Influence of Elastic Effects on Capillary Flow
of Molten Polymers

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Synopsis

Capillary viscometer measurements for a number of polyethylenes and polystyrenes reveal deviations from linearity in plots of applied pressure versus capillary length to diameter ratio, at constant rates of shear, resulting in apparently negative end corrections. This is contrary to previous physical considerations. Some polymers obey Hooke's law in shear permitting the separation of the end correction into two components. A Couette correction, dependent upon the capillary dimensions, is constant for any given polymer, shear rate, and temperature; an elastic shear strain correction, dependent upon the transit time through the capillary, may be determined by post-extrusion measurements. Determination of these two corrections leads to linear plots of pressure versus capillary length to diameter ratio and enables flow curves to be calculated independent of the capillary dimensions and the swell properties of the polymer.

Introduction

The capillary viscometer is perhaps the most popular technique for studying the flow properties of molten polymers. In order to obtain true values of shear stress, corrections have to be made to the raw data. Bagley[1] considered capillary entrance effects (Couette losses) which represent viscous losses encountered by the fluid as a result of velocity gradients near the capillary entrance. Philippoff and Gaskins[2] showed that in the case of viscoelastic fluids, the entrance correction is composed of two factors. These are Couette losses and an elastic component (recoverable shear) which arises through the elastic energy stored in the melt as it is sheared.

Bagley's entrance correction requires linearity between the applied pressure and the capillary length, at constant radius, for each shear rate. It has now been found that in the case of viscoelastic fluids, such as polyethylene and polystyrene, this is not necessarily observed. This paper gives an alternative procedure for calculating corrected shear stresses and also a means for separating elastic and viscous effects in capillary viscometer experiments.

Theory

For flow in a capillary of diameter D and length L, the nominal shear

stress τ_w at the wall is calculated according to

$$\tau_w = P_t D/4L \qquad (1)$$

and the corresponding shear rate $\dot{\gamma}$ is

$$\dot{\gamma} = 32Q/\pi D^3 \qquad (2)$$

where Q is the volumetric flow rate and P_t is the applied pressure difference across the ends of the capillary.

This nominal shear rate may be corrected for non-Newtonian behavior by multiplying the shear rate by[3,4] $(3N + 1)/4N$, where

$$(N = d \log \tau_w/d \log \dot{\gamma}) \qquad (3)$$

It is generally found that the capillary geometry affects the flow data for polymer melts and an entry correction has to be made to the shear stress. Bagley[1] suggested that this might be accomplished by extrapolating the linear plot of pressure versus L/D ratio, at constant shear rate, to obtain the correction term. The shear stress then becomes

$$\tau_{cw} = P_t/2[2L/D + e] \qquad (4)$$

where e, the total end correction, is equal to the intercept on the x axis in the plot of P_t versus L/D, and τ_{cw} is the corrected shear at the wall. Philippoff and Gaskins[2] consider that the end correction e should be divided into two components, a geometrical end correction, n, and a second component, equal to one-half the recoverable shear strain at the wall, $S_R/2$, which corrects for the elastic energy stored by the melt under shear. The total end-correction in this case becomes

$$e = n + S_R/2 \qquad (5)$$

and eq. (4) on rearrangement, becomes

$$P_t = \tau_{cw}[(4L/D) + 2n + S_R] \qquad (6)$$

In some capillary rheometry the velocity of the extrudate may be quite high and can result in noticeable kinetic losses. This correction is generally not great for most work with high polymers. Calculations showed that the kinetic energy correction may be neglected in eq. (6) under our conditions.

Equation (6) leads to the conclusion that the applied pressure P_t is a linear function of L/D, at constant shear rate, with an x intercept of $-1/2(n + S_R/2)$, y intercept of $\tau_{cw}(2n + S_R)$, and slope $4\tau_{cw}$. Examples generally quoted in the literature support linearity,[1,2,5-7] but two publications recently showed the presence of curvature. Toelcke et al.[8] reported curvature in the plot of P_t versus L/D for polystyrene but chose to discard the results with the longer dies. Duvdevani[9] also found curvature in the case of some low-density polyethylenes and was successful in representing his viscosities in an exponential relationship involving the applied pressure, namely

$$\mu = \mu_0 \exp\{bp\} \qquad (7)$$

where μ was the viscosity and μ_0 a reference viscosity, p the applied pressure and b constant characteristic of the polymer and may be dependent upon temperature and shear rates.

We have also observed curvature in the plot of P_t versus L/D for numerous high-density, polyethylenes, copolymers with ethylene, and for several polystyrenes. It has been found that in Bagley's correction procedure while plotting P_t versus L/D it was not possible to obtain straight lines which, when extrapolated to zero P_t, would give the end correction, e. If the best straight line was used then often negative values of e might be obtained, which are obviously unacceptable on the basis of physical considerations.

Duvdevani's treatment implied that the melt is compressible, or that the viscosity changes with pressure. Although evidence exists[10,11] to support this view, it is generally accepted that polymer melts are incompressible at the pressures normally encountered in rheological studies. Again, if the melt is compressible, shear rates calculated from piston motion, as in the Instron capillary rheometer, might be in error. However, it has been found[12,13] that shear rates obtained from weight measurements are essentially the same as those calculated from piston motion. Thus, if compression occurs, it cannot be measured by this experimental technique.

An alternative to Duvdevani's approach may be obtained through eq. (6). The straight-line relationship between the applied pressure and the capillary length/diameter ratio implies that the capillary flow does not change along the axis of the capillary after the entrance section has been passed. This also implies that the time of transit through the capillary, which has been discussed by Smith,[14] is of no importance for the flow of viscoelastic fluids. It is well known that when a polymer is extruded through a capillary the extrudate swells to a size greater than the diameter of the capillary. It has also been shown that the degree of swelling may depend upon the transit time through the capillary.[13,15] Several explanations have been proposed to explain the post-extrusion swelling[16-19,27] but for the purposes of the present paper, post-extrusion swelling is considered to be due to a recoverable elastic shear strain.[20]

The usual approach to the experimental determination of the recoverable shear strain, has been by means of rotational viscometers. However, if Hooke's law in shear is obeyed,[21] S_R values can be obtained from capillary experiments. Spencer and Dillon[17] proposed that the elastic shear strain λ_e was related to the degree of swelling, α, by

$$\lambda_e = \bar{\alpha} - 1/\bar{\alpha} \tag{8}$$

$$\bar{\alpha} = (D_e/D_c)^2 \tag{9}$$

where D_e is the diameter of the extrudate and D_c the diameter of the capillary. If we equate Spencer and Dillon's elastic shear strain to Philippoff and Gaskins recoverable shear strain, then eqs. (6), (8), and (9) give us a means of calculating the true shear stress at the wall, τ_{cw}.

Further, in view of the experimental result[13,15] that the extrudate swelling may depend upon the transit time in the capillary it seems probable that some relaxation of the polymer occurs during its passage through the capillary. This relaxation could thus create an "elastic backpressure" which would oppose the driving force transporting the melt. As the capillary length is increased, at constant radius and constant shear rate, one would obtain an applied pressure greater than that expected from the linear relationship expressed in eq. 6 by an amount equal to the elastic backpressure. As a consequence, the plot of P_t versus L/D would deviate from linearity.

Experimental

Capillary flow data were obtained with a constant rate rheometer manufactured by the Instron Engineering Corporation.[22] Five accurately bored tungsten carbide capillaries, with a 90° tapered entrance angle and 0.030413 in. internal diameter were used. The lengths expressed in terms of length/diameter ratios were: 10.02, 19.90, 33.15, 65.50, and 130.3. A further set of capillaries of nominal diameter 0.04 in. and length/diameter ratios of 2.5, 7.5, 10, and 20 were also used. Experiments were conducted over a range of shear rates and for temperatures from 170 to 240°C. The diameters of the extrudates were measured approximately $1/4$ in. from the initially extruded end of the cooled filament. Care was also taken to minimize drawdown effects. Strictly speaking, the diameters of the molten extrudates should have been measured. This is difficult experimentally, however, the errors introduced using the diameter of the cooled extrudate were found to be within the reproducibility of the experiment.

Five commercial polyethylenes and polyethylene copolymers and two commercial polystyrenes were used to test the theory. Different production lots were also examined, making eleven samples tested. The results are typified by sample D-6, a 0.96 g/cc density ethylene homopolymer having 0.75°C/min melt index, and sample N-1 a medium impact polystyrene, similar to some samples previously studied in this laboratory.[23,24]

Results and Discussion

Equation (6) predicts that a plot of observed force versus capillary length/diameter ratio should be linear and, as shown by Bagley,[1] the negative intercept on the L/D axis is equal to the end correction. Figures 1 and 2 show typical plots of measured force versus L/D for samples D-6, N-1, and many others. The number on the curves refer to the shear rate and cover the range from the lowest obtainable on the Instron, to the point of melt fracture. With increasing L/D and/or increasing shear rates, the deviation from linearity increases rapidly. When the best straight line is drawn through the experimental points to determine the end correction, its value becomes negative. This is illustrated in Figure 3, where the end
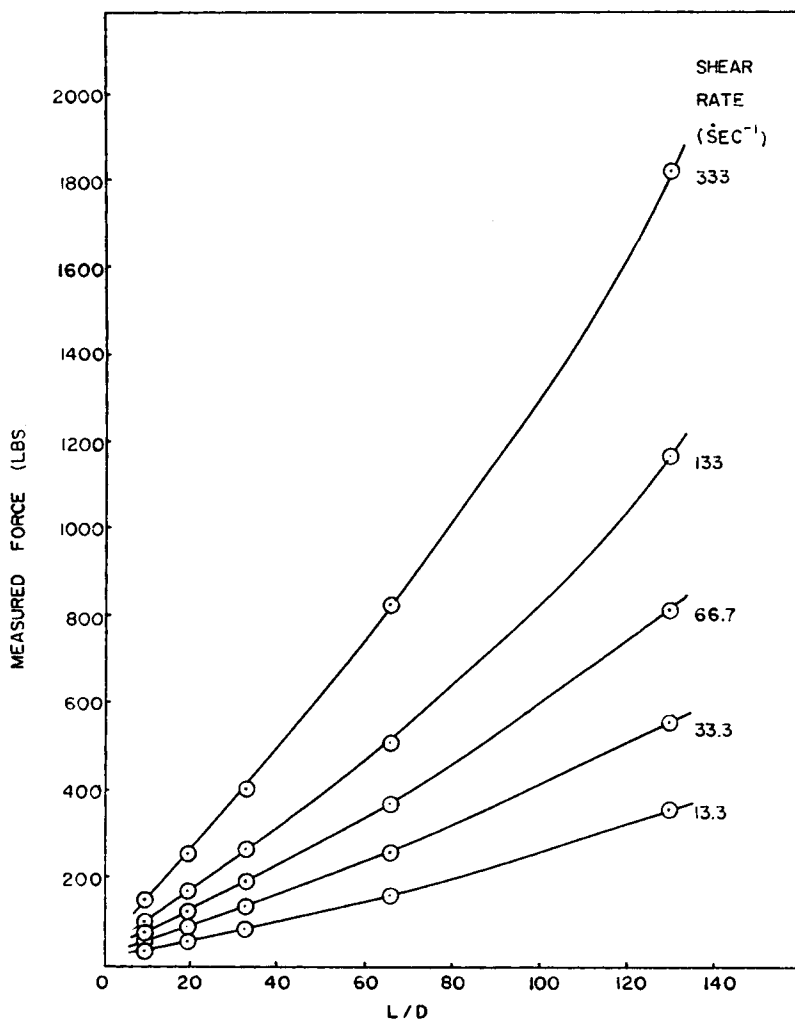
Fig. 1. Curves showing the relationship between measured force and capillary dimensions at constant shear rates; sample D-6; melt temperature 200°C; 0.03 in. diameter capillaries.

correction is plotted as a function of the shear rate for different sets of capillaries containing increasing L/D ratios. With short dies the end correction becomes increasingly more positive, with increasing shear rate, as observed by Bagley. However, the introduction of longer capillaries leads to increasing negative end corrections. These apparently anomalous results are contrary to physical considerations but have been observed so frequently with different polymers and various operators that they cannot be accounted for by experimental errors.

If the two components of the end correction are again considered [eq. (6)], the geometric correction n must be constant for any set of capillaries
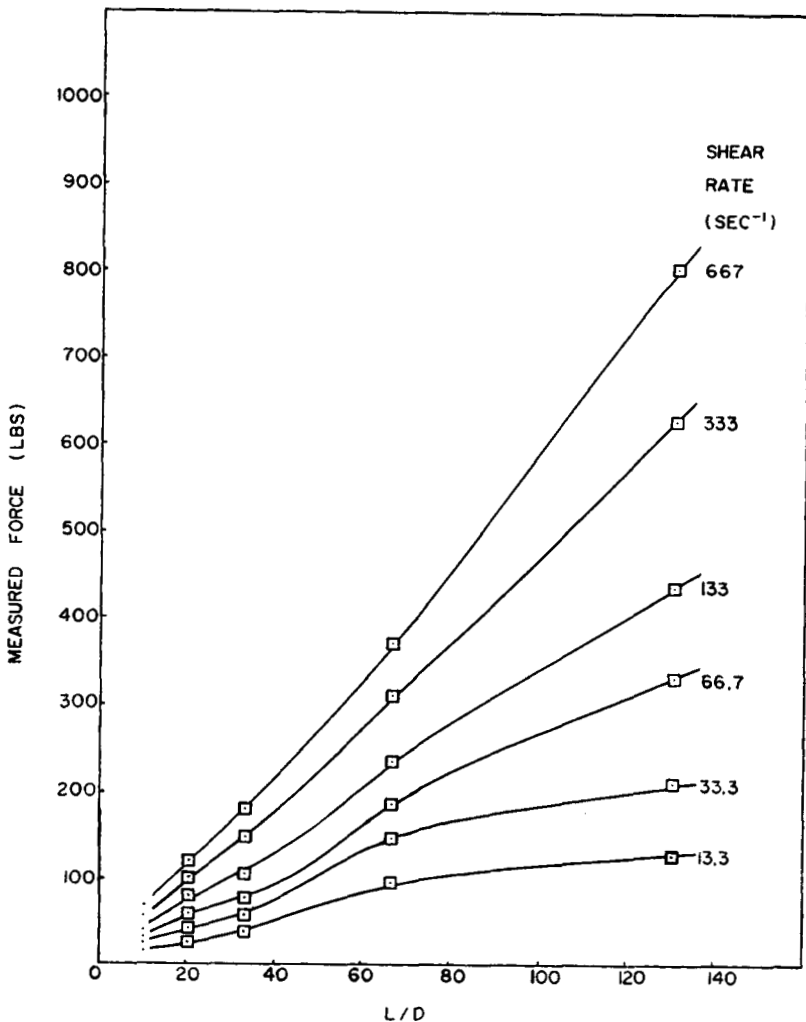
Fig. 2. Curves showing the relationship between measured force and capillary dimensions at constant shear rates; sample N-1; melt temperature 240°C; 0.03 in. diameter capillaries.

of constant diameter and at any given shear rate. Then to account for negative and positive values for the total end correction we must assume that the recoverable shear strain, must change with the capillary length.

Quantitative measurements of the degree of extrudate swelling α ($= D_e/D_c$) below the onset of melt fracture show that swelling decreases as the shear rate decreases or as the capillary length increases (Fig. 4). Tordella[25] showed that the elastic strain could vary down the capillary, but he was unable to measure the associated energy dissipation. The results of Bagley et al.[19] also indicated that changes occur in elastic strain
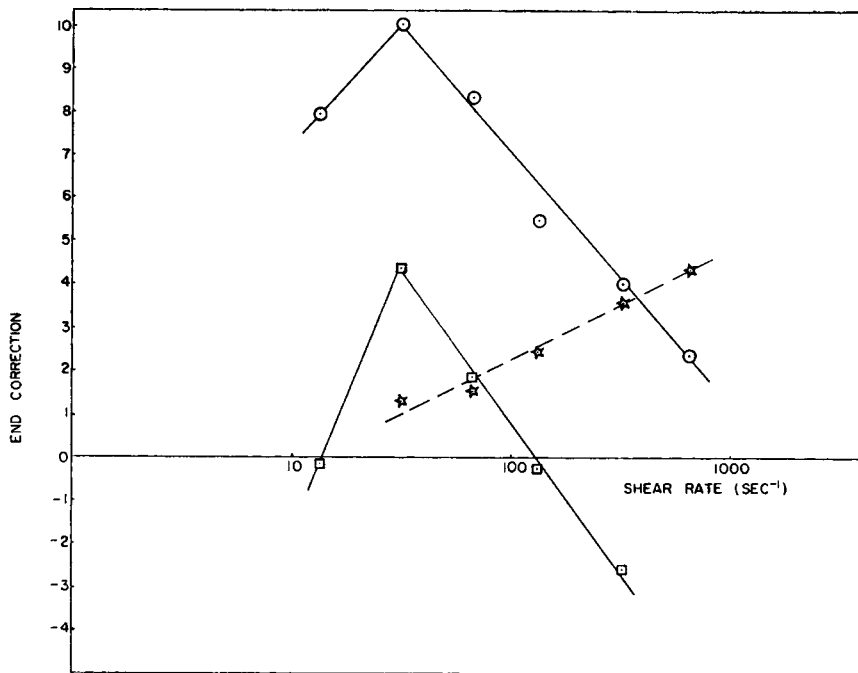
Fig. 3. Effect of capillary dimensions on the end correction: (□) 10/1, 20/1, 33/1, 66/1, and 130/1, L/D capillaries; (⊙) 10/1, 20/1, 33/1, and 66/1, L/D capillaries; (☆) 10/1, 20/1, and 33/1, L/D capillaries. Sample D-6; melt temperature 200°C.
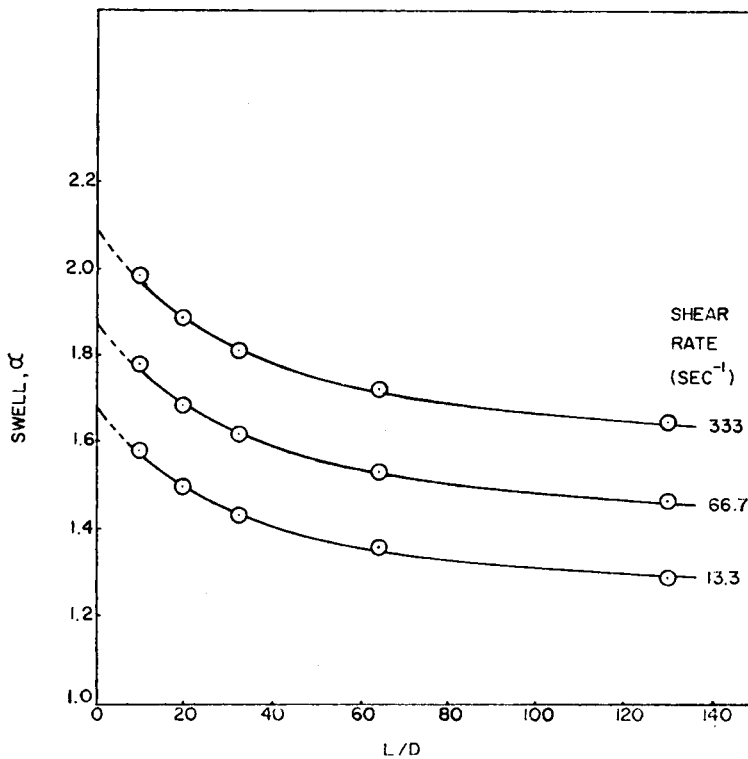

Fig. 4. Effect of capillary dimensions on extrudate swell at constant shear rates; sample D-6; melt temperature 200°C.
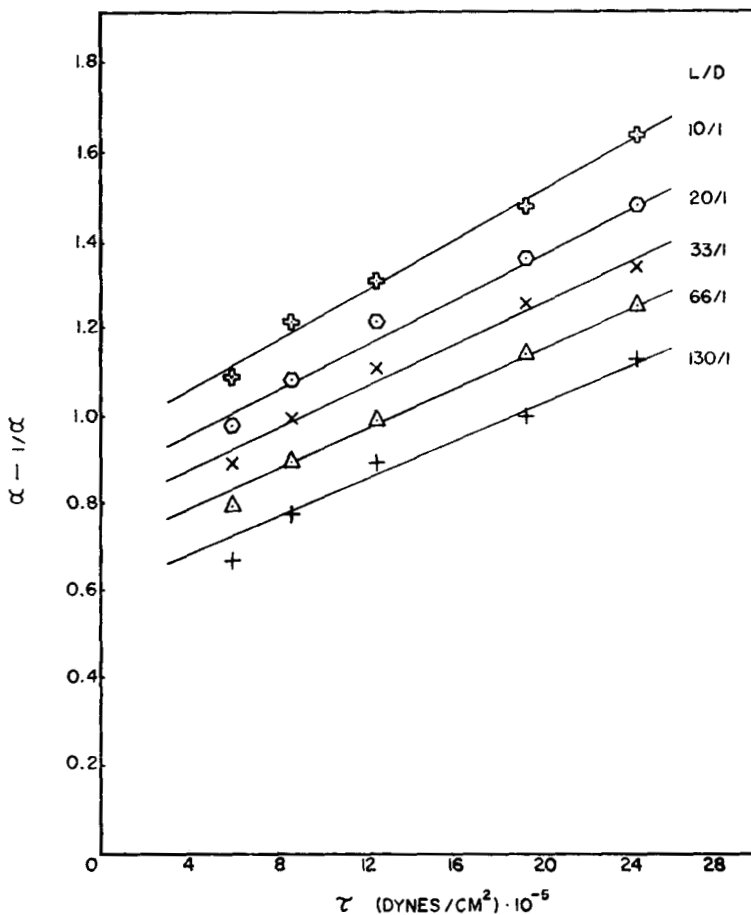
Fig. 5. Linear plot of shearing strain versus corrected shear stress at the wall; sample D-6; melt temperature 200°C.

in the capillary, although they obtained linear plots of pressure versus capillary length/diameter ratio. Bagley et al. concluded that extrudate swelling was not accompanied by any change in the measured viscosity or, at least, the degree of swelling "pressure" had no measureable effect on the viscosity. Curvature in the pressure versus capillary L/D plots might then be taken to indicate that in our case the elastic strain is large enough to be measureable or the polymer melt has time to relax sufficiently to build up an elastic backpressure which can influence the measured viscosity. For short capillaries and high shear rates, the average transit time in the capillary is small and the polymer will have little time to relax. In this case it is probable that a graph of applied force versus L/D would be linear, as observed by Bagley[1] and Philippoff and Gaskins.[2]

The theory of elasticity predicts that if Hooke's law in shear is obeyed

$$\tau = G(\alpha - 1/\alpha) \tag{10}$$

where $(\alpha - 1/\alpha)$ is the shearing strain and G is the shearing modulus. Spencer and Dillon[17] found that in the case of polystyrene, eq. (10) gave linear plots if the shearing stress at the capillary wall was substituted for τ and the average relative length $\bar{a}$, for α. As chain molecules become
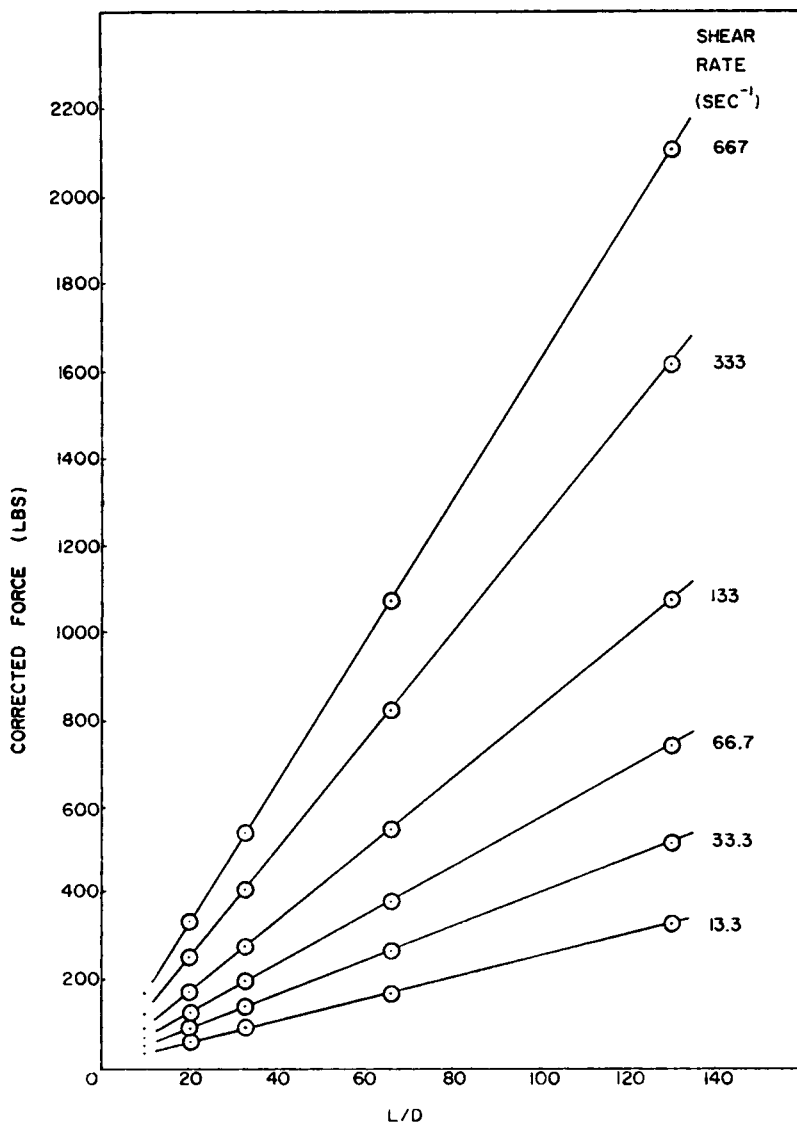

Fig. 6. Curves showing linear relationship between corrected force and capillary dimensions at constant shear rate; sample D-6; melt temperature 200°C.
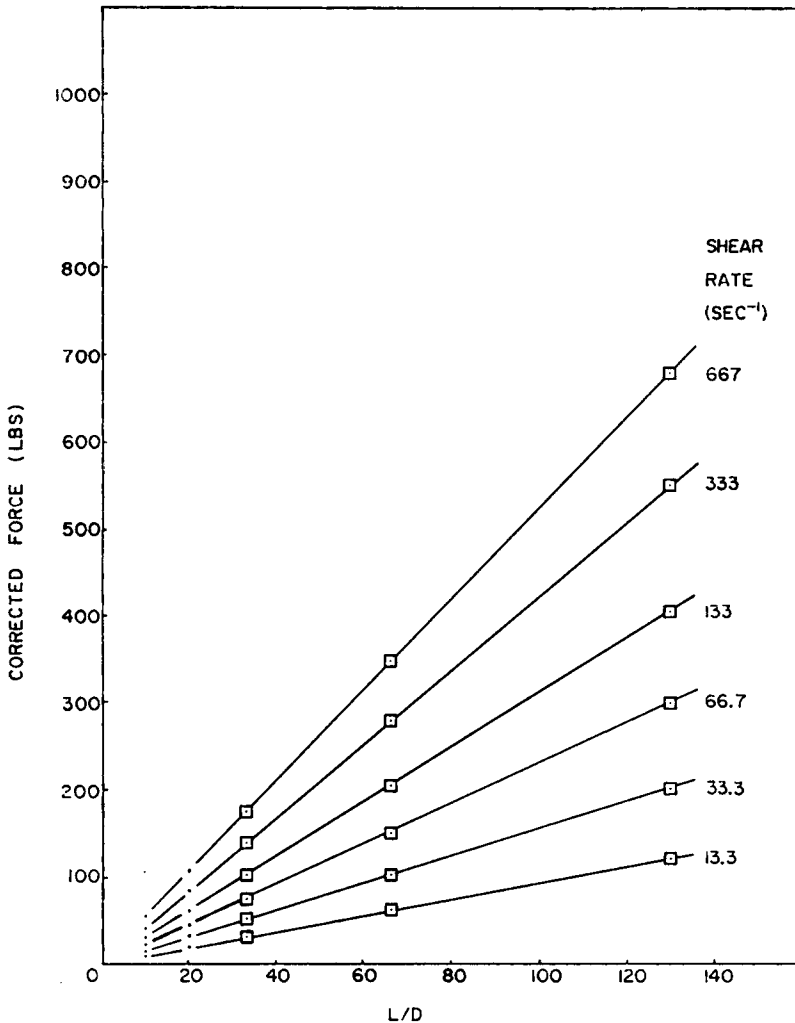
Fig. 7. Curves showing linear relationship between corrected force and capillary dimensions at constant shear rate; sample N-1; melt temperature 240°C.

aligned and parallelized in a certain direction, the polymer shows increased swelling perpendicular to this direction. For capillary flow experiments, $\bar{\alpha}$ or α is therefore a diametric ratio. The polymers tested were found to be best represented by eq. (10) where τ^0_{cw}, calculated from the initial slopes of the curves in Figures 1 and 2, was substituted for τ and the shearing strain by $(\alpha - 1/\alpha)$ (Fig. 5); that is, eq. (8) becomes

$$S_R \equiv \lambda_e = (\alpha - 1/\alpha) \tag{11}$$

If, in Figure 4, we project the swell versus L/D curve, at constant shear rate, to the $L/D = 0$ axis, substitution of this value, α_0 into eq. (11) gives a measure of the recoverable shear S^0_R at $L/D = 0$ that is, for a sharp-
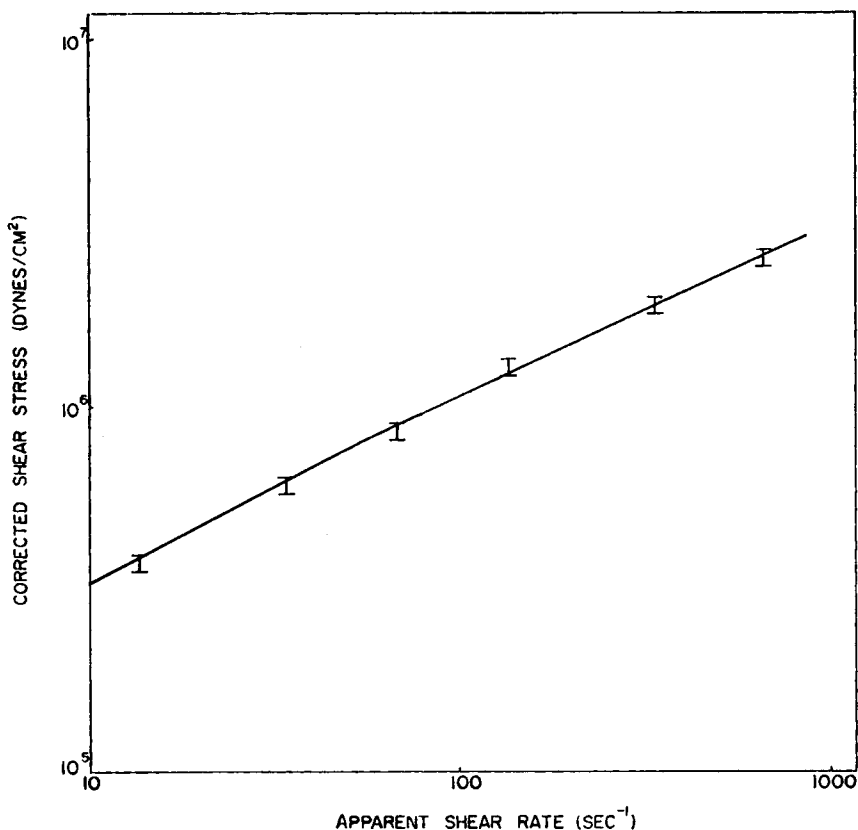
Fig. 8. Corrected flow curve for sample D-6 calculated by using eq. (14).

edged orifice. This value, together with the corresponding intercept
$[= \tau^0_{cw}(2n + S^0_R)]$ obtained by extrapolating the curves of Figures 1
and 2 to $L/D = 0$, gives a measure of the geometric end correction. A
similar numerical value will be determined by extrapolation to zero force.
For this case the x intercept equals $-^1/_2[n + ^1/_2 S^0_R]$. Typical values
obtained for samples D-1 and N-1 are given in Table I.

Equation (6) now becomes

$$P_c = \tau^0_{cw}(4L/D + 2n + S_R) \qquad (12)$$

where P_c is the corrected pressure, τ^0_{cw} and n have been defined, and S_R
is the recoverable shear strain, at constant shear rate, for the various
capillaries. Substituting the appropriate values into eq. (12) leads to the
linear plots shown in Figures 6 and 7. As expected, little difference was
observed between the measured experimental pressure and the calculated
pressure for short capillaries, but as the length of the capillary increased,
divergence occurs due to build-up of the elastic backpressure through the
relaxation of the polymer melt in the capillary.

Generally the corrected pressure versus L/D passed through the origin.

TABLE I
Geometric End Corrections n Calculated From Equation (5)

Shear rate, sec^{-1}	n	
	Sample D-6	Sample N-1
13.34	2.9	3.2
33.36	3.3	2.5
66.74	3.4	2.5
133.4	3.4	2.6
333.6	3.5	2.9
667.4	4.0	3.9

Schott[26] considers a third correction due to the taper of the inlet of the capillary. This correction is a function of shear rate and temperature as well as polymer type. Unfortunately, in the present case the effect of inlet angle could not be determined.

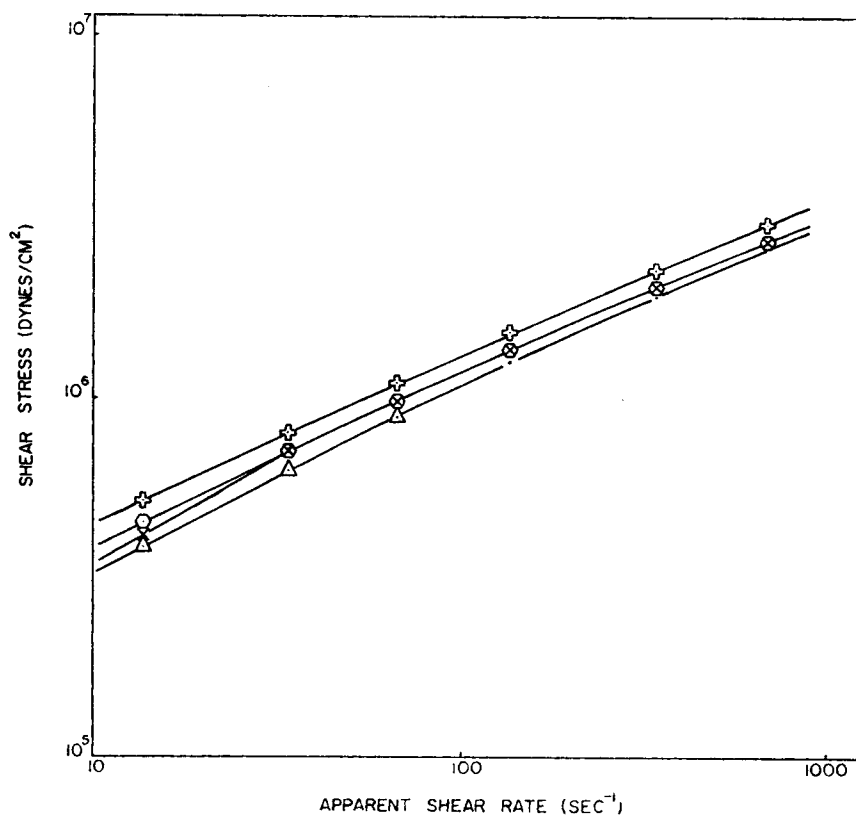Further confirmation of the theory may be seen by rearrangement of

Fig. 9. Logarithmic plot or flow behavior for sample D-6; melt temperature 200°C.

eq. (6).   We can calculate an apparent shear stress, τ_a, from the dimensions of the capillary and the applied pressure:

$$P_t = (4L/D)\tau_a \tag{13}$$

Substituting eq. (13) into eq. (6) and rearranging leads to

$$\tau_a = \tau_{cw}[1 + (D/4L)(2n + S_R)] \tag{14}$$

The plot of τ_{cw} versus shear rate, $\dot\gamma$, gave a curve independent of the L/D ratio and the polymer swell (Fig. 8) compared with the series of curves obtained when the correction for swell was not made (Fig. 9).   The shear stress obtained with the 0.03 in. diameter capillaries with L/D ratios 10/1, 20/1, 33/1, 65/1, and 130/1 is represented as a spread due to cumulative experimental errors.

   Thus there appears to be three procedures for calculating shear stress values which are independent of the capillary dimensions and the elastic properties of the polymer.   First, the shear stress at the wall, τ_{cw}, may be calculated from the initial slope of P_t versus L/D, that is, by using short
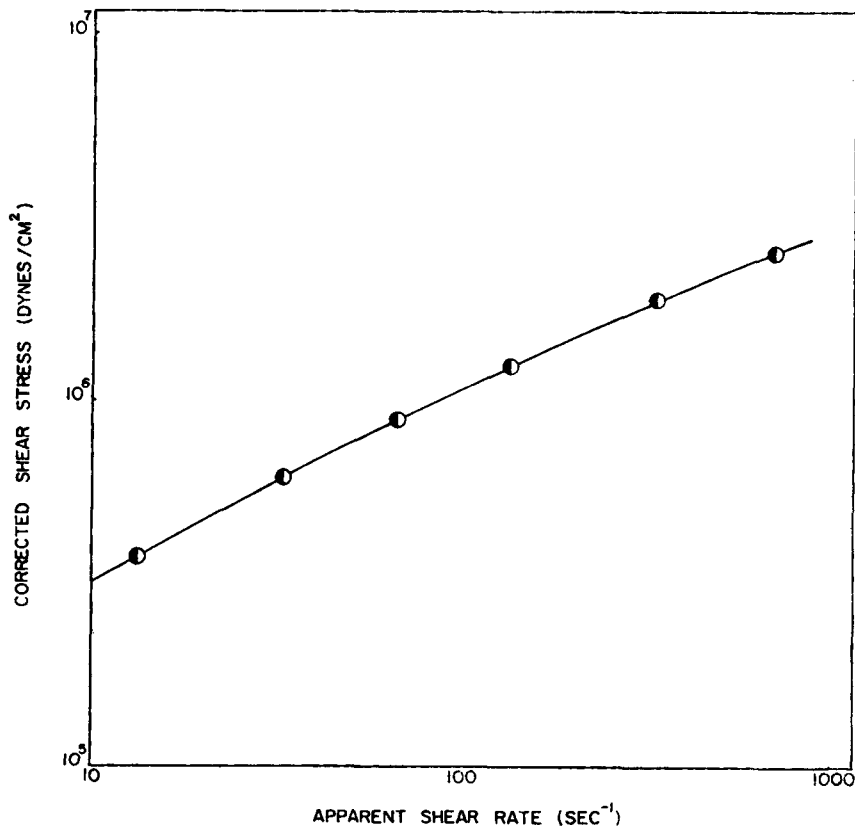

Fig. 10. Comparison of corrected flow curves for sample D-6: (●) eq. (14); (▢) calculated from the initial slope of Fig. 1; (○) calculated from the slope of Fig. 6.

capillaries; secondly, τ_{cw} may be calculated from the slope of the cor-rected pressure versus L/D plot, and thirdly from eq. (14). A comparison of the three methods is shown in Figure 10. In all cases only the apparent shear rates have been calculated and should strictly be corrected as in eq. (3). However, this correction does not affect the corrections to the applied pressure.

Conclusions

Experimental results have shown that the Philippoff and Gaskins[2] theoretical development for the end correction in capillary rheometer measurements must be modified for some polymers to take into account relaxation processes during transit through the capillary. It has also been shown that these relaxation processes can set up elastic forces which are sufficiently large to cause deviations from linearity in the plot of applied pressure versus capillary length to diameter ratio. This deviation implies that the normal stress is not constant for each shear rate as found by Philippoff and Gaskins but varies down the length of the capillary. How-ever, if the transit time through the capillary is short in comparison with the relaxation processes then the applied pressure is a linear function of the capillary length.

Corrected shear stresses, independent of capillary dimensions and the swell properties of the polymers, may be calculated.

References

1. E. B. Bagley, *J. Appl. Phys.*, **28**, 624 (1957).
2. W. Philippoff and F. N. Gaskins, *Trans. Soc. Rheol.*, **2**, 263 (1958).
3. B. Rabinowitsch, *Z. Physik. Chem.*, **A145**, 1 (1929).
4. A. B. Metzner and J. C. Reed, *AIChE J.*, **1**, 434 (1958).
5. S. N. Chinai and W. C. Schneider, *J. Appl. Polym. Sci.*, **7**, 909 (1963).
6. D. E. Grant and S. F. Dieckmann, *J. Appl. Polym. Sci.*, **9**, 3231 (1965).
7. A. B. Metzner, E. L. Carley, and I. K. Park, *Mod. Plastics*, **37**, 133 (July 1960).
8. G. A. Toelcke, C. G. Goyos, and J. A. Biesenberg, paper presented at S.P.E. 13th Antec Meeting, May 1967, *Technical Papers*, 98 (1967).
9. I. Duvdevani and I. Klein, paper presented at S.P.E. 13th Antec Meeting, May 1967; *Technical Papers*, 445 (1967).
10. R. F. Westover, paper presented at S.P.E. 6th Antec Meeting, January 1960; *Technical Papers*, 80 (1960).
11. B. Maxwell and A. Jung, *Mod. Plastics*, **35**, 174 (Nov. 1957).
12. A. P. Metzger and C. W. Hamilton, *S.P.E. Trans.*, Vol. **4**, No. 2 (April 1964).
13. M. G. Rogers, unpublished data.
14. T. L. Smith, *J. Polym. Sci.*, **14**, 37 (1954).
15. A. P. Metzger and J. D. Matlack, paper presented at S.P.E. 13th Antec Meeting, May 1967; *Technical Papers*, 389 (1967).
16. S. Middleman and J. Gavis, *Phys. Fluids*, **4**, 355, 963, 1450 (1961).
17. R. S. Spencer, and R. E. Dillon, *J. Colloid Sci.*, **3**, 163 (1948).
18. E. B. Bagley, *Trans. Soc. Rheol.*, **5**, 355 (1961).
19. E. B. Bagley, S. H. Storey, and D. C. West, *J. Appl. Polym. Sci.*, **7**, 1661 (1963).

20. D. L. McIntosh, doctoral thesis, Washington University, St. Louis, 1960.

21. E. B. Bagley, *J. Appl. Phys.*, **31**, 1126 (1960).

22. E. H. Merz and R. E. Colwell, *ASTM Bull.*, **No. 232**, 63 (1958).

23. R. W. Ford, R. A. Scott, and R. J. B. Wilson, *J. Appl. Polym. Sci.*, **12**, 547 (1968).

24. R. W. Ford, J. D. Ilavsky, and R. A. Scott, paper presented at 155th American Chemical Society Meeting, San Francisco, April 1968.

25. J. P. Tordella, *J. Appl. Polym. Sci.*, **7**, 215 (1963).

26. H. Schott, *J. Polym. Sci. A*, **2**, 3791 (1964).

27. P. L. Clegg, *Rheology of Elastomers*, P. Mason and N. Wookey, Eds. Pergamon Press, London, 1957, p. 174.