

Pressure Effects in Polymer Melt Rheology

PAUL D. DRISCOLL* and DONALD C. BOGUE, *Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996*

Synopsis

Wide ranges of pressure and temperature are encountered in polymer processing operations, as, for example, in injection molding. While the temperature dependence of viscosity has been widely studied, the pressure dependence has not. The present work focuses on the measurement of the melt viscosity of polystyrene at high pressures (up to 124 MPa or 18,000 psi) and high shear rates ($1\text{--}100\text{ s}^{-1}$) at 180°C . The apparatus was a capillary rheometer with the downstream chamber being held at a high back pressure by means of a needle valve. The data so obtained were combined with zero shear viscosity data from the literature; and then correlated with a shear-dependent rheological model of the authors, using a shift factor suggested by Utracki (based on the Simha-Somcynsky equation of state). The final correlation calls for making both the elastic modulus and the time constant dependent on pressure, with the modulus being the dominant factor at high shear rates.

INTRODUCTION

Although the effect of temperature on rheological behavior has been widely studied, the effect of pressure has not. In other work at the University of Tennessee (Ko and Bogue¹) we have set down a generalized constitutive equation which would allow one, in principle at least, to deal with arbitrary non-isothermal, non-isobaric and non-isochoric histories. Such an equation will be necessary to deal carefully with such complicated processes as injection molding, where plunger pressures of 100 MPa ($\approx 15,000$ psi or ≈ 1000 atm) are not uncommon, with some specialty machines going as high as 700 MPa. The melt flows from the plunger chamber into a mold which ultimately ends up at atmospheric pressure and a temperature not far above ambient. These large and rapid changes of pressure and temperature affect not only the flow properties of the melt but also carry over to produce nonequilibrium pressure/volume/temperature (PVT) effects in the final part. In separate work we are dealing with the coupling of flow-induced stresses with V - T -time effects.² We here consider another part of the long-term general formulation: the effect of high pressure on viscosity, with special emphasis on reconciling the data at low shear rates with those at high shear rates.

There is a relatively small literature on the effect of pressure on viscosity for polymeric materials, although work on pressure effects in low molecular

*Present Address: Research Center for Medical Polymers and Biomaterials, Kyoto University, Sakyo-ku, Kyoto 606, Japan.

weight materials has a longer history. In a classic work in 1931 Bridgman³ reviewed the literature as it then existed and went on to develop a theoretical and experimental understanding of the effect of pressure on ordinary liquids. Although there were a few early studies which included polymers, major work began in the 1950s and will be reviewed here briefly.

Capillary rheometers in various forms have been used by several investigators (Maxwell and Jung,⁴ Westover,⁵ Carley,⁶ Choi,⁷ and Ito et al.⁸). The general conclusion is that pressure causes the melt viscosity to increase very substantially at high pressures; for example, for polystyrene at 195°C and 125 MPa, the viscosity increases by a factor of 135 compared with atmospheric pressure,⁴ although the factor may be less at high shear rates.⁸ Smaller factors, of the order of 4–14, have been reported for polyethylene.^{4,7} Related measurements involving the nonlinearity of pressure drop with die length (in experiments in which the polymer flows from a very high pressure to atmospheric pressure) have been reported by Penwell and Porter⁹ and Penwell, Porter and Middleman¹⁰; a review on these and related experiments is provided by Goldblatt and Porter.¹¹

A pressurized Couette (rotational) viscometer was used by Cogswell and McGowan¹² to determine viscosities for various liquids, including a number of polymer melts; the polymeric data were extrapolated to low, but unstated, shear rates. For polystyrene 55- to 500-fold increases in viscosity were reported at 210 and 170°C, respectively. Subsequent work by Cogswell¹³ on the same instrument quantified the analogy between increasing the pressure and decreasing the temperature. Other work using the Couette geometry is that of Hellwege et al.,¹⁴ who found that the zero shear viscosity of a narrow molecular weight distribution polystyrene to be much more pressure sensitive than polyethylenes. Of interest in connection with our results here is an earlier paper from the same group (Semjonow¹⁵), which reported a much smaller factor of viscosity increase (2.2 times the atmospheric data at 100 MPa) at a high shear rate (40 s⁻¹). Finally, a falling sphere experiment reported by Ramsteiner¹⁶ produced low shear rate data for polystyrene.

The analysis of high pressure viscosity data is intimately connected with matters of free volume and the effect of pressure (as well as of temperature) on the glass transition. Havlicek et al.¹⁷ reported experimental work of Oels and Rehage,¹⁸ which showed a large increase of T_g with increasing pressure. O'Reilly¹⁹ and Goldblatt and Porter¹¹ summarize a great deal of data of this kind for several polymers. Although a considerable literature on PVT equations exists (see, for example, Ref. 20), little of it deals with free volume explicitly. Utracki has pointed out the usefulness of the Simha–Somcynsky equation of state (Simha and co-workers^{21–23}) in which a parameter directly related to free volume (y , the occupied hole fraction) occurs. With some empiricism in the choice of the normalizing pressure, Utracki has used this theory to bring together the effects of both temperature and pressure on viscosity, for a number of low molecular weight and polymeric materials.^{24–26} Because our analysis is similar to Utracki's, the details of these correlations will be presented in a later section. In recent work Kühnle²⁷ used a Carreau constitutive equation and various shift factors to bring together data over a range of temperatures, pressures, and shear rates. This work will be commented on again in a later section.

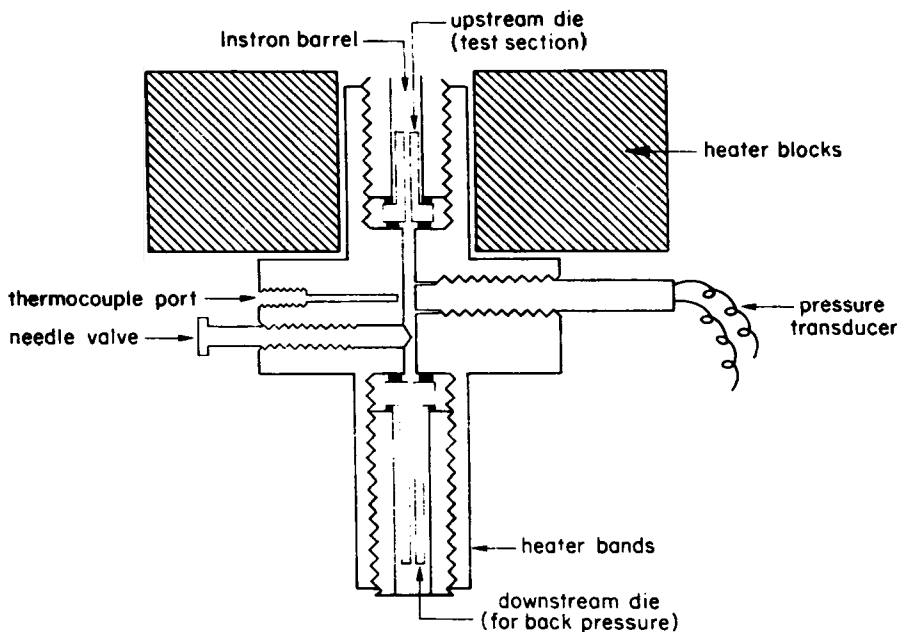


Fig. 1. Schematic diagram of the equipment.

EXPERIMENTAL

Material

The material studied was a commercial polystyrene (Shell TC 3-30), which has been used in several other rheological studies.^{28,29} The molecular weight parameters for this polymer are $M_w = 280,000$ and $M_w/M_n = 4.6$.

Apparatus and Experimental Procedures

The basic instrument was an Instron capillary rheometer, modified in such a way that high pressures (up to about 124 MPa or 18,000 psi) could be developed in the die. This was done by building a die assembly with a downstream chamber in which a back pressure could be developed by means of two restrictions: a second die and a needle valve (see Fig. 1). The upstream die is the test capillary tube; the downstream die serves only to help produce high pressures in the intermediate chamber. The pressure was measured with a Tuffage pressure transducer with a range of 0–15,000 psi. The downstream chamber was kept at isothermal conditions by means of several band heaters, controlled by a Variac. Various gasketing materials were tried, with silver gaskets finally providing the necessary seals. Two dies were used, the first with a diameter of 0.125 in. ($L/D = 15$) and the second with a diameter of 0.071 in. ($L/D = 20$).

Runs were made by running the crosshead of the Instron at some given speed and determining the pressure drop as the difference between that measured in the Instron barrel and that measured by the pressure transducer

in the downstream chamber. The average of these two pressures was taken as the absolute pressure characteristic of that run. During the run at the highest pressures, the pressure was about 170 MPa in the barrel and 80 MPa in the downstream chamber, giving a pressure drop of 90 MPa and an (average) absolute pressure of 125 MPa. With such high pressure drops, one must worry about the possibility of significant viscous heat generation, as will be discussed further below. In more typical runs (excluding that at the highest pressure) the pressure drop was a lesser percentage (typically less than 30%) of the upstream pressure.

Adding the needle valve to the system would, in principle, allow setting the downstream pressure independent of the flow rate, but this was not completely successful. At low shear rates, the downstream pressures were increasingly difficult to hold, precluding the measurement of viscosities at low ("zero") shear rates. The useable data of the work are in the shear rate range of about $1\text{--}100\text{ s}^{-1}$.

Runs in the temperature range from 170 to 190°C were made. The 190°C runs were made early in the work when there was considerable difficulty holding a high downstream pressure. This temperature was not pursued further and runs at 170 and 180°C were subsequently made. At 170°C the pressure drop increased drastically and not always in a consistent manner. In particular, the pressure readings were not constant with time, often showing temporary plateaus for several minutes but then undergoing upward excursions to the limit of the transducer. Our observation of pressure excursions is not unlike the comment of Maxwell and Jung⁴ that their polystyrene "acted like a plug" above 20,000 psi.

The possibility that the high pressures are inducing the glass transition must certainly be considered. Values for dT_g/dP range from about 0.03 to 0.04°C/bar^{11,19}; for our run at the highest average pressure (124 MPa average die pressure), this would result in ΔT_g 's of 37–50°C, or T_g 's in the range 137–150°C (taking T_g to be 100°C at 1 atm). In this run, the chamber pressure was 170 MPa, giving a T_g of 167°C in the worst case; the detailed dilatometric data of Oels and Rehage¹⁸ give, however, a transition temperature of only about 137°C at this pressure. Given these considerable differences, we cannot rule out the possibility that the material in the upstream chamber, at 170°C, might have been at or near the glass transition. That seems unlikely, however, at 180°C, given the higher temperature and also the fact that most of our runs were at pressures substantially below 124 MPa. This is consistent with our experimental observation that the time excursion problem disappeared at 180°C, the temperature used in the subsequent work. The entire matter of time dependence at high pressures does, however, need further study. In particular, the dilatometric data of Oels and Rehage¹⁸ suggest that the difference between the rubbery and glassy states is less distinct at higher pressures.

Data Treatment

Data treatment in capillary rheometry starts with the well-known relation usually referred to as the "Mooney–Rabinowitsch equation,"³¹ which should, however, probably be attributed to Weissenberg (see White³²). In that equa-

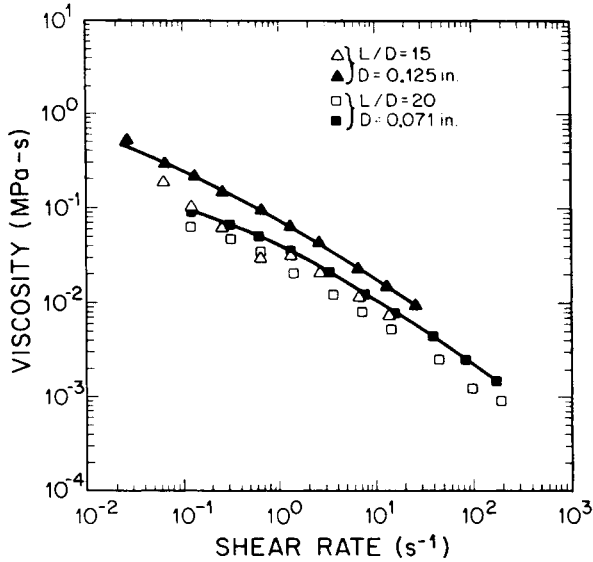


Fig. 2. Uncorrected viscosity data at atmospheric pressure and 180°C, showing the effect of die dimensions and the downstream chamber: (open symbols) data with downstream chamber removed; (solid symbols with lines through them) data with downstream chamber in place.

tion one takes the measured flow rates, pressure drops and die dimensions and obtains finally the shear stress as a function of shear rate. Because we lacked a set of completely isobaric data at different flow rates, the appropriate slope in this procedure was estimated from the similar data of Ito et al.⁸ At any shear rate the apparent viscosity (η) can be calculated by dividing the shear stress by the shear rate. Two corrections to the raw viscosity data were considered, one having to do with possible interference to the flow patterns from the upstream and downstream chambers, the other having to do with viscous heat generation.

The former effects could be quantified by making measurements with dies of various diameters and lengths; and by making atmospheric pressure runs with the downstream chamber in place and then again with the chamber removed (i.e., a free exit). Data from these runs are shown in Figure 2. It is clear that the effects of the die dimensions and of the upstream/downstream geometry are significant. In the absence of extensive data for various L/D ratios, a "Bagley plot" was not possible; fortunately, however, in the high pressure runs, the data from the two dies superimposed well and thus neglect of a correction for L/D was felt to be acceptable. The effect of the downstream chamber was accounted for by introducing a correction factor to the subsequent (high pressure) data in the form $\Gamma = \eta(\text{free})/\eta(\text{chamber})$. That is, the calculated viscosities were corrected by multiplying them by the factor Γ , as determined from Figure 2, for the particular shear rate and die in question. This correction procedure presumes that the disturbance created by the downstream chamber is primarily a viscous one. Our experience with time excursions at 170°C, the relatively high end correction suggested by Figure 2, and finally our emphasis on the modulus as a correlating parameter (as discussed in the next section) suggest that the physical picture should some-

how be one of a "yielding soft solid" rather than that of a simple fluid. Given this complex picture, the corrections made are not, of course, rigorous but seem to us reasonable. Because one must turn to the capillary geometry for high shear rates, correction of this or a similar kind will be necessary for dealing with high shear rate data. The problems noted here have not received adequate attention in the past and further studies are clearly needed before the picture is fully understood.

The problem of viscous heat generation must be considered in any capillary flow with a large pressure drop. The early work of Porter and co-workers,^{9,10} involving the flow from a high pressure upstream chamber to atmospheric pressure, did not consider temperature changes due to viscous heat generation, a difficulty noted by Cogswell.¹³ However, if one considers the combined heat transfer/heat generation problem, the difficulty is not as serious as one might suppose. Viscous polymers flowing through small capillary tubes approach the heat transfer limit of low Graetz numbers: that is, $h_{in}D/k = 3.66$,³³ where h_{in} is the heat transfer coefficient based on a log mean temperature difference, D is the tube diameter, and k is the thermal conductivity of the polymer. Using this asymptote, one concludes that the polymer remains essentially at the wall temperature, even in the presence of significant heat generation. More details are presented in the thesis.³⁰ It was thus concluded that no correction for viscous heat generation was necessary in the present work; a similar conclusion may very well apply to earlier capillary experiments as well.

DATA PRESENTATION AND ANALYSIS

Zero Shear Rate Viscosities and Shift Factors

In any constitutive theory the zero shear rate viscosity (η_0) can be represented as a sum of elastic moduli (G_i) multiplied by the corresponding time constants (τ_i)³⁴:

$$\eta_0 = \sum_i G_i \tau_i \quad (1)$$

When temperature is the only variable to be considered, the G_i are typically shifted by making them proportional to the absolute temperature, although this small shifting is sometimes neglected. The big effect of temperature is on the time constants τ_i , which are shifted by means of the well-known Williams, Landel, and Ferry (WLF) equation, given here in terms of constants for polystyrene melts at temperatures in °C³⁴:

$$\log a_T = -6.3 (T - 160)/(T - 48.5) \quad (2)$$

This shift factor would be used in the form $\tau_i = \tau_{0,i} a_T$, where $\tau_{0,i}$ is the time constant at the reference temperature (160°C in the present case).

As discussed previously, Utracki has been successful in bringing together both temperature shift factors and pressure shift factors by using the free volume factor (γ) in the Simha-Somcynsky (S-S) equation of state. In terms

of shift factors the equation becomes

$$\log a_{TP} = Y - Y_0 \tag{3}$$

where $Y = 1/(1 - y)$ and where y is obtained from the S-S theory. Because of the complicated mathematical form of that equation we here approximate the expression for Y with the empirical equation

$$Y = K_1(\bar{T}) + K_2(\bar{T})\bar{P} \tag{4}$$

where $\bar{T} = T/T^*$ and $\bar{P} = P/P^*$ are the reduced temperature and pressure, respectively, of the S-S theory. For polystyrene the characteristic reference parameters are $T^* = 12,680$ K and $P^* = 745$ MPa.²⁶ The fact that Y is essentially linear in P was noted by Utracki³⁵ and results in a considerable simplification. We note further that $K_1(\bar{T})$ can be approximated by the WLF form, which allows easy reduction to classical results. The final correlating forms for $K_1(\bar{T})$ and $K_2(\bar{T})$ are

$$K_1(\bar{T}) = 0.1665/(\bar{T} - 0.01915) \tag{5}$$

and

$$K_2(\bar{T}) = 0.44/(\bar{T} - 0.0224) \tag{6}$$

Using eq. (5), a reference temperature of 160°C, and considering low pressures ($P = 1$ atm), eq. (3) can be approximated by

$$\log a_T = Y - Y_0 = -11.1(T - 160)/(T + 30.3) \tag{7}$$

where now T is expressed in °C. The various temperature shift factors noted above [that is, eq. (2), eq. (3) with $P = 1$ atm in the S-S theory, and eq. (7)] are compared in Figure 3. From this figure one would conclude that they are all essentially the same at temperatures above T_g (about 100°C); because of the scale of the plot, however, values of a_T itself (as opposed to the logarithm) can be considered the same only above about 140°C.

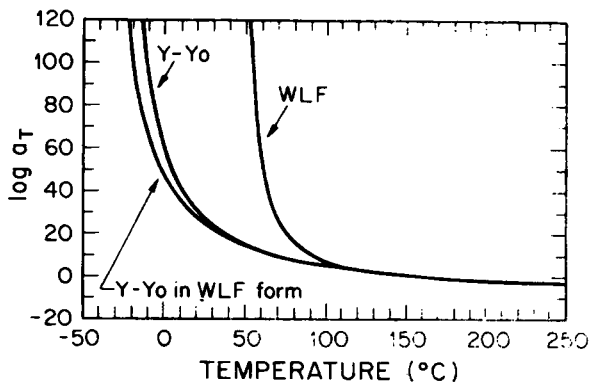


Fig. 3. Temperature shift factors in various forms. The curve marked "WLF" is eq. (2); the curve marked $Y - Y_0$ is that of Utracki,²⁶ based on eq. (3) and the S-S theory; and the curve marked $Y - Y_0$ in WLF form is eq. (7).

Utracki²⁶ has been successful in bringing together both temperature and pressure-dependent zero shear viscosity data, principally those of Cogswell and McGowan,¹² by using the shift factor of eq. (3) (with y coming from the S-S theory). In fact, Utracki directly correlated η (not τ_i) and thus we are presuming in summarizing his results in the present notation that the G_i 's of eq. (1) are not significantly dependent on pressure or temperature. Some empiricism was needed, however, in making the pressure data fall on the master curve: specifically, Utracki found it necessary to replace P^* in the S-S theory by $2P^*$. This is equivalent to imagining "effective pressures" which are half those actually measured. Nonetheless, the framework provided by Utracki provides a reasonable basis for bringing together zero shear viscosity data over a wide range of pressures and temperatures. We turn now to the problem of dealing with viscosity data at high shear rates.

Presentation and Analysis of High Shear Rate Data

To provide a base case for comparison, a number of runs were made at atmospheric pressure and 180°C. These data are presented in Figure 4 with a least squares fit (the dashed line) drawn through them. The data are fit with a rheological model which is an adaptation of one we have used in many earlier studies.^{29,36} Specifically, we use a one-element form of eq. (1) with, in the present instance, a constant G (independent of temperature and shear rate) and an effective (shear rate dependent) time constant τ , given by

$$\tau = \frac{\tau_0}{1 + a(\dot{\gamma}\tau_0)^{0.82}} \quad (8)$$

where τ_0 is the time constant at zero shear rate, $\dot{\gamma}$ is the shear rate, and a is

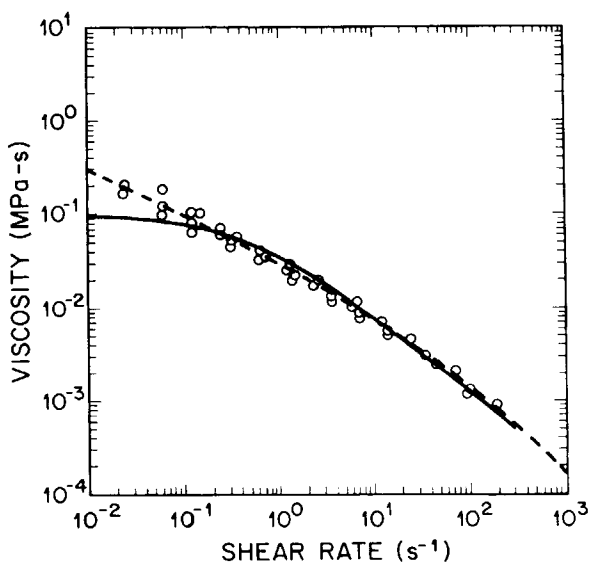


Fig. 4. Shear-dependent viscosity data of the present work at 180°C and 1 atm: (----) least squares fit through the data; (—) fit of the model $\eta = G\tau$, with τ from eq. (8).

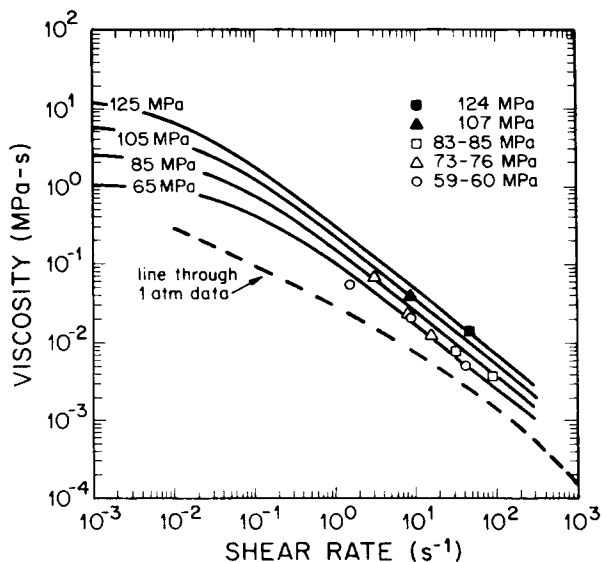


Fig. 5. Comparison of high pressure viscosity data of the present work with predictions from the model [eq. (9)]: (—) model predictions; (---) least squares line through the 1 atm data, from Figure 4.

an adjustable constant. If the exponent 0.82 is replaced by 1.0, this becomes the model suggested earlier by Bogue and White,³⁷ as used in our prior work. Dietz and Bogue³⁸ and others have observed that an exponent of 1.0 is too high; based on the extensive data of Masuda et al.,³⁹ it is here adjusted to 0.82, which is close to the value predicted by Graessley.⁴⁰ The theoretical line of Figure 4 is, then, a fit of a one element model to the data, with the numerical values being $G = 0.05$ MPa, $\tau_0 = 2.0$ s (at 180°C), and $\alpha = 1.0$. Additional fitting of this and earlier shear data with a multielement model is shown in the thesis.

The high pressure data of the present work are presented in Figures 5 and 6; the dashed line is a least squares fit through the atmospheric data, as a basis for comparison. Except for the data at the lowest pressures (13–17 MPa), the internal consistency and reproducibility are good. The scatter at the lower pressures is due to the error in reading small pressure drops and to the difficulty of holding a constant back pressure under these conditions (as noted earlier).

Postponing for the moment any discussion of the theoretical lines in Figures 5 and 6, it is clear that the change of viscosity with pressure, while substantial when compared with the atmospheric data, is considerably smaller than the corresponding change at low shear rates (a factor of 10 or less at high shear rates compared with a factor of 100 or more at low shear rates). This lower factor at high shear rate is consistent with capillary viscosity data for polystyrene reported by Ito et al.⁸ The tendency of viscosity curves to approach each other at high shear rates is not limited to pressure changes: in particular, when molecular weight is the parameter, there is a large difference at low shear rates but a much smaller one at high shear rates³⁹; similarly, when temperature is the parameter under consideration.⁴¹ The reason for this

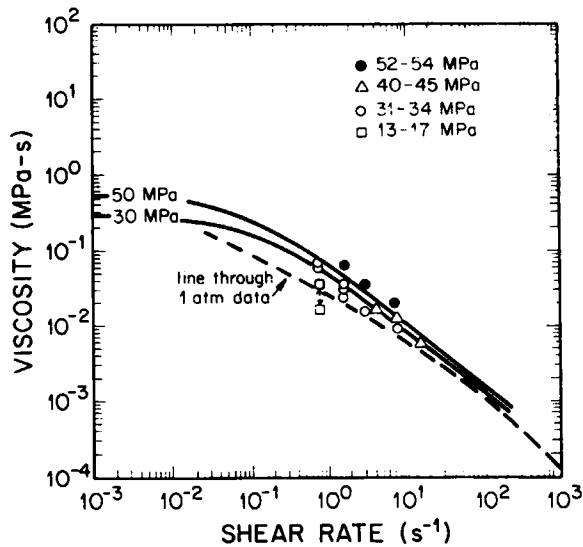


Fig. 6. Comparison of medium pressure viscosity data of the present work with predictions from the model [eq. (9)]: (—) model predictions; (----) least squares line through the 1 atm data, from Figure 4.

effect can be understood by inspecting eq. (8) at high shear rates, that is, τ becomes proportional to $\tau_0^{0.18}/a\dot{\gamma}^{0.82}$. (For the earlier Bogue-White model, with an exponent of 1.0 in the denominator, the limit is $1/a\dot{\gamma}$.) In either case the effective time constant becomes substantially independent of τ_0 at high shear rates; this conclusion follows whether one uses the model of eq. (8) or some other model, the result being forced by the experimental observations just cited. Since the viscosity is product of the modulus and the effective time constant ($\eta = G\tau$), one concludes that the behavior at high shear rates is largely governed by G , not τ_0 . This conclusion is similar to that of Kühnle,²⁷ who observes that the pressure dependence of viscosity is diminished ("veiled") at high shear rates. One must, therefore, deal carefully with how the modulus G varies with pressure (or temperature or molecular weight) when high shear rates are being considered.

There is a limited literature of the effect of pressure on modulus in the melt state. Key data, that of Hellwege et al.¹⁴ and Zosel,⁴² are shown in Figure 7. The Hellwege data cover a range of values as indicated by the vertical arrows. Our task is to reconcile the high shear rate data of Figures 6 and 7 with the low shear rate data of Cogswell and McGowan,¹² which are fortunately for a material of a molecular weight ($M_w = 295,000$) very close to that of our work ($M_w = 280,000$). Temperature shifting of their data (ranging from 170 to 210°C) to our temperature of 180°C was accomplished using eq. (7). The question is, then, of correlating the effect of pressure over the entire range of pressures and shear rates.

We have noted above the need to place most of the pressure dependence of viscosity (at high shear rates) in the modulus $G(P)$; this fact, however, must be reconciled with the need to make both the modulus G and the time constant τ , especially the latter, dependent on pressure at low shear rates.

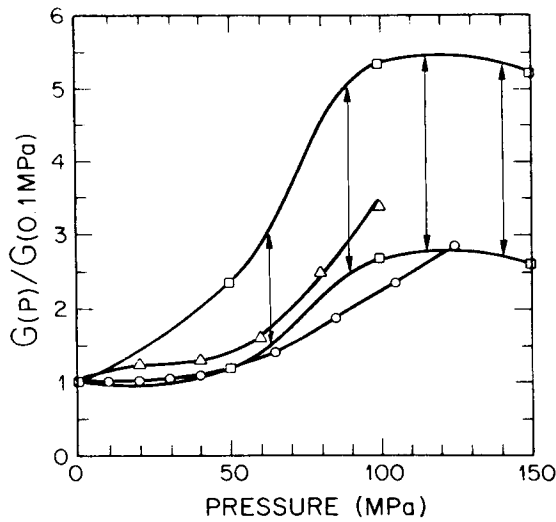


Fig. 7. Shear modulus as a function of pressure: (□) two lines showing range of data of Hellwege et al.¹⁴ for PS; (Δ) data of Zosel⁴² for PVC; (○) from fit of the data for the present work for PS.

These requirements led finally to the following correlations:

$$\eta(T, P) = \frac{G(P) \tau_0(T, P)}{1 + a[\tau_0(T, P) \dot{\gamma}]^{0.82}} \tag{9}$$

where $G(P)$ is obtained from the empirical function sketched in Figure 7 (marked “present work”), which can be fit with a polynomial as follows:

$$G(P)/G(0.1 \text{ MPa}) = 1 - 2.37 \times 10^{-3}P + 1.041 \times 10^{-4}P^2 \tag{10}$$

where P is in units of MPa and $G(0.1 \text{ MPa}) = 0.05 \text{ MPa}$. The small effect of absolute temperature on the modulus in the rubbery state is neglected. In eq. (9) the parameter $a = 1.0$ and the time constant τ_0 is given by

$$\tau_0(T, P) = \tau_0(0) a_{TP}(T, P) \tag{11}$$

where

$$\log a_{TP} = Y - Y_0 = [K_1(\bar{T}) - K_1(\bar{T}_0)] + [K_2(\bar{T})\bar{P} - K_2(\bar{T}_0)\bar{P}_0] \tag{12}$$

where $\tau_0(0)$ is the zero shear time constant at the new reference temperature (180°C) and reference pressure (0.1 MPa) [$\tau_0(0) = 2.0 \text{ s}$]; $K_1(\bar{T})$ and $K_2(\bar{T})$ are the function of eqs. (5) and (6) with \bar{T} being the reduced temperature; \bar{P} and \bar{P}_0 are, respectively, the reduced pressure corresponding to the experimental pressure and that corresponding to the reference pressure; and \bar{T} and \bar{T}_0 are the corresponding reduced temperatures. Following Utracki,²⁶ it is necessary to introduce some empiricism in the selection of the S-S scaling pressure; he used $P_r^* = 2.0P^*$, whereas we used $P_r^* = 3.25P^*$, where P_r^* is the “effective”

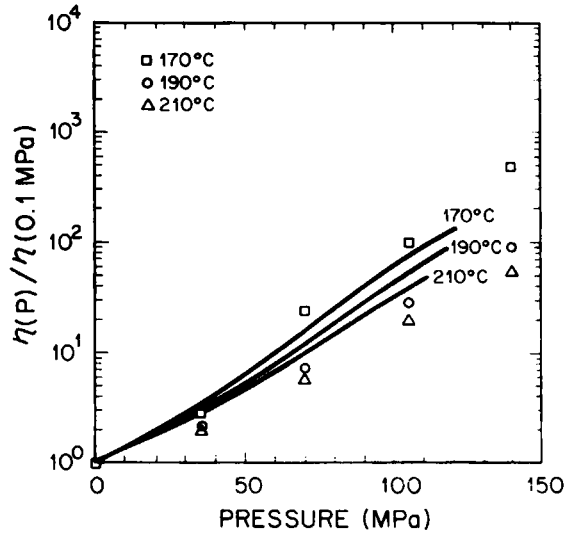


Fig. 8. Ratio of the zero shear viscosity data at high pressure to that at low pressure (≈ 1 atm), data of Cogswell and McGowan¹²: (—) model predictions based on eqs. (9)–(12), with $P_r^* = 3.25P^*$.

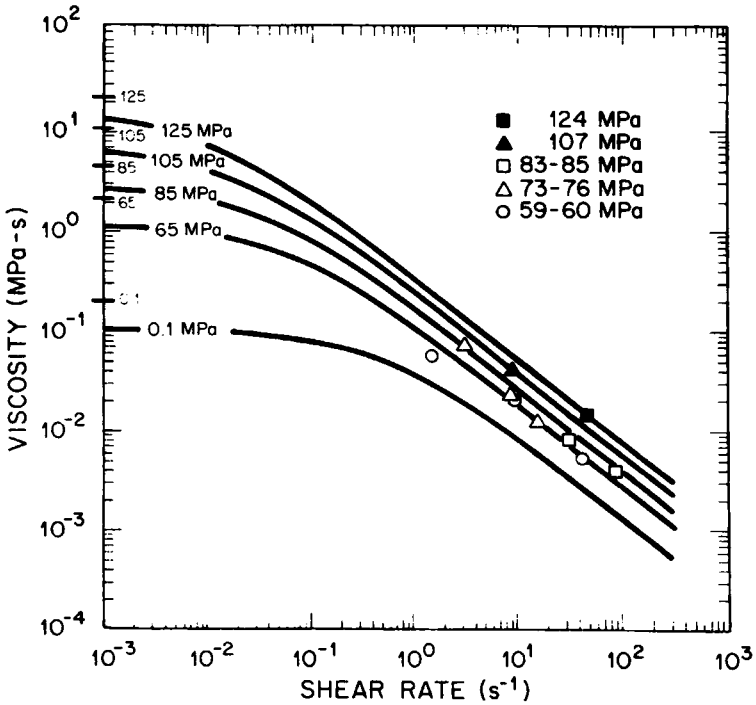


Fig. 9. Summary plot of high pressure viscosity data, showing zero shear data of Cogswell and McGowan¹² and high shear rate data of the present work. The zero shear data, measured at low but unknown shear rates, are marked with short horizontal bars, corresponding to the pressures shown (in MPa); (—) model predictions based on eqs. (9)–(12), with $P_r^* = 3.25P^*$.

(rheological) scaling pressure. This magnitude of adjustment is within the range noted by Browstow and Szymanski,⁴³ who have reviewed the "scaling pressures" which are needed in various transport processes. The theory lines shown in Figures 5, 6, 8, and 9 are, then, calculated from eqs. (9)–(12). The final figure (Fig. 9) brings together in summary form the important data from our work and the correlation of these data with respect to the zero shear data of Cogswell and McGowan.¹² Their data are represented by horizontal marks at the appropriate viscosity value, since they do not state the shear rate at which the data were measured (though low, no numerical values are given). One sees then that the formulation of eqs. (9)–(12) provides a reasonable correlation over a considerable range of pressures and shear rates.

CONCLUSIONS

The behavior of polymer melts at high pressure is not simple. At low shear rates there is a rough analogy between increasing the pressure and decreasing the temperature, both of which cause the viscosity to increase: very dramatically if one is near the glass transition and less so if one is far into the rubbery state. These effects can be accounted for by introducing a generalized shift factor, such as the one suggested by Utracki based on the Simha–Somcynsky equation of state. At high shear rates, however, the physical picture shifts to a dependence on the elastic modulus. If one recalls that the viscosity is the product of an elastic modulus and a time constant (or, more generally, of a spectrum of elastic moduli and time constants), one can say that the effect of pressure (and also of temperature and molecular weight) is strongly dependent on the time constants at low shear rates but changes to a strong dependence on the elastic moduli at high shear rates.

The experiments of the present work were made in a capillary rheometer, which allows measurements at high shear rates but which presents several experimental difficulties in practice. The difficulties have to do with entrance and exit effects, not all of which were resolved definitively in the present work. At high shear rates and high pressures the physical picture appears to be one of a "soft yielding solid" rather than that of a simple fluid. A reasonable, but not completely rigorous, procedure for the data treatment was developed, based on a shear-dependent rheological model.

The model consists of a temperature/pressure/shear-dependent time constant and a pressure-dependent elastic modulus. Using it, we are able to bring together the extensive low shear rate viscosity data of Cogswell and McGowan (in which both temperature and pressure were varied) with the high shear rate data of the present work (in which the pressure and shear rate were varied). There is, finally, good agreement between experiment and model predictions over a range of temperatures, pressures and shear rates.

The authors acknowledge with thanks the support of the Polymer Consortium at the University of Tennessee and also partial support for the first author from the Plastics Institute of America. Finally, the help of Dr. L. A. Utracki in providing a computer printout of results from the Simha–Somcynsky equation, and for a number of helpful suggestions, is greatly appreciated.

References

1. W.-C. Ko and D. C. Bogue, *J. Rheol.*, **31**, 425 (1987).
2. W.-C. Ko, Ph.D. dissertation, Univ. of Tennessee, Knoxville, 1989.
3. P. W. Bridgman, *The Physics of High Pressure*, Macmillan, New York, 1931.
4. B. Maxwell and A. Jung, *Mod. Plast.*, **57** (1), 174 (1957).
5. R. F. Westover, *SPE Trans.*, **1**, 14 (1961).
6. J. F. Carley, in *SPE 17th ANTEC Technical Papers*, Paper No. 25-4, Jan. 1960.
7. S. Y. Choi, *J. Polym. Sci. A-2*, **6**, 2043 (1968).
8. K. Ito, M. Tsutsui, M. Dasajima, and T. Ojima, *Appl. Polym. Symp.*, **20**, 109 (1973).
9. R. C. Penwell and R. S. Porter, *J. Polym. Sci. A-2*, **9**, 463 (1971).
10. R. C. Penwell, R. S. Porter, and S. Middleman, *J. Polym. Sci. A-2*, **9**, 731 (1971).
11. P. H. Goldblatt and R. S. Porter, *J. Appl. Polym. Sci.*, **20**, 1199 (1976).
12. F. N. Cogswell and J. C. McGowan, *Brit. Polym. J.*, **4**, 183 (1972).
13. F. N. Cogswell, *Plast. Polym.*, **41**, 39 (1973).
14. K. Hellwege, W. Knappe, F. Paul, and V. Semjonow, *Rheol. Acta*, **6**, 164 (1967).
15. V. Semjonow, *Rheol. Acta*, **2**, 138 (1962).
16. V. F. Ramsteiner, *Rheol. Acta*, **9**, 374 (1970).
17. I. Havlicek, M. Ilavsky, and J. Hrouz, *J. Macromol. Sci. Phys.*, **B21**, 425 (1982).
18. H. Oels and G. Rehage, *Macromolecules*, **10**, 1036 (1977).
19. J. M. O'Reilly, *J. Polym. Sci.*, **57**, 429 (1962).
20. Symposium on Applications of Equations of State in Rheology, 57th Annual Meeting, Society of Rheology, Ann Arbor, 1985; collected papers published in *J. Rheol.*, **30**(4) (August 1986).
21. V. S. Nanda, R. Simha, and T. Somcynsky, *J. Polym. Sci. C*, **12**, 277 (1966).
22. R. Simha and T. Somcynsky, *Macromolecules*, **2**, 342 (1969).
23. R. Simha, *Macromolecules*, **10**, 1025 (1977).
24. L. A. Utracki, *Polym. Eng. Sci.*, **23**, 446 (1983).
25. L. A. Utracki, *Can. J. Chem. Eng.*, **61**, 753 (1983).
26. L. A. Utracki, *Polym. Eng. Sci.*, **25**, 655 (1985).
27. H. Kühnle, *Internat. Polym. Proc.*, **1**, 89, 116 (1987).
28. T. Matsumoto and D. C. Bogue, *Trans. Soc. Rheol.*, **21**, 133 (1977).
29. R. Racin and D. C. Bogue, *J. Rheol.*, **23**, 263 (1979).
30. P. D. Driscoll, MS thesis, Univ. of Tennessee, Knoxville, Dec. 1986.
31. C. D. Han, *Rheology in Polymer Processing*, Academic, New York, 1976.
32. J. L. White, in *Science and Technology of Rubber*, Academic, New York, 1978, Chap. 6.
33. R. B. Bird, W. E. Lightfoot, and E. N. Stewart, *Transport Phenomena*, Wiley, New York, 1960.
34. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York, 1980.
35. L. A. Utracki, private communication.
36. D. A. Carey, C. J. Wust, Jr., and D. C. Bogue, *J. Appl. Polym. Sci.*, **25**, 575 (1980).
37. D. C. Bogue and J. L. White, *Engineering Analysis of Non-Newtonian Fluids*, NATO Agardograph No. 144, Clearinghouse for Fed. Tech. Info, Springfield, VA, 1970.
38. W. Dietz and D. C. Bogue, *Rheol. Acta*, **17**, 595 (1978).
39. T. Masuda, M. Takahashi, and S. Onogi, *Appl. Polym. Symp.*, **20**, 49 (1973); see also T. Masuda, Ph.D. dissertation, Polymer Chemistry, Kyoto Univ., Kyoto, 1973.
40. W. W. Graessley, *J. Chem. Phys.*, **43**, 2696 (1965).
41. R. C. Penwell, W. W. Graessley, and A. Kovacs, *J. Polym. Sci. Polym. Phys. Ed.*, **12**, 1771 (1974).
42. A. Zosel, *Kolloid Z.*, **199**, 113 (1964).
43. W. Browstow and W. Szymanski, *J. Rheol.*, **30**, 77 (1986).

Received April 6, 1988

Accepted March 20, 1989