen in Figure 6, this is indeed found to be the case from replotting the data in Figure 5. A similar argument applied to the inspection of the equation for η' as related[6] to the relaxation spectrum indicates that η'/η_0 plotted vs. $\omega\eta_0$ should give a single curve for all oil levels. These predictions are confirmed in Figure 7.

From the preceding it follows that knowledge of the dynamic rheological data for the neat polystyrene and the oil level allows us to predict the dynamic curves as a function of frequency for samples containing arbitrary levels of mineral oil. Additionally, the reduced variables should also allow us to predict the curves at arbitrary temperatures from knowledge of the activation energy in the η_0 relationship and either knowledge of the dynamic functions as a function of frequency or as a function of the molecular weight distribution.[5] One possible application of these ideas is that, by combining measured rheological behavior with predictions of the Bersted model[6] (from MWD data as obtained by gel permeation chromatography on the sample containing mineral oil) for a sample with unknown oil level, estimation of the oil level can be effected.

CONCLUSIONS

The small strain dynamic rheological functions as functions of frequency for polystyrene, containing arbitrary levels of mineral oil, are shown to be simply related to the oil content and the dynamic functions of the neat polystyrene. Alternatively, one could predict the rheological behavior of samples containing

oil directly from the molecular weight distribution and the oil level, since the Bersted model has previously been shown to be capable of predicting the relaxation spectrum and rheological functions from the MWD of the neat polymer. The similarity between the effects of oil on the small strain dynamic functions and on the steady shearing viscosity, together with considerations of the magnitude of the effects of the oil on the rheological behavior and the effects of the mineral oil on the glass transition of the polystyrene, suggest the mineral oil acts as a plasticizer. Analogous to the effects of temperature, reduced variables for samples, containing various levels of oil, can be successfully employed. The employment and form of these reduced variables are shown to be dictated by the Bersted model.

References

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