

Some Melt Flow Properties of Polypropylene

D. E. GRANT and S. F. DIECKMANN, *Research Center,
Hercules Powder Company, Wilmington, Delaware*

Synopsis

The ability to express laboratory melt flow data in generalized terms serves both the fabricator and the resin producer: the fabricator can reduce the relations to the particular conditions of his process; the resin producer can assess the effect of polymer composition and structure on melt flow properties. An empirical method of correlating and generalizing laboratory capillary viscometer data has been developed which allows prediction of pressure-output relations for any cylindrical orifice. It is based on the Rabinowitsch and Bagley methods of calculating the correct shear rate and shear stress. The pressure drop across a die is made up of two terms, the entry pressure and the land pressure. Each is a function of the shear rate, but only the latter is a function of the die dimensions. Six key rheological parameters are developed, using polypropylene as an illustrative example. The effect of molecular weight and molecular weight distribution of polypropylene on the parameters is shown. In addition, some examples of practical uses of the generalized formulations are given. In the examples, the shear rate range of 10-1000 sec.^{-1} is covered, although the method could be applied to any experimentally attainable shear rates.

INTRODUCTION

The two current approaches to the study of melt rheology of polymers are the theoretical synthesis of bulk properties from considerations of molecular segmental motions and the empirical correlation of experimental observations. At the present stage of development the phenomenological approach yields more fruitful results, although the theoretical approach will eventually dominate the scene. One reason for this situation is that experimental techniques are still being explored and perfected. Many simple propositions regarding the effects of imposed conditions on polymer melts await experimental demonstration. The much-discussed viscous heating effect is one example of this. If a thin layer of flowing polymer close to the wall is raised to a very high temperature, many of the observed bulk phenomena could be accounted for. However, experimental demonstration of the viscous heating effects is not at hand. A number of such questions must be settled before rational application of theoretically derived equations can be made. Therefore the phenomenological approach has been adopted in this work.

A useful means of expressing polymer melt flow analytically serves two purposes. First, it allows the fabricator to predict the behavior of a resin

in his process and provides him with a rational basis for designing equipment; second, it allows the resin producer to correlate molecular structure and composition with flow behavior and to tailor his products to fit particular end uses. The objective of the work reported here was to develop a means of correlating melt flow data which would fill these practical needs. The method will be developed with polypropylene as an example.

EXPERIMENTAL

Experimentally, data are generated by runs in a capillary viscometer of the type shown schematically in Figure 1. This is a gas-driven instrument, commonly referred to as the CIL viscometer. To collect data with this instrument, the resin is melted in the reservoir, pressure is applied at the desired level, and an extrudate sample is collected over a timed interval by snipping it off at the die face. Rates are determined at twelve pressures, by starting at a high pressure, going in six steps to a low pressure, and then returning in six steps to the high pressure level. The upper and lower pressure levels were chosen to cover the desired rate range—in this work, 0.003–0.5 g./min., which corresponds to a shear rate range of 10–1000 sec.^{-1} . The intermediate pressure levels are chosen to be about equally spaced on a logarithmic scale.

To get meaningful results from a capillary viscometer experiment, four precautions must be taken. First, to make pressure drop from laminar flow in the barrel negligible, the die diameter must be less than one-tenth the barrel diameter. The measured pressure is applied to the top of the

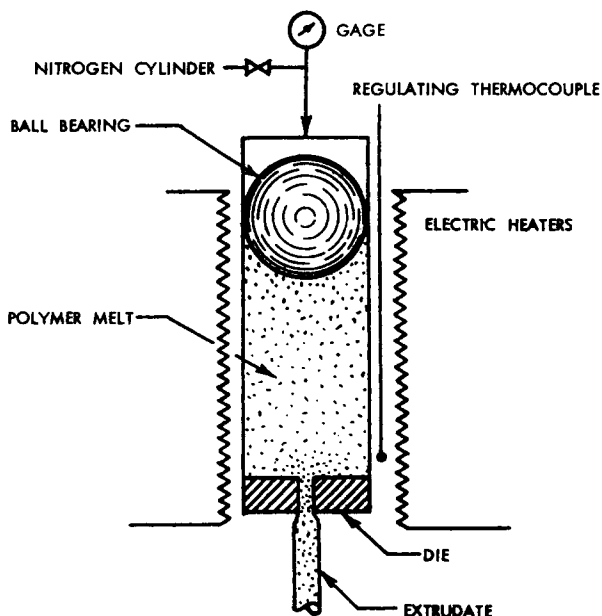


Fig. 1. Capillary viscometer (schematic).

resin column in the barrel. The pressure drop due to laminar flow in the barrel is normally assumed to be zero, but it is zero only if the die diameter is small with respect to the barrel diameter. The ratio of die to barrel diameter in the work reported here was 1:31; the die diameter was 20 mils, and the barrel diameter was 625 mils. Experiment confirmed that no barrel pressure drop occurred under these conditions.

Second, degradation of the resin must not occur during a run. It takes about 45 min. to complete a run, which is a rather long exposure time for some polymers at temperatures well above their melting point, even though oxygen is in limited supply. In the procedure described, an internal check on degradation exists: the first and last rate measurements are made at the same pressure. If degradation occurs, the last rate will be higher than the first and the results of that experiment can be discarded.

The third precaution necessary is to measure the capillary diameters with high precision. In the data analysis, the capillary radius is raised to the third power, so a small error in diameter measurement is magnified in the calculations. The most satisfactory method of measuring die diameters is to observe dependence of flow rate on pressure drop with a Newtonian oil of known viscosity. Poiseuille's equation can then be applied to calculate the diameter of the capillary to a 95% confidence range of 1% of the measured value. The equipment used for this experiment is different from that used for the melt flow experiments, since pressure differences of a few centimeters of mercury are quite adequate for an oil of 10 poise viscosity. In principle, the experiments are the same, however.

Fourth, use of fairly short capillary dies is desirable. The CIL viscometer pressure is limited to the available nitrogen cylinder pressure of 2000 psi unless a compressor is used. To achieve a shear rate of 1000 sec.^{-1} for high viscosity resins with this pressure capability, a length-to-radius (L/R) ratio of about 20 is a practical maximum. The alternative to limiting die length is to increase the driving pressure into the range where viscosity is affected by hydrostatic pressure.¹ This complication has been avoided by dealing with dies of length-to-radius ratios of 20 or less and limiting the pressure used to the 2000 psi available in a commercial nitrogen cylinder.

Typical data obtained on the CIL viscometer are shown in Figure 2. Here the logarithm of the applied pressure is plotted against the logarithm of the observed output rate for a single polypropylene resin (Pro-fax 6323*, melt flow rate 10.3) as measured on three dies at 230°C. The dies were all about 20 mils in diameter but of different lengths, leading to the three levels of L/R : 0, 3.6, and 18.2. The zero-length die is a sharp-edged orifice with a 45° approach angle.

To generalize these data, they are cast into terms of the shear rate which is a function of the output rate, the capillary dimensions, and the resin—and shear stress, which is a function of the applied pressure, the capillary dimensions, and the resin. Two types of corrections must be made to the standard formulation of these functions when dealing with

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viscoelastic melts: the Rabinowitsch correction to account for a non-parabolic velocity profile² and the Bagley correction to account for losses in the capillary entrance region.³

The Rabinowitsch Correction

An analytical expression which describes the raw data quite well is

$$\log P = A_1 + B_1 \log Q + C_1(\log Q)^2 \quad (1)$$

where P is the applied pressure, Q the output rate, and A_1 , B_1 , and C_1 constants which are functions of the resin and the die. The Rabinowitsch equation, which allows calculation of the true shear rate without knowledge of the actual velocity profile of the melt, can be cast into the form

$$D = \left(3 + \frac{d \log Q}{d \log P} \right) \frac{Q}{\pi R^3 \rho} \quad (2)$$

where D is the corrected shear rate and ρ the melt density. Differentiation of eq. (1) yields the required slope and leads to

$$D = \left(3 + \frac{1}{B_1 + 2C_1 \log Q} \right) \frac{Q}{\pi R^3 \rho} \quad (3)$$

Here the true shear rate is in terms of the output rate, the die radius, melt density, and the known constants B_1 and C_1 . This allows correlation of the true shear rate with the applied pressure, which is cast in the form

$$\log P = A_2 + B_2 \log D + C_2(\log D)^2 \quad (4)$$

The coefficients for this and the other equations are calculated by computer. At this stage of the calculations the coefficients still depend on die dimensions as well as on the resin and the temperature.

The Bagley Correction

To determine the true shear stress at the capillary wall, Bagley's approach has been taken. He has shown that

$$S = P/[2(L/R + e)] \quad (5)$$

or in an analogous form

$$P = P_0 + 2(L/R)S \quad (6)$$

where S is the land shear stress, e the Bagley end correction, and P_0 the pressure drop upstream of the capillary. The useful property of this equation is that at constant shear rate, the total pressure is a linear function of the L/R ratio of the dies, with a slope of $2S$ and an intercept P_0 . Through eq. (4) with its constants determined for two or more dies, the proper data to construct a Bagley plot can be generated by simple substitution of a value for shear rate. An example of such a plot for the representative lot of polypropylene at 100 sec.⁻¹ shear rate is shown in

Figure 3. Individual values calculated from eq. (4) and the least-squares line are shown.

As shown in Figure 3, the intercept on the pressure axis is P_0 , the pressure drop upstream of the capillary. The slope, $dP/d(L/R)$ is equal to twice the land shear stress, S . By making Bagley plots at a series of shear rates, a series of values for S and P_0 can be determined. These functions are independent of the experimental die dimensions and depend only on the resin, temperature, and shear rate. The latter dependence is shown in Figure 4. The relation between these rheological functions and the shear rate can be expressed as

$$\log S = \alpha + \beta \log D + \gamma(\log D)^2 \quad (7)$$

and

$$\log P_0 = A_3 + B_3 \log D + C_3(\log D)^2 \quad (8)$$

The six coefficients in these two equations are unique functions of the resin and temperature. They serve to characterize the melt flow properties of a given resin at a given temperature. The values for the parameters and the 95% confidence limits found for the lot of polypropylene used as an example are:

$$\alpha = 3.89 \pm 0.09$$

$$\beta = 0.84 \pm 0.10$$

$$\gamma = 0.09 \pm 0.02$$

$$A_3 = 5.07 \pm 0.13$$

$$B_3 = 0.50 \pm 0.14$$

$$C_3 = 0.02 \pm 0.04$$

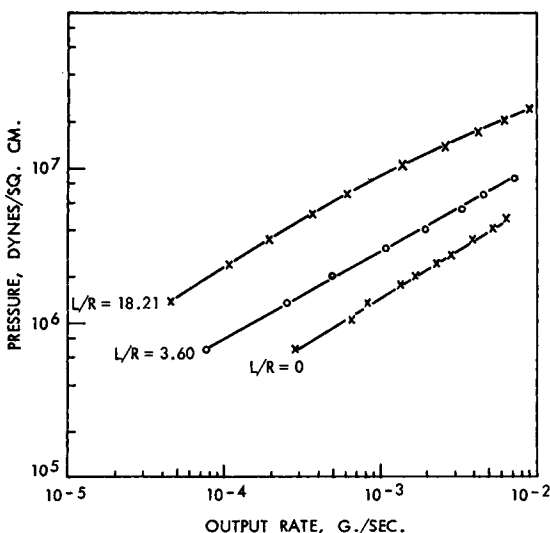


Fig. 2. Effect of pressure and die length on output rate for Pro-fax, melt flow rate 10.3; 230°C.

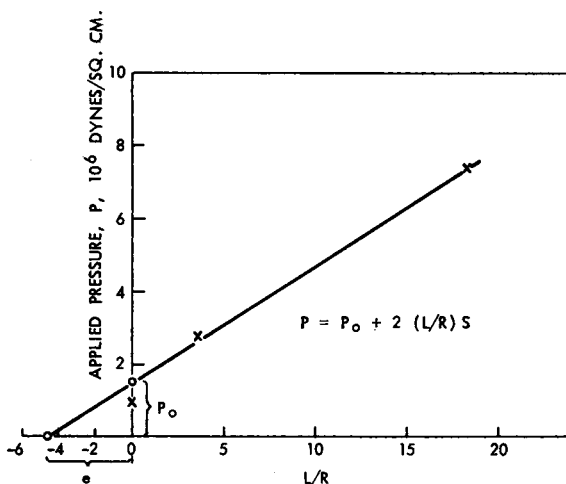
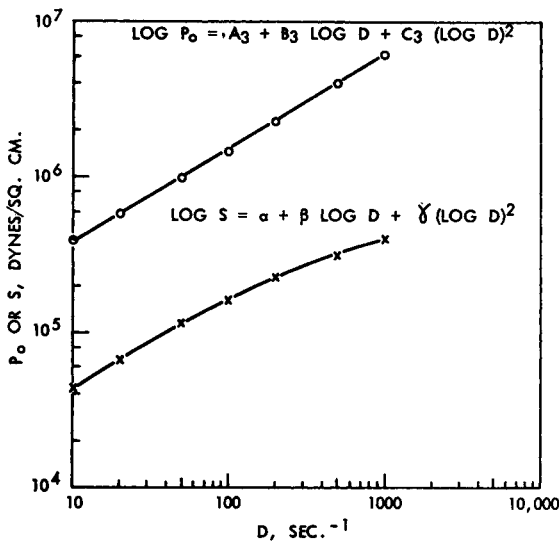
Fig. 3. Bagley plot at 100 sec.⁻¹.

Fig. 4. Effect of shear rate on land shear stress and entry pressure for Pro-fax; melt flow rate 10.3; 230°C.

EFFECTS OF MOLECULAR WEIGHT AND POLYDISPERSITY

The molecular weight of a polymer has a dominating effect on its melt flow behavior. Intrinsic viscosity is the most convenient method of measuring the molecular weights of the polypropylene resins being considered. For polypropylene, the relation between intrinsic viscosity and molecular weight is

$$\log [\eta] = -3.79 + 0.77 \log \bar{M}_v \quad (9)$$

where \bar{M}_v is the viscosity-average molecular weight. This type of molecular weight average is nearly equal to the more familiar weight-average

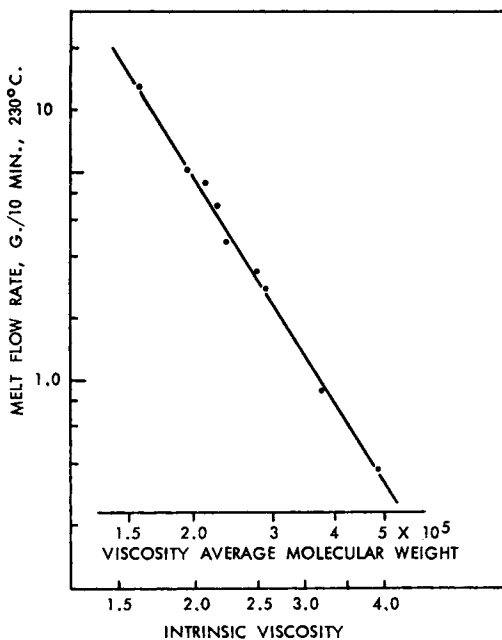


Fig. 5. Relation between intrinsic viscosity, viscosity-average molecular weight, and melt flow rate for polypropylene.

molecular weight. According to Chiang,⁴ the two are equal for monodisperse polymers, and the weight-average molecular weight is 20% higher than the viscosity-average molecular weight for commercial polypropylenes, which have a polydispersity characterized by a weight-average to number-average molecular weight ratio of about five.

Commercially the melt flow rate⁵ is used to give a measure of molecular weight. This property of a resin is determined by measuring the efflux rate of the polymer melt from a capillary on imposing a dead load weight which corresponds to 43.25 psi. Thus, it is a constant stress measurement. As a consequence, the shear rate will depend on the fluidity of the resin. Because of the dependence of viscosity on shear rate in polymer melts, correlation of melt flow rate with molecular weight is unreliable.

For orientation, Figure 5 shows the relation between intrinsic viscosity, viscosity-average molecular weight, and melt flow rate for polypropylene, in the commercially available range of melt flow rates (0.2–80).

To investigate the effect of molecular weight on the flow properties of polypropylene, the rheological parameters were measured for a series of resins which covered the commercially available range of molecular weights. In Figure 6, the term α is seen to be a linear function of the logarithm of the intrinsic viscosity. This relation is expected, for α is the logarithm of the melt viscosity at a shear rate of 1 sec.⁻¹. Analytically the observed relation reduces to

$$\alpha = \log \eta_1 = 2.87 + 3.62 \log [\eta] \quad (10)$$

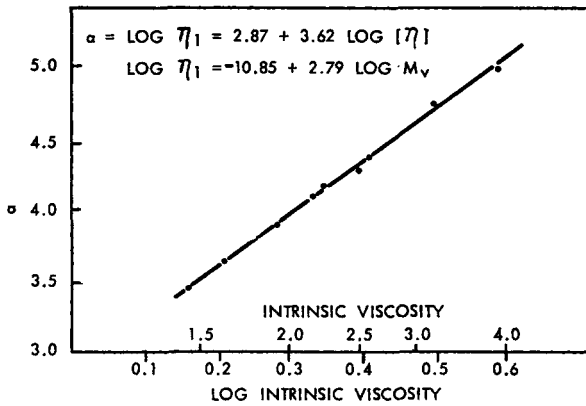


Fig. 6. Effect of molecular weight on the land stress parameter α .

or, by substituting \bar{M}_v for $[\eta]$ through eq. (9),

$$\alpha = \log \eta_1 = -10.85 + 2.79 \log \bar{M}_v \quad (11)$$

The interesting point here is that the coefficient of $\log \bar{M}_v$, 2.79, is substantially lower than the 3.4 coefficient observed in the Newtonian flow regime, which occurs at lower shear rates. This reduction in dependence of melt viscosity on molecular weight with increasing shear rate has been discussed in some detail by Schreiber, Bagley, and West.⁶ The ability to calculate separately the viscosity associated with flow in the die land by isolation of entry effects is a valuable feature of the present method of treating melt flow data. Correlations of the individual rheological parameters with molecular parameters allow the resin producer the maximum freedom to tailor a resin for a particular situation.

Figure 7 shows the dependence of β , the first coefficient in the $\log S$

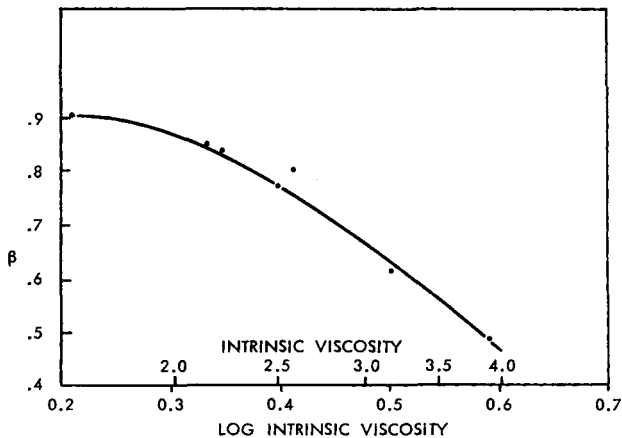


Fig. 7. Effect of molecular weight on the coefficient β .

versus $\log D$ equation, on intrinsic viscosity. As $[\eta]$ increases, β decreases monotonically. This behavior implies that melt viscosity becomes more dependent on shear rate in the intermediate shear rate range as the molecular weight increases.

Values of γ were not precisely enough determined for a good correlation with intrinsic viscosity. For commercial polypropylene, γ ranges from -0.09 to -0.11 . This coefficient equals one-half the rate of change of the slope of the $\log S$ versus $\log D$ curve, which is numerically important only at the high end of the experimental range of shear rates.

Figure 8 shows the linear relation observed between A_3 , the value of $\log P_0$ at a shear rate of 1 sec.^{-1} , and $\log [\eta]$. The slope of this line is much lower than the slope of the line relating α to $\log [\eta]$. This means that, at low shear rates, entrance pressure drop is less sensitive to molecular weight than land shear stress is.

B_3 shows no clear trend with intrinsic viscosity. For commercial polypropylene, B_3 ranges from 0.5 to 0.7. C_3 is negligible compared to the uncertainty in its determination.

Equations (5) and (6) imply that the Bagley end correction can be calculated by:

$$e = P_0/2S \quad (12)$$

e is clearly a function of shear rate. Figure 9 shows the dependence of e on intrinsic viscosity at two values of shear rate. The end correction is not sensitive to molecular weight. However, the values found for a polypropylene of narrow molecular weight distribution are substantially lower than those of commercial polypropylenes. This leads to the conclusion that narrow molecular weight distribution can be associated with small end correction. The correspondence between low end corrections and low polydispersity has been observed in studies of polyethylene and other polymers as well as polypropylene.

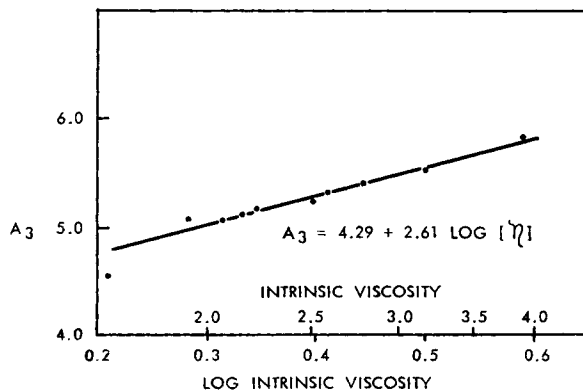


Fig. 8. Effect of molecular weight on the entry pressure parameter A_3 .

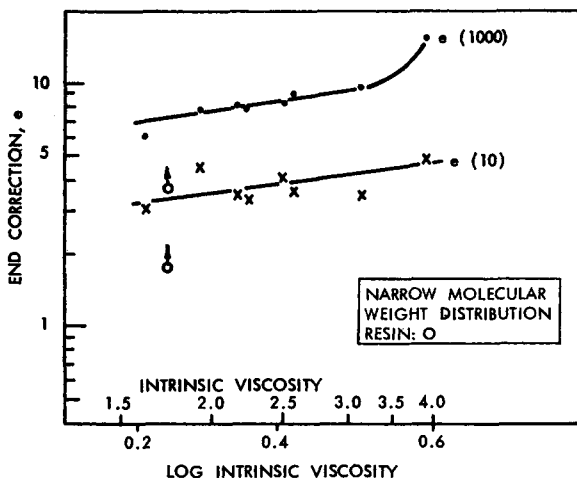


Fig. 9. Effect of molecular weight on the Bagley end correction at 10 and 1000 sec.^{-1} .

PRACTICAL APPLICATIONS

One advantage of having the melt flow properties of a resin in analytical form is that it affords the opportunity to calculate the behavior of the melt under specific conditions of interest. By proper application of this device a better appreciation of the effect of certain variables can be gained. As an example, Figure 10 shows how the land shear stress S varies with intrinsic viscosity at two selected shear rates, 10 and 1000 sec.^{-1} . On the log-log scale, the relation is linear at both shear rates. The relation at 1 sec.^{-1}

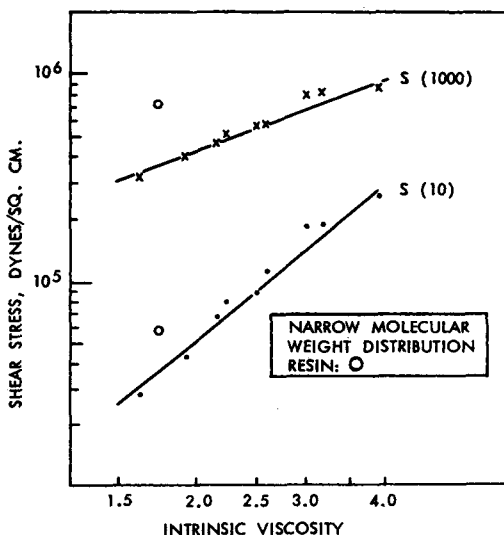


Fig. 10. Effect of molecular weight on the land stress S at 10 and 1000 sec.^{-1} .

has already been presented (Fig. 6) when the dependence of α on intrinsic viscosity was examined.

Two points of interest are revealed in these relations between S and $[\eta]$. First, at the higher shear rate, the slope is substantially lower. Lower slope means that an operation at high shear rate would be less affected by a change in molecular weight than one at low shear rate would. The second point has to do with the values observed for the narrow distribution polypropylene sample. This material requires a greater stress to attain a given shear rate than resin of the usual distribution. The apparent viscosity of a narrow distribution resin in the land of the capillary is therefore higher than that of the commercial resin of the same solution viscosity.

Turning to the entry pressure term, Figure 11 shows how P_0 varies with molecular weight at the same two shear rates. The slope is about the same for the two shear rates, contrary to the observation made with the shear stress. Also in contrast to the effect of molecular parameters on S , the narrow distribution resin does not exhibit a significantly different value of P_0 than the resin of usual distribution.

The reason for dwelling on the relation of S and P_0 to molecular weight and molecular weight distribution is that they are simply related to the total pressure through eq. (6), which has been considered previously:

$$P = P_0 + 2(L/R)S \quad (6)$$

This equation states a very significant point which is not well recognized: the total pressure required to force a polymer melt through an orifice is the sum of two terms and one of the terms is independent of the orifice

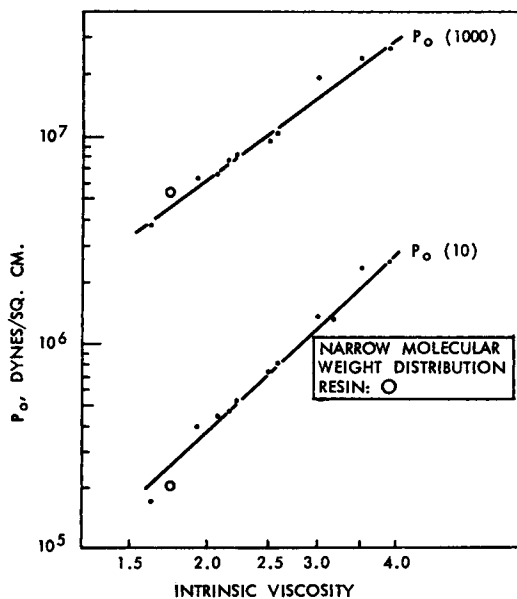


Fig. 11. Effect of molecular weight on entry pressure P_0 at 10 and 1000 sec.⁻¹.

face dimensions. The significance of this situation can be appreciated by die designers. For resins which have a large entry pressure term, the die land length can be extended considerably without affecting the total pressure requirement proportionally. As an illustration of this effect, consider two dies, one short, with an L/R of 1.0, and the other long, with an L/R of 10. In Figure 12 the total pressure across the system is shown as a function of shear rate for two resins of about the same melt flow rate: one narrow-distribution material and the other of wider distribution. For the short-land die, the narrow-distribution resin requires less pressure to attain a given shear rate—less by as much as 30% at the lower shear rate level. Quite the opposite is true for the long-land die: the narrow-distribution resin requires up to 60% more pressure to attain a given shear rate. There are several interesting facets to this graph. For one, the melt flow rate of the two resins is about the same: 13 for the narrow-distribution resin, 10 for the wide-distribution resin. Yet the difference in behavior in a long-land die is substantial. This is a clear demonstration that equivalence of melt flow rate does not necessarily imply that two resins will behave similarly over a range of conditions. Another point of interest is the small increase in pressure required to overcome a 10-fold increase in land length. For the wide-distribution material a factor of 1.7–3 is adequate, whereas for the narrow-distribution material, the factor varies from 3 to 4. Thus, a die designer has much more leeway on increasing die lengths than a direct proportionality of length to pressure drop would suggest.

SUMMARY

An empirical method of treating laboratory capillary viscometer data to arrive at six rheological parameters has been presented. By application

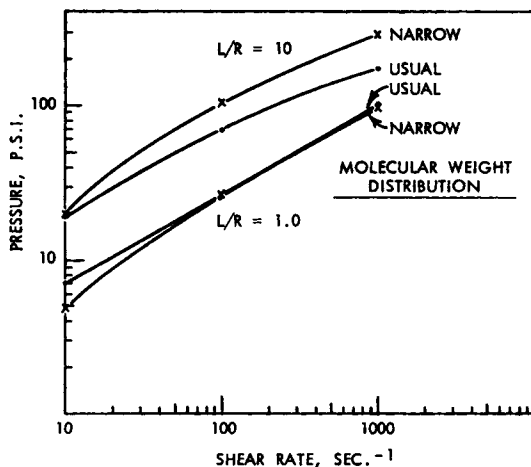


Fig. 12. Effects of molecular weight distribution on pressure requirements in long and short dies for polypropylene.

of the parameters the melt flow behavior of polymer melts in cylindrical orifices of any dimensions can be calculated. The results of such calculations for certain specific conditions can be used to aid in achieving a practical grasp of the effects of both resin and operational parameters on flow behavior.

The generalized parameters are cast in terms of shear rate, which fundamentally depends on the velocity profile of the resin flowing through a channel. The Rabinowitsch method of calculating shear rate is adequate to treat the cylindrical capillary case, but demonstration of the validity of extension to flow channels with noncircular cross sections must precede application of these equations to more complex geometries. Work along these lines is in progress.

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Résumé

La possibilité d'exprimer les résultats de laboratoire concernant l'écoulement à l'état fondu en termes généralisés rend tout autant service au fabricant qu'au producteur de résines: le fabricant peut adapter les relations obtenues aux conditions particulières de son processus; le producteur de résines peut évaluer l'influence de la composition et de la structure du polymère sur les propriétés d'écoulement à l'état fondu. Une méthode empirique de corrélation et de généralisation des données du laboratoire obtenues par viscosimétrie capillaire a été développée et permet de prédire des relations pression-sortie pour n'importe quel orifice cylindrique. Elle est basée sur les méthodes de Rabinowitsch et Bagley pour le calcul de la vitesse exacte de cisaillement et de la tension de cisaillement. La chute de pression à travers une filière est composée de deux termes, le pression d'entrée et la pression en operation. Chacun de ces termes est fonction de la vitesse de cisaillement mais seulement la dernière est fonction des dimensions de la filière. On déduit six paramètres rhéologiques faisant usage du polypropylène comme illustration. L'influence du poids moléculaire et de la distribution du poids moléculaire du polypropylène, sur les paramètres est démontré. En plus, on donne quelques exemples de l'usage pratique des formules généralisées. Le domaine de vitesse de cisaillement de 10 à 1000 sec^{-1} est couvert par les exemples, bien que la méthode puisse être appliquée à n'importe quelles vitesses de cisaillement accessibles par l'expérience.

Zusammenfassung

Die Möglichkeit, Schmelzfließdaten in verallgemeinerter Form darzustellen, ist sowohl für den Fabrikanten als auch den Harzerzeuger dienlich: der Fabrikant kann die Beziehungen auf die besonderen Bedingungen seines Prozesses reduzieren; der Harzerzeuger kann den Einfluss der Polymerzusammensetzung und -struktur auf die Schmelzfließeigenschaften bestimmen. Eine empirische Methode zur Korrelation und Verallgemeinerung von Ergebnissen mit Laboratoriums-Kapillarviskosimetern wurde entwickelt, welche Aussagen über die Druck-Ausstossbeziehungen für eine beliebige zylindrische Öffnung erlaubt. Sie beruht auf der Methode von Rabinowitsch und Bagley

zur Berechnung der korrekten Schubgeschwindigkeit und Schubspannung. Der Druckabfall in einer Spritzgussform ist durch zwei Terme gegeben, den Eintrittsdruck und den Seitendruck. Beide sind Funktionen der Schubgeschwindigkeit, aber bloss der letztere der Formdimensionen. Sechs rheologische Schlüsselparameter werden an Polypropylen als Musterbeispiel hergeleitet. Der Einfluss des Molekulargewichts und der Molekulargewichtsverteilung auf die Parameter wird gezeigt. Zusätzlich werden einige Beispiele für die praktische Anwendung der verallgemeinerten Beziehungen gegeben. In diesen Beispielen wird ein Schubgeschwindigkeitsbereich von 10 bis 1000 sec^{-1} verwendet, die Methode kann jedoch auf jede beliebige, experimentell erreichbare Schubgeschwindigkeit angewendet werden.

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