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Polymer Flow Through Capillaries of Variable Diameter

K. K. CHEE and Y. H. YAP, *Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia*, and A. RUDIN, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada*

Synopsis

A polystyrene melt has been extruded through successive capillaries arranged to produce converging and diverging flow patterns through the twin orifices. Applied pressure at fixed mass flow rate through the combined dies is equal to the sum of the pressure drops in the single capillaries in both flow modes. The Bagley end correction was found to apply to each die in the sequence. Bagley plots were linear with a particular upper capillary at given apparent shear rate in the lower die. No effect of shear history could be detected on the viscous behavior of the polymer, but preshearing in converging flow produced a slight reduction in die swell.

INTRODUCTION

Rheological properties of polymer melts have been studied extensively in flow through orifices with various shapes and dimensions. To the best of our knowledge, the behavior of polymers flowing successively through two flat-entry capillaries with different radii has only been touched on recently. Ito and Shishido[1] extruded a polystyrene solution in an overall converging flow pattern through a very large orifice leading into a much smaller capillary.

This article includes the results of a study of polystyrene melt extrusion through successive orifices arranged so as to produce diverging as well as converging flow when the melt exited from the first capillary. Apparent flow curves, Bagley[2] end corrections, and die swell values have been examined.

EXPERIMENTAL

A commercial polystyrene was used. This sample had $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ equal to 1.41×10^5, 3.04×10^5, and 6.18×10^5, respectively, from GPC measurements; M_v in toluene[3] was 2.73×10^5. The polymer was found to be thermally stable for at least 1 hr at 190°C as manifested by steady torque readings in a Brabender Plastograph. Antioxidant was, therefore, not added to the polystyrene.

The extrusion apparatus was a dead weight-driven piston capillary rheometer adapted from a Davenport Melt Indexer (Model III). The dimensions of the piston and reservoir are as specified in the melt index test methods.[4] Driving weights on the piston were varied to provide different apparent

TABLE I
Die Dimensions

Die designation	Length L, cm	Diameter D, cm	L/R[a]
w_3	0.5122	0.0731	14.01
w_4	0.7602	0.0720	21.12
w_5	1.0080	0.0751	26.84
w_6	0.6860	0.1010	13.58
w_7	0.8905	0.1000	17.81
w_8	1.4891	0.1015	29.34
w_9	0.7924	0.1530	10.36
w_{10}	0.9125	0.1520	12.01
w_{12}	0.7920	0.2001	7.97

[a] R = radius of the die.

shear stresses. The maximum load used was about 20 kg. All extrusions were at 190.0° ± 0.2°C.

Nine capillaries were machined from stainless steel. The orifice dimensions were measured at about 190°C with a micrometer and traveling microscope. Table I contains a list of the die designations and dimensions.

Granule samples were packed into the rheometer reservoir and allowed to stand for 10 min to attain temperature equilibrium.

A standard annealing procedure was followed closely to obtain die swell measurements on stress-free extrudates. This procedure, which is a variation of that reported by Mendelson and Finger[5] for polyethylene, used liquid paraffin to eliminate drawdown of the extrudate.

Two different series of extrusions were performed. In one set of experi-

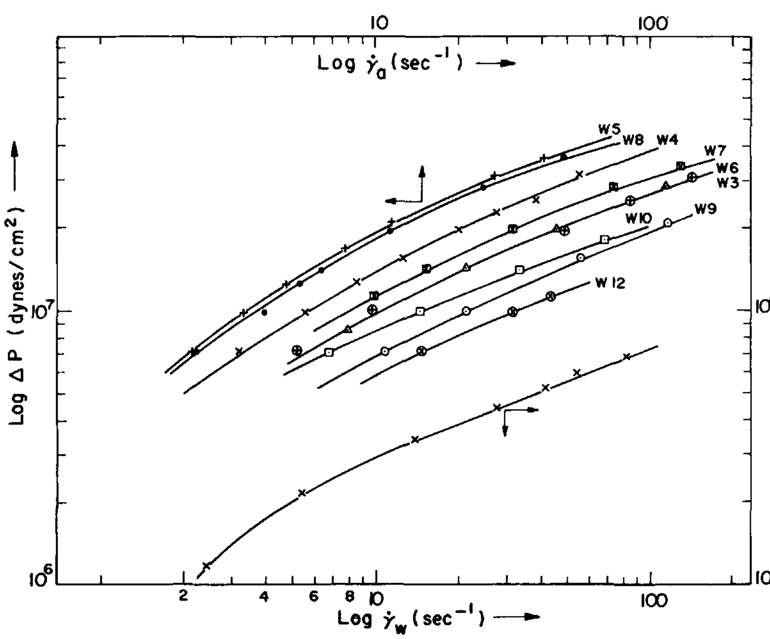

Fig. 1. Plots of extrusion pressure (ΔP) vs. apparent shear rate ($\dot{\gamma}_a$) for orifices with dimensions listed in Table I. Also shown is the true flow curve of shear stress (τ_w) against shear rate ($\dot{\gamma}_w$) at the capillary wall for the polystyrene studied. Temperature = 190.0°C.

ments, a single capillary was used in the usual manner. The other series employed one die on top of the other. Great care was taken to ensure proper alignment of the capillaries in the latter case. The following die alignments were studied (the top die is listed first; codes refer to the designations in Table I).

Converging flow:

w_6–w_3, w_7–w_3, w_8–w_3, w_9–w_3, w_{10}–w_3, w_{12}–w_3, w_7–w_4, w_{10}–w_6, w_{12}–w_6, w_{12}–w_9.

Diverging flow:

w_3–w_6, w_3–w_7, w_3–w_8, w_3–w_9, w_3–w_{12}, w_4–w_7, w_6–w_{10}, w_9–w_{12}.

Mass output data were found to be reproducible to within better than 5% of the mean replicate results.

Viscous Behavior

Figure 1 shows the apparent flow curves obtained with the nine individual dies used in this study. Mass flow rates were converted to apparent shear rates by equating the density of the melt to 0.9748 g/cm^3.[6] Figure 1 also includes the true flow curve calculated from the apparent data by application of Bagley[2] and Mooney-Rabinowitsch[7,8] corrections for end effects and nonuniform velocities across the capillary cross section, respectively.

End corrections[2] are shown in Figure 2. As expected,[2,9] the end correction becomes practically independent of shear rate at low shear rates.

The raw data (pressure and volumetric flow rate) obtained in converging and diverging flows with die w_4–w_7 combination are shown in Figure 3. The corresponding figures from extrusion with the individual capillaries are also plotted in this figure. It is clear that the applied pressure at a given volumetric flow rate (Q) through the combined dies equals the sums of the pressure

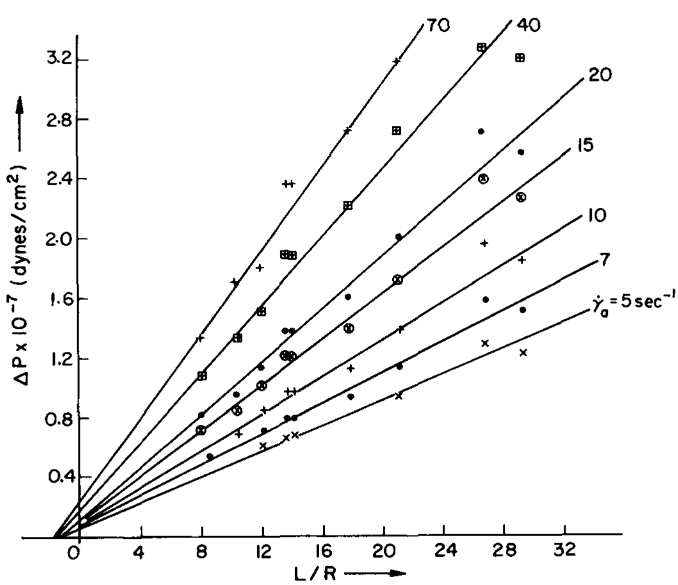

Fig. 2. Bagley end correction plots at various apparent shear rates.

drops in the single capillaries regardless of the order in which the dies are placed.

This observation applies to all the other capillary combinations which were investigated and holds whether the top die is narrower or wider than the succeeding capillary.

The empirical observation which has just been stated can be expressed as

$$\Delta P_{i+j} = \Delta P_i + \Delta P_j \qquad (Q \text{ constant}) \tag{1}$$

where the ΔP's refer to the pressure drops at given volumetric flow rate and temperature through the subscripted dies. Pressure drops are not additive at fixed shear rate since this parameter is not the same for both capillaries at a fixed volumetric flow rate.

It is clear that the pressure drop between the ends of the top or the bottom die in the sequence would be equal to that of the corresponding orifice in single-die extrusion if the flow patterns were not perturbed by the presence of the other capillary. Similar observations have been made in studies in which the orifice and reservoir diameters have been changed to vary the so-called contraction ratio.[10,11] When the diameter of the reservoir in single-die extrusion or the upper die in a sequential capillary extrusion is sufficiently larger than the diameter of the final orifice, the normal stress measured at the entrance to this capillary will be independent of the diameter of the upper member of the sequence because the deviatoric stress contribution will be negligible compared to the magnitude of the hydrostatic pressure.[11]

The Bagley end correction applies to each orifice in the sequence in the sense that the pressure drop between the ends of any die (but not the total

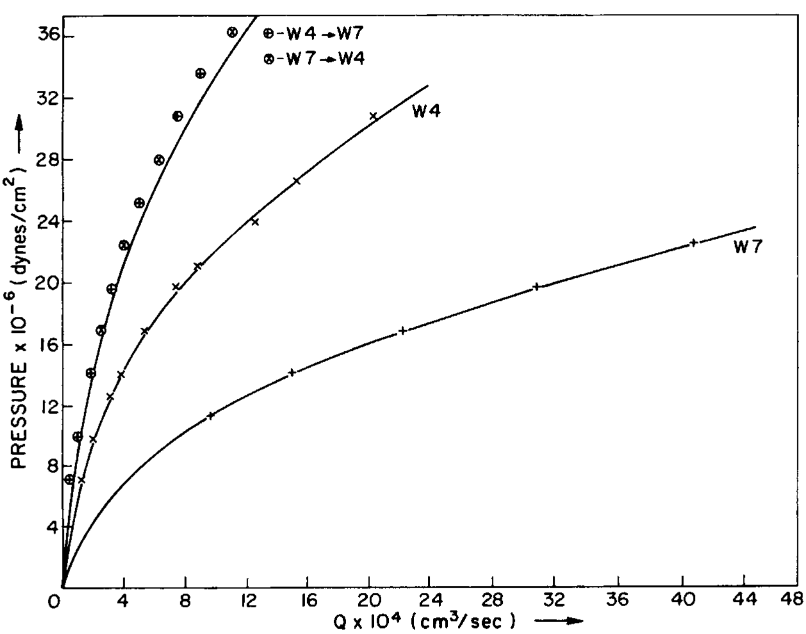

Fig. 3. Pressure drops and corresponding volumetric flow rates (Q) with dies w_4 and w_7 and the combinations w_4–w_7 and w_7–w_4.

applied pressure) varies linearly with the aspect ratio of that die at given apparent shear rate. Application of the Bagley end correction technique to the die combination is not strictly practical because the shear rate in each section of the orifice combination will vary with the cube of each capillary radius. It is useful to note that the total pressure drop can be estimated from end correction plots if the pressure drop for each orifice is taken at the apparent shear rate which pertains in that capillary. This analysis has implications for extrusions with tapered dies,[12] since the pressure drop in the tapered section, which is similar to that in the upper orifice in converging flow in our case, should be subtracted from the total applied pressure whenever the Bagley technique is applied. This procedure agrees in principle with the analysis of converging flow given by Cogswell.[13]

Our observations are consistent with Hyun's[11] analysis of the nature of end corrections in the capillary flow of polystyrene melts. Hyun showed that the pressure correction due to the ends effect obtained by the Bagley graphic procedure is equal to the difference between the hydrostatic pressure drops at the die entrance and at its exit. It was further demonstrated, with a polystyrene similar to the sample used in this study, that the exit pressure (including hydrostatic and deviatoric stress contributions) can be neglected if capillary dies with length/diameter ratios greater than 4 are used. This aspect ratio happens fortuitously to be the lower limit used in our studies.

Equation (1) implies that the shear history of the polystyrene has no effect on its viscous behavior in subsequent flow. This conclusion applies whether the shear history is expressed in terms of total shear[14] or as a function of apparent values of shear stress and shear rate.[15] It will be noted that the melt which was sheared in the upper die was immediately discharged to the bottom die, for further shearing, in contrast to most other studies in which the presheared melt had some opportunity to relax and reentangle before the second extrusion step.[16] The present results agree with the findings of Rudin and Leeder[17] who reported that shear and thermal pretreatment of a similar commercial polystyrene resulted in significant variations in time-dependent flow behavior but not in the equilibrium flow curve.

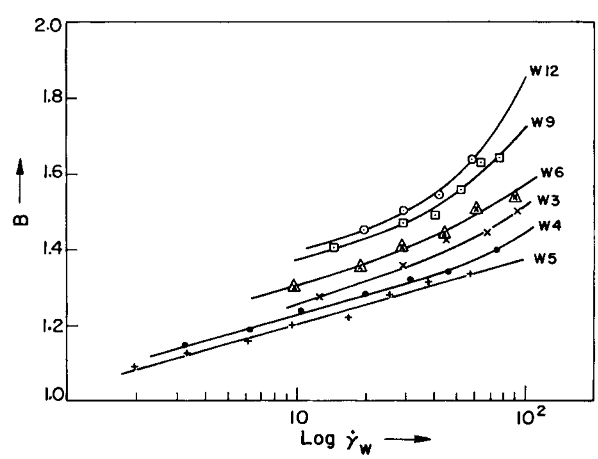

Fig. 4. Die swell B, eq. (2), as a function of shear rate at the die wall.

Melt Elasticity

Elasticity of the polymer melt is manifested in capillary extrusion by the swelling of the extrudate to a larger diameter than that of the orifice. The die swell ratio B is calculated from[5]

$$B = \frac{D_e}{D_c} (\rho V_t)^{1/2} \tag{2}$$

where D_e is the diameter of the extrudate measured at room temperature, D_c is the capillary diameter, ρ is the polymer density at room temperature, and V_t is the specific volume of the polymer melt at the extrusion temperature.

The results of die swell measurements are shown in Figure 4, where B is plotted against the logarithm of the true shear rate at the orifice wall, for single die extrusions. The usual[18] asymptotic trend of decreasing B with increasing L/R would be apparent if a cross plot were constructed.

Figure 5 shows die swell in converging flow into die w_3 and diverging flow into die w_7. Several points should be noted here. The converging flow data show somewhat lower die swells for presheared melt flowing into die w_3. This effect is most noticeable at lower shear rates and vanishes at shear rates near 50 sec^{-1}. These differences are not pronounced since the swelling ratio values are very low in any case.

It has been pointed out that die swell due to melt elasticity is superimposed on the die swell of slow Newtonian flows[19,20] for which $B \sim 1.10$.[21,22] This is the value attained at low shear rates in converging flow into die w_3. It seems likely, then, that the polystyrene used here is not very elastic in the first case and any effects of shear history on melt elasticity will not be pronounced. Within this limit, some effect of shear history on melt elasticity is perhaps indicated in the converging flow data shown in Figure 5. There is no detectable evidence of shear history on die swell in diverging flow into orifice w_7.

It has been suggested[21,22] that the die swell can be represented as

$$B^2 = P_i \exp(-t/\lambda) + 1 \tag{3}$$

where P_i is the stress at the capillary inlet, t is the transit time through the capillary, and λ is a relaxation time. P_i in the bottom die is unaffected by

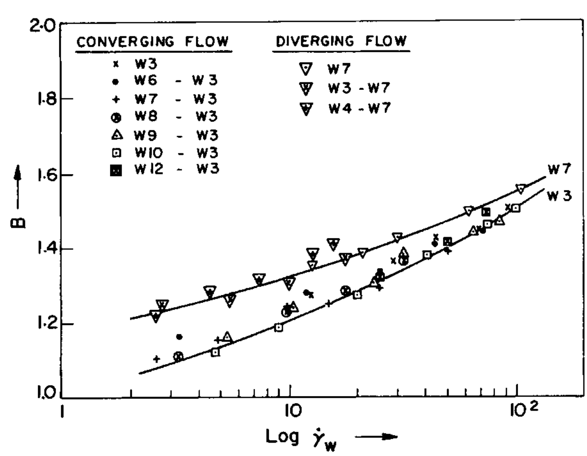

Fig. 5. Die swell in converging flow into capillary w_3 and in diverging flow into capillary w_7.

shear history and t ($= \pi R^2 L/Q$)[14] is fixed at given flow rate and die dimensions. The relaxation time seems to be little affected by shear history with this polymer, and the die swell is therefore not significantly different in flow through single or combined capillaries.

It will be noted, however, that the die swell measured with the die sequence w_3–w_7 in diverging flow is higher than when the same capillaries were used in the reverse sequence.

DISCUSSION

The data obtained reveal no detectable effect on the upper die in combination on viscous behavior and only a slight effect on melt elasticity in converging flow at low shear rates. These results are consistent with the ideas of Schreiber et al.[25] that any change in interchain couplings (as from die transit) will produce proportionately greater changes in melt elasticity than in viscosity.

The slight changes observed in die swell reflect the fact that the melt was not highly entangled in the first place, as evidenced by low B values in single-die extrusion. It is likely that the conclusions of this work will apply to many other commercial thermoplastics in which melt elasticity is not relatively great. Examples would be many branched polyethylenes, polypropylene, and so on. Melt elasticity of linear polyethylene may be expected to be influenced more strongly by shear history, since this material behaves as a relatively more rubbery fluid. Fully fluxed plasticized poly(vinyl chloride) is also probably more sensitive to shear history.[26,27]

With these possible exceptions, the conclusions of this study appear to be generally applicable. Viscoelastic properties of most polymer melts are seen to be single-valued functions of output rate in low shear rate extrusion. Pressure drop across dies is fixed for constant output rate in the sense that Bagley's end correction is valid for converging and diverging flows.

In laminar flow at sufficiently high total shear,[14] intermolecular couplings which existed at the die entrance will have been disrupted, but others may have formed during die transit if the molecular chains are sufficiently mobile. The tendency is toward reduced viscosity and melt elasticity, but the latter phenomena are affected much more strongly since a molecule must be coupled to at least two other polymers to be elastically effective, while a single entanglement will hinder molecular movement.

This study has shown that preshearing of polystyrene in the top die does not alter its flow behavior in the bottom die. In diverging flow, the molecules which emerge from the first capillary seem to be restored to their original rheological state because of the opportunity for reacting and reentanglement in the entrance region of the lower bottom die. In converging flow, it is mainly the melt flowing near the center of the upper die under relatively low shear stresses and total shear which discharges into the bottom die. Hence, the original rheological structure of the polymer may be essentially maintained in both flow modes.

An interesting extension of this work involves a study of other polymers and an investigation of the effects of higher shear stress conditions which may involve extrudate distortion and other melt flow defects. This work is underway.

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