

## Reliability of Capillary Rheometer Measurement of Polymer Melts

### Introduction

It is generally found that capillary geometry affects the flow data of polymer melts in capillary extrusion rheometers, and entrance corrections have to be made.<sup>1</sup> This correction term may be obtained by graphical means or, as has been customary in these laboratories for several years, a suitable computer program may be written based on Bagley's observation<sup>1</sup> that a plot of pressure versus capillary length-to-diameter ratio, at constant shear rate, is linear. It has now been found that for some viscoelastic fluids, such as polyethylene and polystyrene, apparently negative end corrections may be obtained. Closer examination of the results revealed deviations from linearity in the plots of pressure versus capillary length-to-diameter ratio.

The measured pressure drop in a capillary rheometer similar to that manufactured by the Instron Engineering Corporation<sup>2</sup> contains frictional losses in the entrance and exit regions, a loss during developed flow in the capillary, kinetic energy losses and elastic effects. Nieve and Bogue<sup>3</sup> have discussed these losses in detail for capillary experiments with polymeric solutions. The present authors have also considered sources of pressure losses in attempting to explain the nonlinear plots of pressure versus capillary length-to-diameter ratio previously mentioned. Some results are reported herein, based on a 0.96 g/cc density ethylene homopolymer, 0.75 dg/min melt index, similar to those studied previously in this laboratory.<sup>4,5</sup> The capillaries were 0.03 in. in nominal diameter, and the melt temperature was 190°C.

### Discussion

In the extrusion-type rheometer a certain amount of energy is spent in order to move the molten polymer in the barrel. If the barrel is regarded as a capillary in series with the test capillary, then the ratio of the pressure drop across the barrel to that across the capillary is given as:

$$P/p = (L/l) (r/R)^{3/n+1}$$

for a power law fluid where  $n$  is the flow index,  $L$  and  $R$  the length and radius of the barrel, and  $l$  and  $r$  the length and radius of the capillary. Calculations for the Instron rheometer show that the maximum pressure loss in the barrel is 1½% and occurs with the shortest die (10/1 length:diameter ratio and 0.03 in. diameter) and at the lowest shear rate. As the die length or shear rate increases the relative magnitude of the pressure loss in the barrel diminishes. Similar results were observed by Metzger and Knox.<sup>6</sup>

Pressure losses can also arise in the barrel due to back flow past the piston. Table I shows some typical results when the polymer was extruded at a constant shear rate through the entire length of the barrel. The change in force (pressure) along the barrel was less than ±1%.

When the molten polymer flows under high shear stresses temperature gradients may arise. In his treatment of heat generation and conduction for flow in a round tube, Toor<sup>7,8</sup> showed that initially the fluid in the center of the tube cools, and after a sufficient length of flow, the temperature distribution becomes essentially constant. Calculations for our case showed this distance to be negligibly small. Any temperature rise due to intermolecular friction<sup>8</sup> would decrease the rate of increase of the applied pressure, with increasing shear rate and not increase the rate as observed. Further losses occur when the fluid stream discharges directly from the capillary into air. The stream carries an amount of kinetic energy which represents a portion of the total force. Thus the observed pressure may be corrected for kinetic losses by:

$$\Delta P_{\text{corr}} = \Delta P - \rho v^2_{\text{av}}/\alpha$$

TABLE I

Variation of Force with Distance Along Rheometer Barrel for a Plunger Moving at a Constant Speed (0.03 in. diameter, 65/1  $L/D$  Capillary)

0.5 in./min crosshead speed		5 in./min crosshead speed	
Distance down barrel, in.	Force, lb	Distance down barrel, in.	Force, lb
1.5	285.5	2.0	841
4.5	285	5.0	843
6.5	284	7.0	849
8.35	282.5	8.0	852
9.5	285	9.0	855
11.35	285	11.35	858
Mean	284.5 $\pm$ 0.5%	Mean	850.3 $\pm$ 0.94%

where  $\Delta P_{\text{corr}}$  is the corrected pressure,  $\Delta P$  the observed pressure,  $\rho$  the fluid density, and  $v_{\text{av}}$  the average velocity through the capillary. For a non-Newtonian fluid described by a power-law model,<sup>9</sup>  $\alpha$ , the kinetic energy correction factor, is given by:

$$\alpha = (4n + 2)(5n + 3)/(3n + 1)^2$$

Following Bagley<sup>1</sup> the shear stress is calculated from the slope of applied pressure versus  $L/D$  for each shear rate. Since the plot of applied pressure versus  $L/D$  was not linear, slopes were taken over two portions of the curves, namely, from a  $L/D$  ratio equal to zero to 33/1 and secondly from  $L/D = 33/1$  to 130/1. From the plots of shear stress versus shear rate,  $n$  and hence  $\alpha$ , the kinetic energy correction may be calculated. Combining with the calculated output for each crosshead speed, the corrected pressure,  $\Delta P_{\text{corr}}$ , is readily calculated. Typical values are shown in Table II. Even at the highest crosshead speed, the pressure loss due to kinetic energy is less than 0.1%, which is considered negligible. With longer capillaries, the losses become even more insignificant.

TABLE II

Estimation of Pressure Correction Due to Kinetic Energy Losses (10/1  $L/D$ ; 0.03 in. Capillary)

Crosshead speed, in./min	$\Delta P$ (observed), dynes/cm <sup>2</sup> $\times 10^{-5}$	Kinetic energy correction, dyne/cm <sup>2</sup>
0.02	2.9	0.006
0.05	3.9	0.031
0.1	5.12	0.141
0.2	7.26	0.608
0.5	10.10	3.80
20.0	34.10	5.630

Maxwell and Jung<sup>10</sup> and later Westover<sup>11</sup> reported that polymer melts were compressible. If curvature in the plots of pressure versus capillary  $L/D$  ratio was due to compressive effects, then shear rates calculated from output measurements and those calculated from piston travel might be expected to differ. Since rates of shear calculated by the former procedure are generally based on a constant melt density, determination of the latter at several applied pressures might reveal compressibility. Simultaneous measurements of extrudate weight and piston travel combined with the diameter of the rheometer barrel allow the density to be determined. Although the results (Table III) show some scatter, no obvious trend is evident.

TABLE III  
Effect of Pressure Drop on Melt Density at 190°C

Pressure drop, psi	Melt density, g/cc
2016	0.749
2840	0.728
3149	0.733
4300	0.754
5409	0.762
5432	0.721
5566	0.755
6292	0.763
7804	0.739
8451	0.752
11498	0.730
13287	0.780
16437	0.746

The losses discussed above would indicate that pressure losses are small. Other contributing factors include calibration, temperature stability and packing of the rheometer. Reproducibility tests over a period of several months indicated that the reproducibility of the pressure measurements at low rates of shear was  $\pm 6\%$  while at higher rates,  $10^3 \text{ sec}^{-1}$ ,  $\pm 2\%$  was easily obtained. The temperature gradient along the barrel and capillary was maintained at  $\pm 0.5^\circ\text{C}$ .

In the case of polymeric solutions, LaNieve and Bogue were able to correlate an elastic pressure drop from capillary experiments with the normal stress differenced as measured on a Weissenberg rheogoniometer. Perhaps intuitively one feels that in the case of a polymer melt, pressure energy could be converted into elastic energy at the entrance of a capillary and that this could be recoverable and reversible. The recovery would be manifested as an expansion of the extrudate from the capillary and should be related to the normal stress. Analysis of the expansion of the extrudates was carried out similar to that used by Middleman and Gavis<sup>12</sup> and that by Metzner et al.<sup>13</sup> However, as found by LaNieve and Bogue, this type of analysis gave values for the normal stresses which were too small to account for extrudate expansion.

To summarize, there are several inherent errors in the use of capillary rheometers, the sum of which amount to  $\pm 2\text{--}6\%$  of the applied pressure. These errors do not account entirely for the deviation from linearity of plots of pressure drop versus capillary  $L/D$  ratios observed for some viscoelastic polymers. In another publication,<sup>14</sup> other factors such as relaxation processes and the transit time in the capillary were considered. The approach was successful for calculating corrected shear stresses.

#### References

1. E. B. Bagley, *J. Appl. Phys.*, **28**, 624 (1957).
2. E. H. Merz and R. E. Colwell, *ASTM Bull.*, No. **232**, 63 (1958).
3. H. L. LaNieve, III, and D. C. Bogue, *J. Appl. Polym. Sci.*, **12**, 353 (1968).
4. R. W. Ford, R. A. Scott, and R. J. B. Wilson, *J. Appl. Polym. Sci.*, **12**, 547 (1968).
5. M. G. Rogers, *Ind. Eng. Chem.*, submitted for publication.
6. A. P. Metzger and J. R. Knox, *Trans. Soc. Rheol.*, **9**, 13 (1965).
7. H. L. Toor, *Ind. Eng. Chem.*, **48**, 922 (1956).
8. H. L. Toor, *Trans. Soc. Rheol.*, **1**, 177 (1957).
9. A. B. Metzner, *Advan. Chem. Eng.*, **1**, 113 (1956).
10. B. Maxwell and A. Jung, *Mod. Plastics*, **35**, 174 (Nov. 1957).

11. R. F. Westover, S.P.E. 16th ANTEC Technical Papers, Paper No. 80 (Jan. 1960).
12. S. Middleman and J. Gavis, *Phys. Fluids*, **4**, 355, 963 (1961).
13. A. B. Metzner, W. T. Houghton, R. A. Sailor, and J. L. White, *Trans. Soc. Rheol.*, **5**, 133 (1961).
14. C. McLuckie and M. G. Rogers, *J. Appl. Polym. Sci.*, in press.

MORRIS G. ROGERS  
COLIN MCLUCKIE

Research and Development Laboratory  
Dow Chemical of Canada Limited  
Sarnia, Ontario, Canada

Received December 3, 1968