

## Measurement of the Flow of Molten Polymers Through Short Capillaries

ALFRED P. METZGER\* and ROBERT S. BRODKEY, *Department of  
Chemical Engineering, The Ohio State University, Columbus, Ohio*

### INTRODUCTION

The flow of molten polymers is significant both from a theoretical and a practical standpoint. As knowledge of the factors which influence polymerization grows, the ability to control molecular weight, molecular weight distribution, branching, and even the arrangement of the branches, is increased. The effect of these parameters on the flow of the molten material is of great interest in understanding polymer behavior. The performance of the melt in processing equipment is equally important. For example, successful injection molding of intricate shapes or large parts, and the high-speed extrusion of film or wire jackets, demands an understanding of the flow behavior of the material.

In the laboratory, the response of polymer melts is usually measured by means of either rotational or extrusion viscometers. At high shear rates the rotational instruments are limited by (1) the tendency of the material to climb out of the cylindrical gap and (2) the heat generated by the continuous shearing action. On the other hand, data obtained from capillary extrusion viscometers must be viewed skeptically unless energy losses due to friction and entrance effects are considered. Nevertheless, the behavior of polymer melts extruded through capillaries has been the subject of numerous investigations. It is the purpose of this paper to discuss some experimental data obtained with an extrusion viscometer with the use of capillaries of various length-to-diameter ratio and the application of corrections for obtaining basic shear diagram.

### EXPERIMENTAL EQUIPMENT AND PROCEDURE

The extrusion viscometer employed in this work is similar to that used by other investigators<sup>1-3</sup> and is essentially a modified melt index apparatus.<sup>4</sup> The reservoir temperature is controlled at any desired value by means of resistance heaters and a thermistor sensing element with appropriate electronic circuitry. In this work the temperature was maintained at 190°C. The polymer melt is forced through the capillary by means of nitrogen gas

\* Present address: Continental Can Company, General Packaging R & D, Chicago, Illinois.

which is maintained at any level up to cylinder pressure. The observed pressure is considered to be the pressure drop through the capillary. Any losses in the reservoir or from other sources are lumped into the so-called entrance effect, and the correction to be described should account for these losses. The extrusion rate is determined by weighing samples of the extrudate collected over timed intervals. The volume flow rates are then calculated by the use of the appropriate melt density. Details of the equipment and the basic data obtained are available.<sup>15</sup>

The capillaries were made of Inconel metal annealed to a Rockwell hardness of 70–90 and were precision drilled with square edges and a 180° entry angle. The diameters were determined by examination under a microscope equipped with a calibrated eyepiece. The length-to-diameter ratios varied from approximately 3 to 30.

Experimentally, there are two limitations to measurements made with this type of viscometer. For capillaries with a small length-to-diameter ratio, the flow rates are high. That is, the reservoir is emptied in a short time interval. Therefore the maximal pressure that can be used is limited by the operator's ability to adjust the pressure and collect the sample in this interval. On the other hand, for capillaries with a large length-to-diameter ratio, considerable pressure is required to force the polymer melt through the capillary, and thus the range of shear stress that can be covered is limited by the cylinder pressure.

In addition to the flow measurements, densities were determined,<sup>5</sup> melt indexes were obtained,<sup>6</sup> and the inherent viscosities were measured in tetralin at a concentration of 0.1 g./dl. and a temperature of 100°C. with an Ubbelohde viscometer. These values are shown in Table I.

TABLE I  
Certain Physical Properties of Polyethylenes

	A	B	C	D	E
Melt index	6.0	2.2	0.60	3.9	0.23
Density	0.919	0.920	0.919	0.920	0.920
Inherent viscosity	0.835	0.885	0.962	0.957	1.256

All of the five polyethylenes used in this study were conventional low-density materials obtained from two sources. Three (A, B, C) were from one manufacturer and, presumably, the primary difference is molecular weight, while the other two materials (D, E) were obtained from another manufacturer.

### TREATMENT OF DATA

Polymer flow behavior is often considered in terms of Newton's law, which relates shear stress and shear rate by a proportionality constant. Mathematically this can be expressed as

$$\tau = -\mu (du/dr) \quad (1)$$

where  $\tau$  = shear stress (dynes/cm.<sup>2</sup>),  $du/dr$  = shear rate (sec.<sup>-1</sup>), and  $\mu$  = coefficient of viscosity (poise).

For the flow of a Newtonian fluid through a capillary, the Hagen-Poiseuille law is

$$Q = (\pi r_0^4 / 8 \mu) (dP/dL) \quad (2)$$

where  $Q$  = volume flow rate (cm.<sup>3</sup>/sec.),  $dP/dL$  = the pressure gradient (dynes/cm.<sup>2</sup>-cm.),  $r_0$  = capillary radius (cm.), and  $\mu$  = coefficient of viscosity (poise).

This equation can be rearranged in terms of shear stress and shear rate to become

$$(r_0/2)(dP/dL) = \mu (4Q/\pi r_0^3) \quad (3)$$

that is,

$$\tau_w = (r_0/2)(dP/dL) \quad \text{and} \quad du/dr = 4Q/\pi r_0^3$$

where  $\tau_w$  = shear stress at the wall.

Although these relationships are used in melt flow measurements on polymers, neither one is correct. Calculation of the shear rate is based on the assumption that the material is a Newtonian fluid (which is certainly not true for most polymers) and the equation for shear stress makes no allowance for entrance effects as caused by the sudden contraction and the formation of the velocity profile in the capillary. The non-Newtonian behavior of most polymers is represented schematically in Figure 1. Since the exact shape of the curve depends on the polymer structure, it is apparent that each polymer will have a characteristic flow curve. Furthermore, there is no assurance that the curves for different materials will not intersect. Obviously, single-point determinations of melt flow viscosity are of limited value.

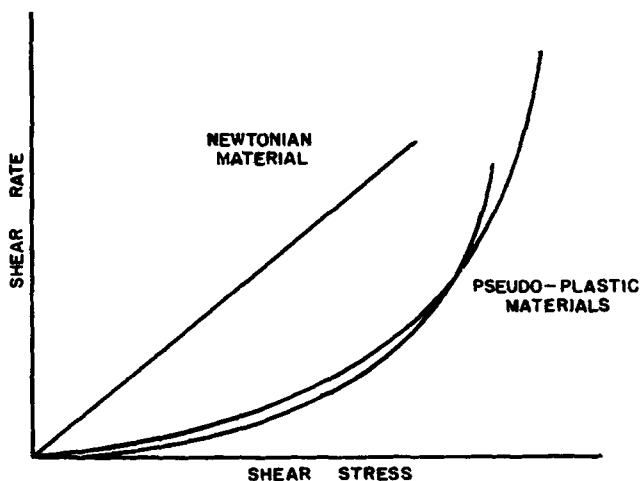


Fig. 1. Schematic representation of flow behavior.

The effect of capillary geometry on the flow data is illustrated by Figure 2 (these curves also show the non-Newtonian behavior of the polymer melts). As the length-to-diameter ratio of the capillary increases, the entrance effect is reduced. For example, it has been reported<sup>7</sup> that for polyethylene the  $L/D$  ratio should be around 30 in order that the viscosity may be unaffected by capillary dimensions. Other investigators<sup>8</sup> and the present work suggests that results may be influenced by  $L/D$  ratios as high as 130. Because of the viscous nature of polymer melts it is difficult to work with long capillaries, and therefore most experiments have been

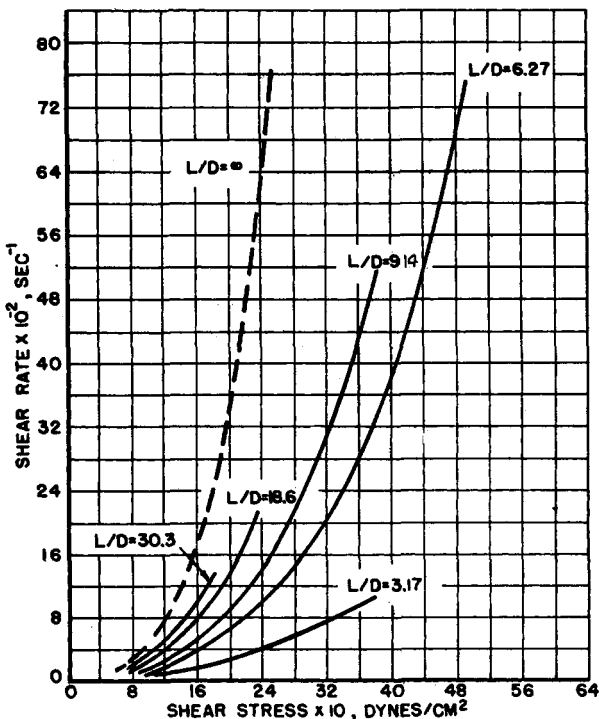


Fig. 2. Linear plot of flow behavior for a commercial low-density polyethylene.

made with relatively short capillaries. Some investigators<sup>9</sup> have attempted to correct for the entrance effect by obtaining data for flow through sharp-edged orifices (no length) of the same diameter. Presumably, the difference between the pressure drop through the capillary and that through the orifice is the driving force for the capillary. However, it has been pointed out<sup>10</sup> that this method may not be valid. A more effective approach has been suggested<sup>1</sup> for making corrections for entrance effects. In this technique, the equation for shear stress is modified by assuming that the entrance effect is a function of the capillary dimensions. If experimental data from a series of capillaries are available, the correction term can be ob-

tained by extrapolating the linear plot of pressure versus  $L/D$  (at constant shear rate). It was demonstrated that this correction term is strongly dependent on the shear rate and that it also varies from one polymer to another. If the correction terms are determined and the shear stresses recalculated, flow data from different capillaries (various  $L/D$  ratios) will reduce to a single curve. Thus, not only does the technique illustrate the importance of correcting for entrance effect but it also permits data obtained with different capillaries to be compared. Probably the greatest objection to the method is the amount of calculations involved and the uncertainty encountered in extrapolating the pressure versus  $L/D$  plots to obtain the correction terms.

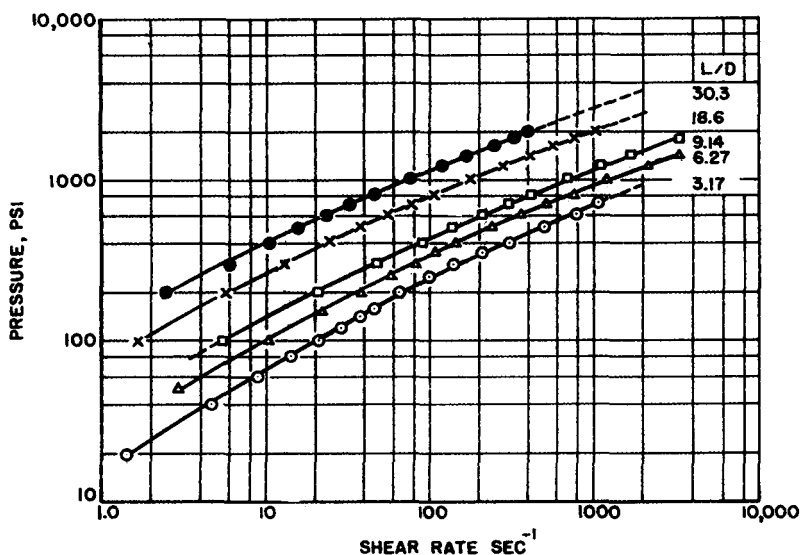


Fig. 3. Effect of pressure on the shear rate of commercial low-density polyethylene through various capillaries.

An alternative, although similar, approach to the correction for entrance effect is suggested by examination of the expression for shear stress, eq. (3), which can be rearranged to

$$\tau_w = 1/4 [dp/d(L/D)] \quad (4)$$

It follows that the wall shear stress can be obtained from the slope of the pressure versus  $L/D$  plot without the necessity of determining the end correction. Thus, experimental data from short capillaries can be used to calculate shear stresses which are independent of geometry and are characteristic of the polymer.

As pointed out previously, the expression for shear rate ( $4Q/\pi r_0^3$ ) is valid only for Newtonian fluids. However, the Rabinowitsch equation<sup>11</sup>

can be manipulated<sup>12</sup> to show that this shear rate can be corrected to conditions at the capillary wall by multiplying by

$$(3n' + 1)/4n' \quad (5)$$

where  $n' = [d \log (r_0/2 dP/dL)]/[d \log (4Q/\pi r_0^3)]$ .

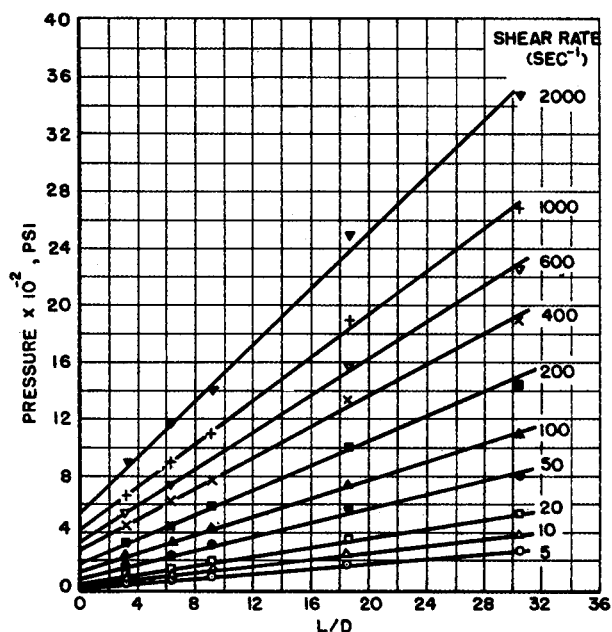


Fig. 4. Curves showing the relationship between pressure and capillary dimensions at constant shear rates.

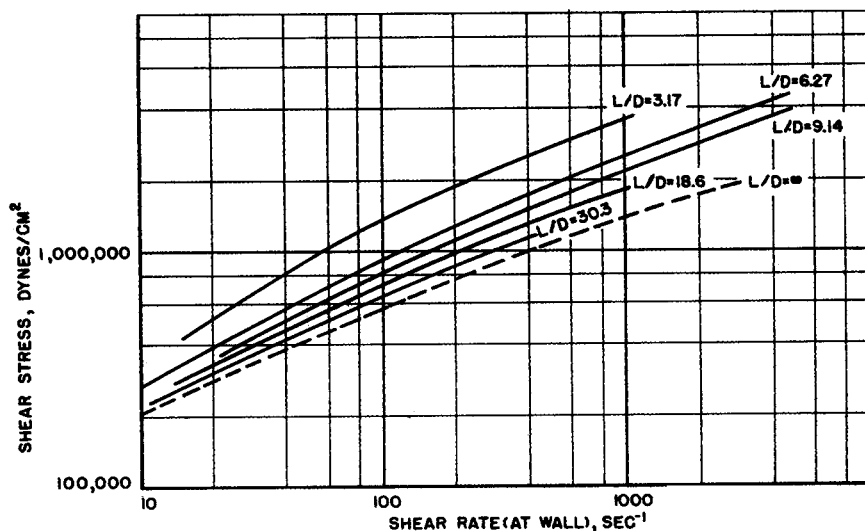


Fig. 5. Logarithmic plot of flow behavior for commercial low-density polyethylene.

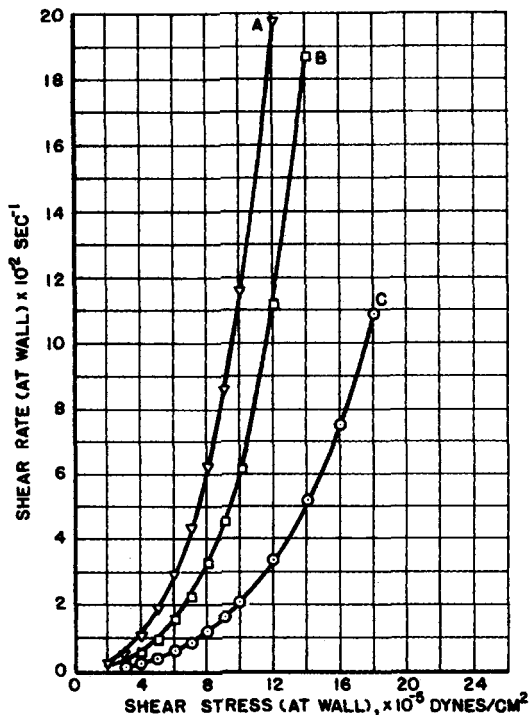


Fig. 6. Linear plot of basic shear data for commercial low-density polyethylenes; temperature 190°C.

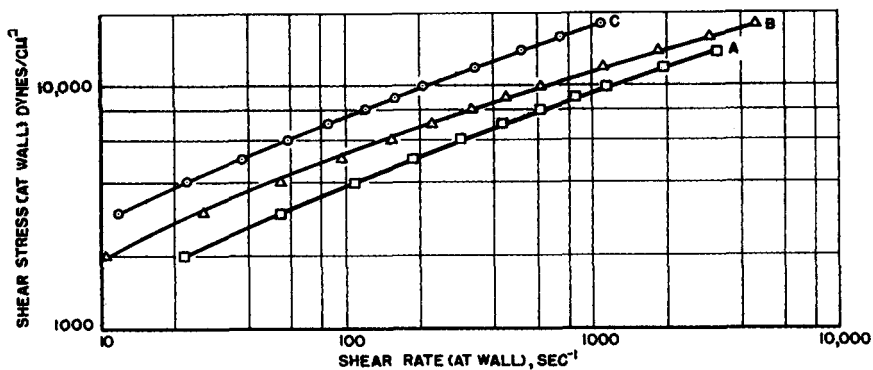


Fig. 7. Logarithmic plot of basic shear data for commercial low-density polyethylenes; temperature 190°C.

Thus, from the slopes of logarithmic plots of shear stress and shear rate it is possible to obtain shear rate conditions at the wall. The true melt viscosities can then be determined from the ratios of corrected shear stresses and corrected shear rates, since both are now measurements at the wall. An example will illustrate the procedure:

1. The calculated shear rates ( $4Q/\pi r_0^3$ ) are plotted against the corresponding pressure for each capillary, as in Figure 3.

2. At arbitrarily chosen values of shear rate the corresponding pressures are obtained and plotted against the  $L/D$  ratio (Fig. 4).

3. The slopes of these lines are used to calculate the corrected shear stresses for a capillary of infinite length. The linearity of the lines demonstrates the validity of eq. (4). In the data reported in Figure 4, both  $L$  and  $D$  were varied to produce the range of  $L/D$  values.

4. From a logarithmic plot of corrected shear stress versus shear rate (Fig. 5,  $L/D = \infty$ ) values of  $n'$  are obtained, and the shear rates at the wall are calculated, the Rabinowitsch correction being used.

The corrected shear rates (at the wall) and shear stresses (independent of capillary dimensions) are shown on a linear plot in Figure 6 and logarithmically in Figures 7 and 8 (basic shear diagrams). For some polymers, it has been reported that the flow behavior, at least over a limited range of shear conditions, can be represented by the empirical expression

$$\tau = K (-du/dr)^n \quad (6)$$

This equation, which has no theoretical basis, is called the power law, and implies that a logarithmic plot would be a straight line if  $n$  were constant. It is apparent from Figure 7 that  $n$  is not constant for these polymers, and therefore the power law cannot be applied. Glasstone et al.<sup>13</sup> used the theory of absolute reaction rates to develop the hyperbolic sine law relating shear stress to shear rate. Subsequently, this was modified by Powell and Eyring<sup>14</sup> and applied to non-Newtonian systems. The Powell-Eyring equation is

$$\tau = \mu(du/dr) + 1/\alpha \sinh^{-1} [(du/dr)/\gamma] \quad (7)$$

where  $\mu$ ,  $\alpha$ , and  $\gamma$  are constants and the other symbols have the meanings given above. Although this equation has a theoretical basis, it is unwieldy

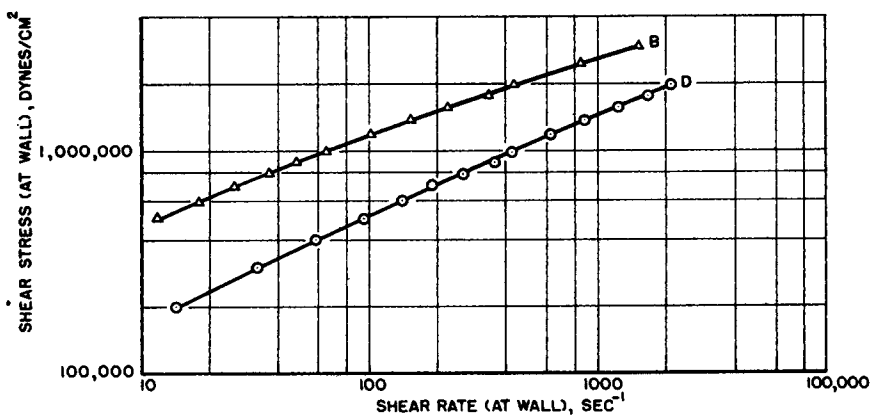


Fig. 8. Logarithmic plot of basic shear data for commercial low-density polyethylenes; temperature 190°C.



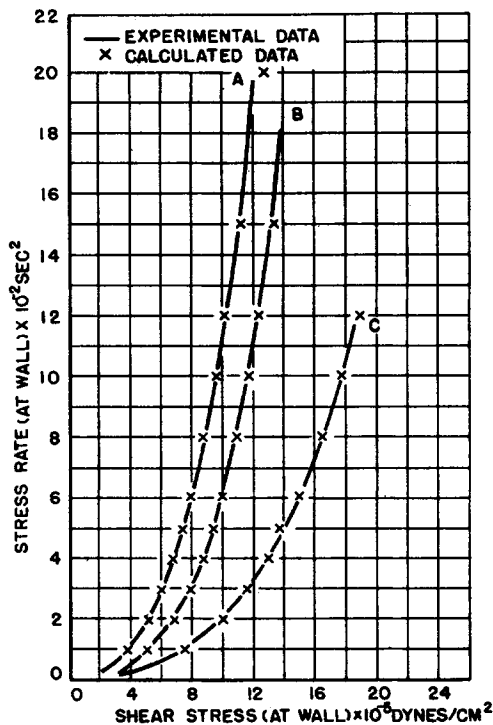


Fig. 9. Comparison of experimental data with results calculated from Powell-Eyring equation.

because of the hyperbolic sine function. However, by choosing three points on the basic shear diagram (Fig. 6) it is possible to write three equations which can be solved simultaneously. A comparison of the calculated values and the experimental data are shown in Figure 9 and the constants for the Powell-Eyring equation for the five materials included in this study are listed in Table II.

TABLE II  
Constants for Powell-Eyring Equation

Material	$\mu$	$\alpha$	$\gamma$
A	200	24.8	$5.87 \times 10^{-6}$
B	106	30.1	$3.95 \times 10^{-6}$
C	273	24.5	$2.96 \times 10^{-6}$
D	470	30.1	$4.16 \times 10^{-6}$
E	416	18.5	$2.12 \times 10^{-6}$

## DISCUSSION

The pronounced influence of capillary geometry in melt flow measurements is apparent from the data plotted in Figure 2. These results il-

lustrate the necessity of applying corrections for entrance effects. It is also evident (Fig. 5) that  $n$  of the power law equation is variable and is affected by capillary dimensions. As the capillary length-to-diameter ratio is increased the instrument effects are minimized. Nevertheless, by the method suggested, experimental data obtained with short capillaries can be corrected to obtain flow diagrams which are independent of instrument geometry. Furthermore, by applying the Rabinowitsch correction, it is possible to obtain the shear rates at the capillary wall for these non-Newtonian materials. With values of  $n$  as low as 0.3, errors greater than 50% can be introduced by neglecting this correction. In addition, the error is not constant with shear rate, since  $n$  is not constant. When these corrections have been made, the resulting flow curves are truly characteristic of the polymers.

The flow data cannot be expressed mathematically by the power law equation. Although the three-constant Powell-Eyring equation seems to fit the values, at least over the range investigated, it is difficult to manipulate. The significance of the constants is also questionable. It has been speculated that they might be indicative of relaxation times or rates but there are insufficient data for drawing conclusions. It should be emphasized that both corrections are necessary before meaningful constants can be obtained. To correct for entrance effects only is not enough.

It is, perhaps, of somewhat more immediate interest to make some observations of the extrudates. In common with other investigators, the extrudates were observed to become irregular at high shear rates. However, the roughness did not occur sharply within a narrow range of pressures. Initially "knots" or "bumps" were noticed in the extruded filament. Gradually, at higher pressure, this "bamboo" structure grew progressively shorter until the entire extrusion was curled and kinky. It will be noticed from the flow diagrams (Figs. 7 and 8) that no "break" in the curves is present. The fact that irregularities occurred over a broad range of shear stresses seems to contradict the concept of a critical shear stress. It might be speculated that imperfections (such as a burr) on the edge of the capillary interfered and obscured or prevented any sudden change in the flow behavior as noted by some investigators.<sup>1,2</sup> However, it seems unlikely that all of the capillaries were affected in the same manner.

Acknowledgment is due Battelle Memorial Institute, Columbus, Ohio, for use of the equipment.

### References

1. Bagley, E. B., *J. Appl. Phys.*, **28**, 624 (1957).
2. Mills, D. R., G. E. Moore, and D. W. Pugh, *SPE Trans.* (1961).
3. Martinovich, P. J., P. J. Boeke, and R. A. McCord, *SPE Journal*, **16**, 1335 (1960).
4. Tordella, J. P., and R. E. Jolly, *Modern Plastics*, **31**, 146 (1953).
5. ASTM D1505-57T.
6. ASTM D1238-52T.
7. Merz, E. H., and R. E. Colwell, *ASTM Bull.*, **232**, p. 63 (1958).
8. Metzner, A. B., E. L. Carley, and I. K. Park, *Modern Plastics*, **37**, 133 (1960).

9. Westover, R. F., B. Maxwell, *SPE Journal*, **13**, 27 (1957).
10. Metzner, A. B., *Ind. & Eng. Chem.*, **50**, 1577 (1958).
11. Rabinowitsch, B., *Z. Phys. Chem.*, **A145**, 1 (1929).
12. Metzner, A. B., J. C. Reed, *A.I.Ch.E., Journal*, **1**, 434 (1958).
13. Glasstone, S., K. J. Lardler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.
14. Powell, R. E., and H. Eyring, *Nature*, **154**, 427 (1944).
15. Metzger, A. P., M.S. Thesis in Chemical Engineering, The Ohio State University, Columbus, Ohio (1960).

### Synopsis

A method of treating experimental flow measurements on high polymers to obtain the basic shear diagram is described. Shear stress data are corrected to eliminate capillary end effects, and shear rate data are modified for the non-Newtonian behavior of the materials. Differences in flow behavior of commercial low-density polyethylenes are illustrated, and the effects of the two corrections are demonstrated. The method is applicable to other polymer melts. Although the data could be expressed by the power law, the fact that logarithmic plots of shear stress versus shear rate are not linear suggests that such relationships would be approximate. The data are expressed better by the three-constant Powell-Eyring equation, although the significance of the three parameters is uncertain. The need to obtain the rheological constants from the basic shear diagram rather than from an uncorrected or partially corrected capillary flow diagram is emphasized. In support of previous investigators, irregularities in the extrudate were observed at high shear stresses. However, it was not possible to determine at what pressure the roughness was initiated. The shear diagrams calculated from the experimental data do not exhibit any point of inflection as reported in some studies.

### Résumé

Ce travail décrit une méthode permettant l'étude expérimentale de l'écoulement des hauts polymères en vue d'obtenir un diagramme de cisaillement de base. Les données concernant la tension de cisaillement sont corrigées en vue d'éliminer les effets de capillarité et les données concernant la vitesse de cisaillement sont modifiées en vue de tenir compte du comportement non-Newtonien des matériaux. Les différences de comportement lors de l'écoulement de polyéthylène commerciaux de basse densité sont illustrées et l'influence des deux corrections sont mises en évidence. La méthode est applicable à d'autres polymères à l'état fondu. Quoique les données puissent être interprétées à l'aide d'une exponentielle, on constate que les diagrammes logarithmiques donnant la tension de cisaillement en fonction de la vitesse de cisaillement ne sont pas linéaires. Ceci suggère que de telles relations ne sont qu'approximatives. Les données sont mieux exprimées par l'équation à trois constantes de Powell-Eyring. La signification de ces trois paramètres est cependant incertaine. En tout cas l'attention est attirée sur la nécessité d'obtenir des constantes rhéologiques à partir de diagrammes de cisaillement de base au lieu de diagrammes d'écoulement dans un capillaire non corrigés ou partiellement corrigés. Des irrégularités lors de l'extrusion ont été observées pour des tensions de cisaillement élevées; ceci confirme les constatations antérieures de divers auteurs. Il n'a cependant pas été possible de déterminer la pression à laquelle la rigidité apparaît. Les diagrammes de cisaillement calculés à partir des données expérimentales ne montrent pas de point d'inflexion ainsi qu'il a été signalé dans certains travaux.

### Zusammenfassung

In der vorliegenden Mitteilung wird eine Methode beschrieben, die es ermöglicht aus Fließmessungen an Hochpolymeren das allgemeine Scherdiagramm aufzustellen. Schubspannungsdaten werden zur Ausschaltung des Einflusses der Kapillarenenden kor-

rigiert und Schubgeschwindigkeitsdaten wegen des nicht-Newtonschen Verhaltens der Stoffe modifiziert. Unterschiede im Fließverhalten von handelsüblichem Polyäthylen niedriger Dichte werden an Beispielen belegt und der Einfluss der beiden Korrekturen gezeigt. Die Methode kann auf andere Polymerschmelzen angewendet werden. Die Ergebnisse können zwar durch das Potenzgesetz dargestellt werden, doch zeigt die Tatsache, dass im logarithmischen Diagramm Schubspannung gegen Schubgeschwindigkeit keine lineare Abhängigkeit erhalten wird, dass eine solche Beziehung nur näherungsweise gilt. Besser werden die Versuchsdaten durch den dreikonstantigen Ansatz von Powell und Eyring wiedergegeben. Die physikalische Bedeutung der drei Parameter ist jedoch ungewiss. Auf jeden Fall wird aber klargemacht, dass die rheologischen Konstanten aus dem grundlegenden Scherdiagramm und nicht aus einem unkorrigierten oder teilweise korrigierten Diagramm des kapillaren Fließens gewonnen werden müssen. In Übereinstimmung mit früheren Autoren, wurden bei hohen Schubspannungen Unregelmäßigkeiten in der extrudierten Masse beobachtet. Es war jedoch nicht möglich den kritischen Druck dafür festzustellen. Ein Wendepunkt im Scherdiagramm, wie er von einigen Autoren angegeben wird, trat bei den Versuchsergebnissen nicht auf.

Received September 29, 1961