

## A Comparison of Equations for the Effect of Pressure on the Viscosity of Amorphous Polymers

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### Synopsis

Several equations which are used to predict the pressure coefficient of viscosity for amorphous polymers have been examined on the basis of type of information required and equation reliability. These equations can be useful in accounting for pressure effects observed in tubular flow and in other shear geometries. The correlations of Penwell and Porter and of Miller are evaluated and in the perspective of expressions by Matheson and by Eyring. Data on linear amorphous polystyrene (PS), polyisobutylene, poly(vinyl acetate), poly(methyl methacrylate) (PMMA), natural rubber, and polycarbonate are examined and presented. Predictions from the Penwell-Porter and Miller equations are compared with experimental coefficients at one atmosphere for all data available. For PS and PMMA, it was found that Miller's equation tends to predict values somewhat higher than experiments but is closer to the data on PS and on a high molecular weight PMMA. The Penwell-Porter equation, on the other hand, tends to predict values somewhat lower than experiments and does a slightly better job for lower molecular weight PMMA. Both equations require WLF or Vogel coefficients and  $T_g$ -pressure-molecular weight data. Miller's equation also requires compressibilities at  $T_g$  and at the temperature of interest, although an alternate method can be used which only requires average "K" values without  $T_g$ -pressure or compressibilities at  $T_g$ .

### INTRODUCTION

Several equations have been developed for the effect of pressure on the viscosity of liquids. This paper tests these equations against the limited literature data on polymers which is assembled here for the first time. Sufficient data are available for polystyrene, polyisobutylene, poly(vinyl acetate), poly(methyl methacrylate), natural rubber, and polycarbonate amorphous polymers which are used as input for these equations.

A correlation was observed<sup>1</sup> some time ago between the density (or specific volume) of liquids and viscosity. This led to the free-volume theory of viscosity. This theory divides the specific volume into a free and a molecularly occupied volume. This concept has been found to work well for liquids, as by the Matheson equation,<sup>2</sup> and for polymers using the WLF equation.<sup>3,4</sup> Occupied volume may be constant or nearly so. Its dependence on temperature and pressure is the subject of some debate. Explanations and evidence have been offered as to the dependencies this volume might take.<sup>5,6</sup>

The effects of pressure on viscosity can be important in the processing in-

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dustry—injection molding and in extrusion—where high pressures are extant.<sup>7</sup> The interpretation is complicated by the high shear rates which usually accompany pressure. These high shear rates can also give rise to viscosity changes due to shear heating. The shear-thinning effects which are induced are not accounted for by free-volume models. Penwell and Porter,<sup>8,9</sup> however, have successfully used viscosity–pressure predictions based on free volume to account for an anomalous increase in viscosities at high shear rate and pressure in a capillary rheometer. This is based on an additivity of free volume and entanglement contributions to viscosity.

A fundamental question arises from the free-volume approach and especially so when dealing with polymers. The question is whether viscosity can be described exclusively by thermodynamic variables, viz., free volume, which are pressure and temperature dependent. For a Newtonian fluid, the continuum hypothesis and the assumption of an isotropic material holds rather well and yields a viscosity coefficient which can be predicted in different modes of flow. The continuum assumptions lead to the conclusion that hydrodynamic and thermodynamic pressures are identical,<sup>10</sup> i.e., polymers are incompressible. However, this is questionable.<sup>10</sup>

Using the WLF equation for expressing pressure effects, it has been assumed that the zero shear, i.e., Newtonian, viscosity is predictable independent of entanglement contributions to viscoelasticity. Thus, the viscosity–molecular weight relation enters only as any change in  $T_g$  with molecular weight. The uncertainty in  $T_g$  will, of course, add error to predictions. The reference temperature in the WLF formulation is also not  $T_g$  but approximately 50° above.<sup>11</sup> The effect of time on the measurement of  $T_g$  is also an effect not accounted for by instantaneous thermodynamic quantities such as compressibility and can be associated with a breakdown of the assumption of continua and isotropy. With all these limitations, the free-volume theory has proved to be of great value because of its utility and apparent wide range of applicability.

It is the purpose of the present note to intercompare several viscosity equations in the literature involving the pressure coefficient at atmospheric pressure. We shall assess the type of data required by each and their relative reliability. The relationships between the compressibility, free volume at  $T_g$ , and the pressure coefficient are also investigated.

### THEORY COMPARISON

A thermodynamic approach presented by Miller<sup>12</sup> has been shown useful for estimating the pressure coefficient of viscosity for amorphous polymers. Miller begins with the exact thermodynamic definition of the pressure coefficient:

$$b = \left( \frac{\partial \ln \eta}{\partial p} \right)_T = - \left( \frac{\partial \ln \eta}{\partial T} \right)_p \left( \frac{\partial T}{\partial p} \right)_\eta$$

where  $b$  is the pressure coefficient,  $\eta$  is the viscosity,  $T$  is absolute temperature, and  $p$  is absolute pressure. Miller then assumes that for any given polymer, the special combination of volume–temperature derivatives,

$$K = \left[ \left( \frac{\partial V}{\partial T} \right)_\eta - \left( \frac{\partial V}{\partial T} \right)_p \right] = \left( \frac{\partial V}{\partial p} \right)_T \left/ \left( \frac{\partial T}{\partial p} \right)_\eta \right.$$

is independent of temperature at atmospheric pressure. This is an exact mathematical equivalence, and the validity of the assumption of constancy with temperature has been demonstrated over a temperature range above  $T_g$ . Using the concept that  $T_g$  is an isoviscous or isomobility state, one can evaluate this constant from  $dT_g/dp$  and experimental compressibilities at  $T_g$ . From the well-known Vogel equation for the viscosity-temperature relationship,

$$\ln \eta = A + \frac{2.3B}{(T - T_0)}$$

Following Miller's derivation,

$$\left. \frac{\partial \ln \eta}{\partial T} \right|_p = - \frac{2.3B}{(T - T_0)^2}$$

and noting that

$$\left( \frac{\partial T}{\partial p} \right)_\eta = \frac{dT_g}{dp}$$

at the glass transition temperature and that

$$K = \left( \frac{\partial V}{\partial p} \right)_T / \left( \frac{\partial T}{\partial p} \right)_\eta$$

which is equal to  $(\beta V)_g / \frac{dT_g}{dp}$  at  $T_g$ ; we obtain for  $\left( \frac{\partial \ln \eta}{\partial p} \right)_T$

$$\left( \frac{\partial \ln \eta}{\partial p} \right)_T = \frac{2.3B}{(T - T_0)^2} \cdot \frac{\beta V}{K}$$

Substituting for  $K$ , we obtain

$$b = \frac{2.3B}{(T - T_0)^2} \frac{dT_g}{dp} \cdot \frac{\beta V}{(\beta V)_g}$$

where  $B = C_1 C_2$ ;  $T_0 = T_g - C_2$ ;  $\beta V$  is the compressibility at temperature  $T$  and 1 atmosphere =  $-(\partial V / \partial p)_T$ ; and  $(\beta V)_g$  is the compressibility at  $T_g$  and 1 atmosphere. One can easily evaluate the pressure coefficient at different temperatures from compressibility data and WLF coefficients noting the equivalence of the WLF and Vogel equation<sup>13</sup> assuming that the WLF coefficients are experimental constants for each polymer as is commonly done.

Another approach has been presented by Penwell, Porter and Middleman<sup>4</sup> which is based on the WLF equation. The main idea here is that the effect of pressure on viscosity can be accounted for by an increase in  $T_g$  but otherwise the viscosity has the same dependence on  $T$  as the WLF equation but with an elevated  $T_g$  under pressure:

$$\log_{10} \frac{\eta}{\eta_g} = \frac{-C_1 [T - T_g(p)]}{C_2 + T - T_g(p)}$$

$$T_g(p) = T_{g0} + A_1 \Delta p$$

$$\Delta p = p - p_{\text{atm}}$$

$$A_1 = \frac{dT_g}{dp}, \text{ independent of } p$$

This assumption ignores the effect of pressure on  $C_2$  as determined by  $f_g$ , the free-volume fraction at  $T_g$ , and  $\alpha_f$ , the expansivity of free volume which principally affects  $C_2$ .<sup>14</sup> The Penwell-Porter equation thus assumes that  $B = C_1C_2$  is independent of pressure and that  $dT_0/dp = dT_g/dp$ . Although this is not necessarily true, the assumptions may be good at low pressure. There is an increase in slope of the P.-P. equation with pressure but this is probably not observed as the experimental pressure coefficient usually decreases with pressure if the pressure is sufficiently low. However, this slope is approximately constant for polymers of lower molecular weight and at lower pressures.

If one wishes the value of  $b$  at one atmosphere, then  $\eta_g$  need not be known if it is not a function of pressure and

$$\left. \frac{d \log_{10} \eta}{dp} \right|_{1 \text{ atm}} = \frac{d \log_{10} \eta_g}{dp} + \frac{C_1C_2}{(C_2 + T - T_g)^2} \frac{dT_g(p)}{dp}$$

If  $B = C_1C_2$  and  $T_0 = T_g - C_2$ , then

$$\left. \frac{1}{2.3} \frac{d \ln \eta}{dp} \right|_{1 \text{ atm}} = 0 + \frac{B}{(T - T_0)^2} \frac{dT_g(p)}{dp}$$

$$\frac{dT_g(p)}{dp} = \frac{dT_g}{dp} = \text{constant at 1 atm.}$$

so

$$b = \left. \frac{d \ln \eta}{dp} \right|_T = \frac{2.3B}{(T - T_0)^2} \frac{dT_g}{dp}$$

Therefore, this is equivalent to Miller's equation, but only at  $T_g$ , since the ratio of compressibilities,  $(\beta V)_T/(\beta V)_{T_g}$ , increases with temperature. This equation should apply in the same range of temperatures as the WLF equation, namely, up to at least 100°C above  $T_g$ . This approximation is good since the thermal expansion coefficient,  $\alpha_f$ , is approximately constant for this range of temperatures. In this paper, the pressure coefficient is defined as the point slope at 1 atmosphere, namely,  $[d(\ln \eta)/dp]_T$ . This is a departure from pressure coefficients defined in some previous papers<sup>9</sup> as  $b = 2.3 A_3/A_4$ , where  $A_3 = C_1 dT_g/dp$  and  $A_4 = C_2 + T - T_{g0}$ , where  $T_{g0}$  is  $T_g$  at 1 atmosphere.

The P.-P. equation here assumes that the effect of compressibility is taken into account entirely through the change in  $T_g$  with pressure. In the calculations presented below, it will be tacitly assumed that an initial and constant slope of  $\log \eta$ -versus- $p$  plot is applicable to polymers since this slope does seem to be constant in the low pressure range for polymers up to about 1000 bars.<sup>15</sup>

An additional equation is available for estimating the pressure dependence of  $\eta$  on free volume. This is due to Matheson.<sup>2</sup> He assumes that both the specific volume and occupied volume are functions of temperature and pressure. The latter assumption may be questionable. Indeed, Matheson has shown that occupied volume does not vary much over a wide range of pressures. He correlates the occupied volume with a function used by Bridgeman for solids and obtains good results for low molecular weight hydrocarbons. His equation,

$$\log \eta = A' + \frac{B'V_0f(p)}{V - V_0f(p)}$$

can be differentiated to give the pressure coefficient noting that  $f(p)$  is a normalized function describing the pressure dependence of  $V_0$  and is equal to  $1 + a\Delta p + b\Delta p^2$  and  $A'$  is independent of pressure:

$$\left(\frac{d \ln \eta}{dp}\right)_T = B'V_0 \left[ \frac{\left.\frac{\partial f}{\partial p}\right|_{1 \text{ atm}}}{V - V_0} - \frac{\beta V - V_0 \left.\frac{\partial f}{\partial p}\right|_{1 \text{ atm}}}{(V - V_0)^2} \right]$$

It is not known how well this equation holds for polymers. The coefficient has not been calculated since we were not aware of sufficient  $V_0$ -versus- $p$  data to allow computation of  $\left.\frac{\partial f}{\partial p}\right|_{1 \text{ atm}}$ . Regarding the temperature dependence, both Matheson<sup>2</sup> and Laughlin and Ullmann<sup>16</sup> indicate that the Doolittle equation does not produce accurate viscosity values near  $T_g$  where the viscosity is extreme and free volume low.

The hole theory proposed by Eyring has provided an alternate link between compressibility-pressure data and the dependence of viscosity on pressure. According to Eyring and Hirai,<sup>17</sup>

$$1/\beta_h = \frac{RT}{V_h} \exp\left(\frac{\epsilon_h + pV_h}{RT}\right)$$

where  $\beta_h$  is the compressibility of the "holes," viz., free volume; and  $\epsilon_h$  and  $V_h$  are the "internal energy" and volume of the holes, respectively. In addition, the same theory predicts

$$\eta = \eta_0 \exp\left(\frac{pV_h}{RT}\right)$$

so one can find  $b = V_h/RT$  from compressibility data using certain approximations by plotting  $\ln(\Delta V/V - \beta_0 p)$  versus  $p$ , where  $\beta_0$  is the limiting compressibility at low temperature. The slope is  $b$ . We realize that this equation has been applied at temperatures in excess of 100°C above  $T_g$ .<sup>5,16</sup> One could assume that the pressure coefficient should be calculated in this temperature range also. Eyring's equation appears to fit compressibility data near  $T_g$ .<sup>17</sup> However, the viscosity data on polystyrene which was correlated was later found to be inaccurate.<sup>18,19</sup> The semilog dependence of viscosity on pressure predicted by Eyring, however, has been found to hold fairly well in several cases at low pressures and temperatures.<sup>4,12</sup>

## DATA COMPARISON

Considerable judgment is needed in choosing literature data for evaluating predictions. In all cases, we attempted to compare data which was felt most consistent for a wide range of polymers. We did not, however, attempt to match data obtained by the same method or same authors although we realize the inherent error and differences in values obtained by one method as opposed to another. For instance, we used the value of 0.016 in Table I for  $dT_g/dp$  of natural rubber from Paterson's data rather than 0.013,<sup>20</sup> because we felt the former was more reliable.<sup>21</sup> Uncertainties exist in the corresponding  $T_g$  measurements. This is especially true with regard to molecular weight dependence. Values of  $T_g$  were chosen, where possible, for compari-

TABLE I  
 Data Used in Viscosity Pressure Equations

| Polymer | WLF Constants, |                        | $T_g, ^\circ\text{K}$ | $A_1 = \frac{dT_g}{dP}, \text{deg/bar}$ |
|---------|----------------|------------------------|-----------------------|---|
|         | $C_1$          | $C_2 (^\circ\text{C})$ |                       |   |
| PS      | 13.7           | 50 <sup>13</sup>       | 362 <sup>18,25</sup>  | 0.03 <sup>18</sup>                      |
| PIB     | 16.6           | 104.4 <sup>13</sup>    | 208 <sup>25</sup>     | 0.0197 <sup>12</sup>                    |
| PVAc    | 15.6           | 46.8 <sup>13</sup>     | 298 <sup>12</sup>     | 0.0217 <sup>26</sup>                    |
| PMMA    | 14.1           | 90.7 <sup>9</sup>      | 377 <sup>25</sup>     | 0.023 <sup>27,28</sup>                  |
| NR      | 16.8           | 53.6 <sup>13</sup>     | 200 <sup>13</sup>     | 0.016 <sup>29</sup>                     |
| PC      | 15             | 72 <sup>30</sup>       | 417 <sup>26,30</sup>  | 0.0434 <sup>26,30</sup>                 |
|         | 16.3           | 23.3 <sup>14</sup>     |                       |   |

 TABLE II  
 Compressibilities<sup>a</sup> at Three Temperatures

| Polymer | $\beta V$ at $T_1$       | $\beta V$ at $T_2$        | $\beta V_g$ at $T_g$ |
|---------|--------------------------|---------------------------|----------------------|
| PS      | 6.5 <sup>18</sup> (130°) | 7.8 <sup>18</sup> (165°)  | 5.2 <sup>18</sup>    |
| PIB     | 3.6 <sup>31</sup> (-40°) | 5.3 <sup>31</sup> (25°)   | 3.1 <sup>31</sup>    |
| PVAc    | 2.2 <sup>26</sup> (50°)  | 11.1 <sup>26</sup> (100°) | 1.1 (extrap.)        |
| PMMA    | 4.6 <sup>18</sup> (130°) | 8.1 <sup>18</sup> (180°)  | 3.0 (extrap.)        |
| NR      | 3.7 <sup>32</sup> (-50°) | 4.9 <sup>32</sup> (0°)    | 3.2 <sup>32</sup>    |
| PC      | 4.5 <sup>33</sup> (169°) | 5.3 <sup>33</sup> (219°)  | 1.6 <sup>33</sup>    |

<sup>a</sup> In cc/g-bar  $\times 10^5$  at 1 atm.

son of the same polymer molecular weight as in studies on polystyrene and poly(methyl methacrylate) (PMMA). Values of the WLF coefficients,  $C_1$  and  $C_2$ , were considered independent of molecular weight for a given polymer. We realize that  $C_1$  and  $C_2$  do change somewhat with molecular weight, although data are scarce on this effect and we felt that the  $T_g$  change was more important and was accounted for in the calculations. The compressibilities were also assumed to be independent of molecular weight over the range tested, which may not be precisely correct.

The  $T_g$  used for PMMA in Table I is for 133,000 MW in order to compare with Casale's data. This is considerably above the 27,500 entanglement MW ( $M_c$ ) for PMMA. The polyisobutylene (PIB) of 40,000 MW is somewhat above its  $M_c$  of 15,200. Compressibilities given in Table II were extrapolated, where necessary, to provide values at the desired temperatures;  $V$  versus  $(\beta V)^{1/2}$  was plotted in a way similar to that used by Miller.<sup>12</sup>

Table III presents the calculation of the pressure coefficient at two temperatures in the range of applicability of the WLF equation and for the Miller and Penwell-Porter equations. The scarce experimental values are listed. The temperatures for calculation in Table III are listed in parentheses. As can be seen, the two figures listed for polycarbonate (PC) reflect the different WLF coefficients available and the sensitivity of "b" to them. Because of the exponential nature of the WLF equation, the pressure coefficient is not extremely sensitive to the WLF parameters  $C_1$  and  $C_2$ . The data of Casale<sup>9</sup> for PMMA was obtained with an Instron capillary rheometer under pressure and so may be somewhat lower than the values at atmospheric pressures. Values of  $f_g/B$  for each polymer are also included in Table III for a compari-

TABLE III  
Predictions of Pressure Coefficient at 1 Atmosphere

| Polymer | $T_g, ^\circ\text{C}$ | Pressure coefficient, bars $^{-1} \times 10^{-3}$ |                |  |                        |                   |   | $T_2$ exptl.        | $f_g/B^a$ |
|---------|-----------------------|---|----------------|--|------------------------|-------------------|---|---------------------|-----------|
|         |                       | $T_1 \approx T_g + 25$                            |                |  | $T_2 \approx T_g + 75$ |                   |   |                     |           |
|         |                       | Miller  | P.-P.          | P.-P.  | Miller                 | P.-P.             | P.-P.                                     |                     |           |
| PS      | 89 <sup>b</sup>       | 7.14 (130°C)                                      | 5.71           | 4.5 (165°C)                                      | 2.98                   | 7.3 <sup>12</sup> | 5.1 <sup>12</sup>                         | 0.032 <sup>13</sup> |           |
| PIB     | -65                   | 5.45 (-40°C)                                      | 4.72           | 3.57 (25°C)                                      | 2.09                   |                   |   | 0.026 <sup>13</sup> |           |
| PVAc    | 25                    | 14.1 (50°C)                                       | 7.08           | 23.85 (100°C)                                    | 2.46                   |                   |   | 0.028 <sup>13</sup> |           |
| PMMA    | 104.3                 | 7.8 <sup>9</sup> (130°C)                          | 5.0            | 6.71 <sup>9</sup> (180°C)                        | 2.45                   |                   | 2.07 <sup>9</sup> (180°C)<br>4.26 (190°C) | 0.030 <sup>13</sup> |           |
| NR      | -73                   | 6.66 (-50°C)                                      | 5.65           | 3.24 (0°C)                                       | 2.07                   |                   |   | 0.026 <sup>13</sup> |           |
| PC      | 144                   | 31.78 <sup>30</sup> (169°C)<br>45.1 <sup>14</sup> | 11.477<br>16.3 | 16.3 <sup>30</sup> (219°C)<br>12.8 <sup>14</sup> | 5.0<br>3.93            |                   |   | 0.029 <sup>30</sup> |           |

<sup>a</sup> B here is the Doolittle equation parameter.

<sup>b</sup> This value for  $T_g$  was used here to compare predicted coefficients with the experimental values listed for a low molecular weight polymer.

TABLE IV  
Predicted Viscosity-Pressure Coefficients for PMMA at Various Temperatures and Molecular Weights

| No. | $M_n$       | Temp., °C | Values of $b$ ,<br>$\text{bar}^{-1} \times 10^{-3}$ |        | $\beta V$ , cc/g-bar<br>$\times 10^5$ | Exptl.<br>( $d \ln \eta_0/dp$ ) <sub>T</sub> |
|-----|-------------|-----------|---|--------|---------------------------------------|--|
|     |             |           | P.-P.   | Miller |                                       |  |
| 1   | 8,000       | 122       | 5.22  | 7.23   | 4.09                                  | 4.37   |
| 2   | 27,000      | 132       | 4.74  | 7.53   | 4.69                                  | 6.11   |
|     |             | 142       | 4.04  | 7.26   | 5.31                                  | 5.17   |
|     |             | 154       | 3.38  | 7.02   | 6.14                                  | 4.18   |
| 3   | 54,000      | 143       | 4.03  | 7.33   | 5.37                                  | 5.38   |
|     |             | 154       | 3.43  | 7.12   | 6.14                                  | 4.70   |
|     |             | 166       | 2.91  | 6.89   | 7.01                                  | 4.04   |
| 4   | 68,000      | 143       | 4.04  | 7.35   | 5.37                                  | 7.94 (6.44)                                  |
|     |             | 166       | 2.92  | 6.91   | 7.01                                  | 1.88   |
| 5   | 54,000 (BD) | 164       | 2.98  | 6.93   | 6.86                                  | 6.95 (5.31)                                  |
| 6   | 145,000     | 164       | 3.01  | 6.98   | 6.86                                  | 3.10   |
|     |             | 178       | 2.52  | 6.76   | 7.94                                  | 6.29 (5.35)                                  |
|     |             | 189       | 2.21  | 6.58   | 8.79                                  | 5.73 (4.98)                                  |

<sup>a</sup> Experimental values were calculated from the slope of data given by Hermann and Knappe.<sup>22</sup> Values in parentheses are averages over an expanded range of pressures rather than the slopes at one atmosphere.

TABLE V  
Predicted Pressure Coefficients for a Polystyrene of 280,000 MW at Three Temperatures

| Temp., °C | $b$ , $\text{bars}^{-1} \times 10^{-3}$ |        |                     |
|-----------|---|--------|---------------------|
|           | P.-P.                                   | Miller | Exptl. <sup>a</sup> |
| 150       | 4.698                                   | 6.597  | 4.2                 |
| 170       | 3.267                                   | 5.071  | 3.9                 |
| 190       | 2.402                                   | 4.10   | 3.9                 |

<sup>a</sup> Experimental values were obtained from data of Ramsteiner.<sup>23</sup>

son of the approximate  $f_g$ 's for different polymers. The constant  $B$  here is the Doolittle equation parameter and not the Vogel constant. This is consistent with the fact that  $B$  does not change much from polymer to polymer. However, it has been pointed out that the values and ordering of the polymers according to  $f_g$ 's would be different than ordering them according to  $f_g/B$ .<sup>34</sup>

The calculated values in Table IV for PMMA are compared with data by Hermann and Knappe<sup>22</sup> for the change of  $\eta_0$  with pressure. The same paper also includes the effect of shear rate on the pressure coefficient at different temperatures and pressures. The values presented here show where the equations accurately predict temperature and molecular weight effects. All pressure coefficients were adjusted for change of  $T_g$  as the molecular weight of PMMA increased.

Table V compares values of  $b$  for a high molecular weight polystyrene at various temperatures. A  $T_g$  of 100°C for PS was used to calculate the pressure coefficients in this case. The experimental data were obtained by Ramsteiner using a sink viscometer.<sup>23</sup>

## DISCUSSION OF RESULTS

It appears that for the data on PS, Miller's equation does the best job of predicting the pressure coefficient as shown in Table III. The Penwell-Porter equation seems to give a slightly better fit for data on a high molecular weight PMMA. The lower values predicted by the Penwell-Porter equation also seem generally near to experiment for lower molecular weights, but Miller's equation generally does better for high molecular weights. The points for no. 4 at 166°C and no. 6 at 164°C in Table IV seems abnormally low. The reason is not known. The values in parentheses are averages given only where the  $\ln \eta$ -versus- $p$  curve was concave downward, although the curve for no 4 at 166°C was concave upward and the others were nearly straight. The constant  $K$  in the Miller equation may change with temperature, but this requires further investigation.

We note that for pairs of polymers PS plus PMMA, and PIB plus NR, interesting comparisons may be made as  $T_g$ 's for each pair are nearly the same. The values of  $f_g/B$  are about the same for the PIB-NR and PS-PMMA pairs. Ordinarily, it is assumed that the more compressible the polymer, the greater is the effect of pressure on viscosity and that those materials whose viscosities are most sensitive to change in temperature are also most influenced by pressure.<sup>24</sup> Our data show that the compressibilities of PS and PMMA are about the same, although the dependence on temperature is greater for PMMA over the same range. However, the pressure coefficients computed in Table III are also fairly close, with the temperature effect on  $b$  more pronounced at the higher temperatures. In the case of PIB and NR, the compressibilities and their temperature dependence are also about the same. However, the  $b$  values at  $T_1$  (the lower temperature) do not agree well.

Table II shows a clear correspondence between the temperature dependence of compressibility and the absolute value of compressibilities at  $T_g$ . However, no clear-cut relationship was observed between the compressibility and the viscosity-pressure coefficient or between  $f_g/B$  at  $T_g$  and the pressure coefficient. There may be a qualitative correlation between  $f_g$  and  $b$ . One may conclude that the mechanism for viscous flow under pressure is influenced by factors in addition to compressibility and the free volume at  $T_g$ . This conclusion may be in agreement to the statement by Ferry<sup>13</sup> that the effect of pressure changes the occupied volume considerably more than the free volume. The occupied volume he refers to is the van der Waal volume of the molecules plus the volume associated with vibrational modes. It is interesting to note, in addition, that Miller's analysis would not necessarily admit a change in  $(\beta V)_g$  with pressure unless one allowed  $K$  to vary with pressure.

The agreement between theory and experiment in Table IV is essentially qualitative. The equations predict a decrease in  $b$  with temperature at constant molecular weight and this is true experimentally at the lower molecular weights but not at the higher. Samples 4 and 6 show an anomaly here. Sample 5 is known to be a broad (BD) distribution polymer. The effect of MWD in this sample seems to be to increase the sensitivity of  $\eta$  to pressure. It is postulated that entanglements may have some effect on the actual value of the pressure coefficient, but this is unsure. Hermann and Knappe reported that the pressure coefficient goes through a minimum with shear rate at several different pressures and temperatures.<sup>22</sup>

Table V indicates that the equations give only approximate estimates for the pressure coefficient. The experimental values confirm Hellewege's<sup>15</sup> low value for a high molecular weight polystyrene at 165°C. Table IV shows perhaps a similarly low value for PMMA.

We have shown that both the Penwell-Porter equation and Miller's equation can predict pressure coefficients for amorphous polymers which agree qualitatively with certain experiments and can be used in a semilog relationship at low pressures to predict viscosity at low shear rates. The effect of shear rate on the pressure coefficient perhaps requires more elucidation as does the effect of entanglements on  $b$ .

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### References

1. A. J. Batchinski, *Z. Phys. Chem.*, **84**, 644 (1913).
2. A. J. Matheson, *J. Chem. Phys.*, **44**, 695 (1966).
3. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701 (1955).
4. R. C. Penwell, R. S. Porter, and S. Middleman, *J. Polym. Sci. A-2*, **9**, 731 (1970).
5. R. N. Haward, *J. Macromol. Sci.* **C4**(2), 191 (1970).
6. D. L. Hogenboom, W. Webb, and J. A. Dixon, *J. Chem. Phys.*, **46**, 2586 (1967).
7. B. Maxwell and A. Jung, *Mod. Plast.*, **35**(3), 174 (1957).
8. R. C. Penwell and R. S. Porter, *J. Polym. Sci. A-2*, **9**, 463 (1970).
9. A. Casale, R. C. Penwell, and R. S. Porter, *Rheol. Acta*, **10**, 412 (1971).
10. A. G. Frederickson, *Principles and Applications of Rheology*, Prentice Hall, Englewood Cliffs, New Jersey, 1964.
11. S. Middleman, *Flow of High Polymers*, Interscience, New York, 1968.
12. A. A. Miller, *Macromolecules*, **4**, 757 (1971).
13. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed. Wiley, New York, 1970, Chap. 11.
14. M. Yamada and R. S. Porter, *J. Appl. Polym. Sci.*, **18**, 1711 (1974).
15. K. H. Hellwege, W. Knappe, F. Paul, and V. Semjenow, *Rheol. Acta*, **6**, 165 (1967).
16. W. T. Laughlin and D. R. Ullmann, *J. Phys. Chem.*, **76**, 2317 (1972).
17. H. Eyring and N. Hirai, *J. Polym. Sci.*, **37**, 51 (1959).
18. K. H. Hellwege, W. Knappe, and P. Lehman, *Koll. Z.*, **183**, 110 (1962).
19. J. F. Carley, *Mod. Plast.*, **39**(4), 123 (1961).
20. L. A. Wood, *J. Polymer Sci. B*, **2**, 706 (1964).
21. A. A. Miller, personal communication.
22. H. D. Herrmann and W. Knappe, *Rheol. Acta*, **8**, 384 (1969).
23. F. Ramsteiner, *Rheol. Acta*, **9**, 374 (1970).
24. F. N. Cogswell, *Plast. Polym.*, to be published.
25. T. G. Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955).
26. J. M. O'Reilly, *J. Polym. Sci.*, **57**, 429 (1962).
27. G. Gee, *Polymer*, **7**, 177 (1966).
28. A. Miyake and M. Sakakibara, *Rep. Progr. Polym. Phys. (Japan)* **6**, 93 (1963).
29. M. S. Paterson, *J. Appl. Phys.*, **35**, 176 (1964).
30. Y. Ishida and S. Matsuoka, *ACS Polym. Prepr.*, **6**, 795 (1965).
31. B. E. Eichinger and P. J. Flory, *Macromolecules*, **1**, 285 (1968).
32. L. A. Wood and G. M. Martin, *J. Res. Nat. Bur. Stand.*, **A68**, 259 (1964).
33. M. M. Martynynk and V. K. Semenchenko, *Koll. Zh.*, **26**, 83 (1964).
34. I. Sanchez, personal communication.

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