

Measurement of the Rheological Properties of Polymer Melts with Annular Rheometer

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Synopsis

An annular die has been designed having a very thin gap distance between two coaxial cylinders. The die was then used to measure wall normal stresses along the longitudinal direction of polymer melts flowing through the thin annulus. The materials investigated were high-density polyethylene, low-density polyethylene, polypropylene, and polystyrene. Also investigated were blends of polystyrene and polypropylene, and blends of polystyrene and high-density polyethylene. The measurements of wall normal stresses were used to determine the rheological properties of the melts, namely, the melt viscosity from the slope of axial wall normal stress profiles and the melt elasticity from exit pressures. The interpretation of the experimental data was made possible by the fact that the narrow-gap annular die can be considered as a substitute for a thin slit die. It has been found that the results obtained in the present study are consistent with those reported earlier by the author, who at that time used both capillary and slit dies.

INTRODUCTION

In the past, some attempts have been made to use annular flow for determining the rheological properties of polymeric materials.^{1,2} As a continuing effort to develop experimental techniques for determining the rheological properties of polymer melts, the author has recently constructed an annular die with a very thin annulus. The primary motivation of the die design was to study the blown film extrusion process. An interesting feature of the annular die, as a rheometer, is the simplicity of data analysis. That is, the flow data obtained from the geometry of a narrow-gap annular die can be treated by essentially the same procedure as that obtained from the geometry of a thin slit die.^{3,4}

The purpose of this paper is to present some recent experimental data on both the viscous and elastic properties of polymer melts (homopolymers and blends) obtained from the newly designed thin slit annular die. For the study, measurements were taken of wall normal stresses along the longitudinal direction of polymer melts flowing through the thin annular slit. The measurements of wall normal stress were used to determine the melt viscous property from the pressure gradient and the melt elasticity from exit pressures.

EXPERIMENTAL

Apparatus and Experimental Procedure

The main features of the apparatus and the operating procedures are similar to those described in the author's earlier publications^{3,5,6} for capillary and slit dies, except for the design of the annular die itself. The annular die used for the experiment is made of cold-drawn steel, and its details of construction are given in Figure 1, which shows the axial positions of the pressure tap holes and other dimensions of the die. Four pressure tap holes are located on 90° centers at distances sufficiently far from the entrance of the straight annular section so that measurements of wall normal stresses can be taken in the fully developed region.

In order to uniformly distribute polymer melt into the annular space, the feed stream flowing from the extruder is split into two lines and then fed

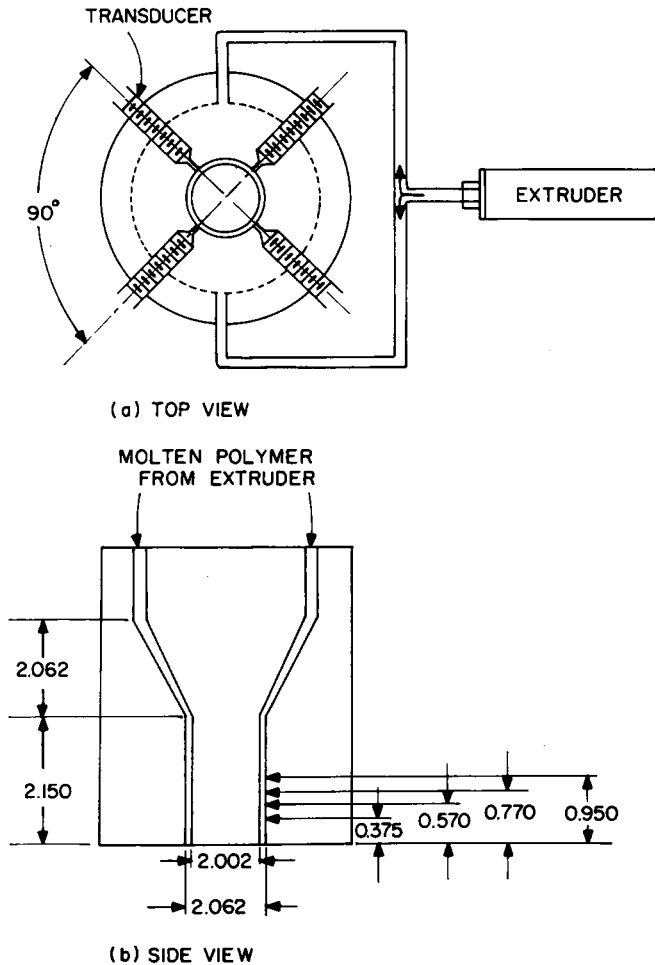


Fig. 1. Schematic of the annular die design.

into the upper straight annular section at two diametrically opposite points (see Fig. 1a). The melt then flows into the lower straight annular section via the converging section. The converging section was provided to ensure the uniform distribution of the melt before it enters the lower straight annular section. Wall normal stresses are measured with Dynisco melt pressure transducers. The entire system is electrically heated and heavily insulated. Other auxiliary equipment and details of the operating procedures are as described in previous publications.^{3,5,6}

Materials

The homopolymers used for the present study were high-density polyethylenes (Union Carbide, DMDJ 4309), low-density polyethylene (Union Carbide, DYNF-1), polypropylene (Enjay Chemical, Resin E115), and polystyrene (Dow Chemical, Styron 686). For studying the behavior of blend systems, blends of polystyrene and polypropylene and of polystyrene and high-density polyethylene were prepared. This was done by mixing two polymers, in the form of pellets, in a tumbling operation, using blending ratios of 20–80, 50–50, and 80–20 wt-%.

RESULTS AND DISCUSSION

Homopolymers

Figure 2 shows typical axial pressure profiles for low-density polyethylene at two different shear rates. It is seen that the pressure profiles become linear in the interval where measurements were taken and that extrapolating the last pressure measurement to the die exit gives rise to a positive non-zero pressure which has been called the "exit pressure."^{3,5,6}

The working equations for the thin slit *annular* die to be used are essentially the same as those for the thin slit *flat* die with the substitution

$$\left. \begin{aligned} h &= R_2 - R_1 \\ w &= \pi(R_1 + R_2) \end{aligned} \right\} \quad (1)$$

where R_1 and R_2 are radii of the inner and outer cylinders, respectively. Earlier, Han^{3,4} used the following expressions for constructing flow curves from slit die data:

$$\tau_w = \left(-\frac{\partial p}{\partial x} \right) \frac{h}{2} \quad (2)$$

$$\dot{\gamma} = \left(\frac{2n+1}{3n} \right) \frac{6Q}{wh^2} \quad (3)$$

where τ_w denotes the true wall shear stress, $-\partial p/\partial x$ is the pressure gradient, $\dot{\gamma}$ is the true wall shear rate, Q is the volumetric flow rate, and n is defined by

$$n = \frac{d \ln (\tau_w)}{d \ln \left(\frac{6Q}{wh^2} \right)} \quad (4)$$

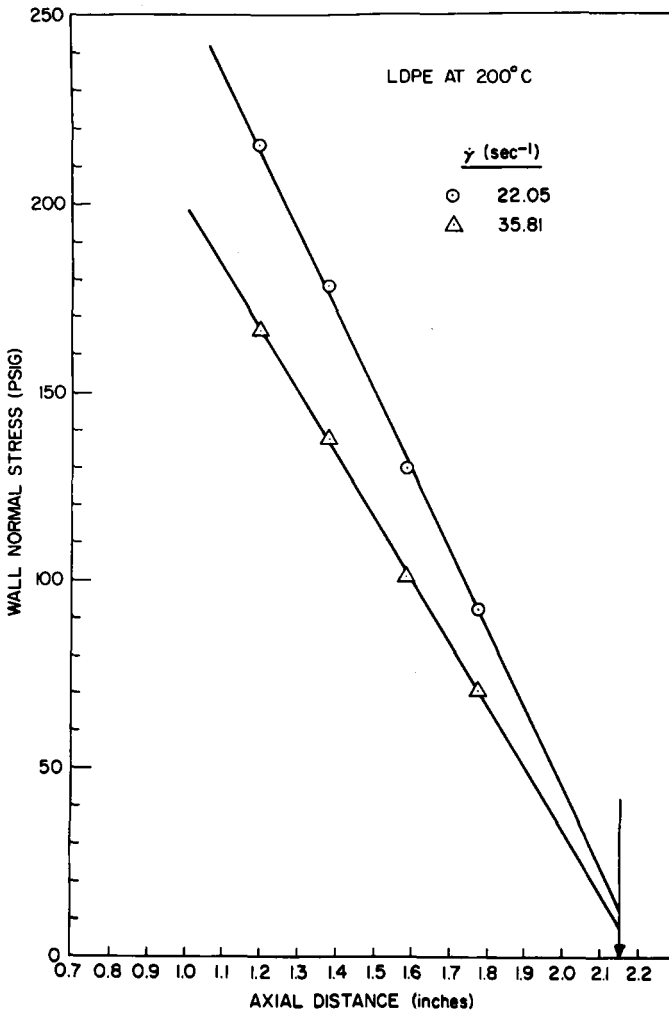


Fig. 2. Representative axial pressure profiles for low-density polyethylene at 200°C.

It should be noted that, in order to have eqs. (2) and (3) applicable to the annular die, the ratio of w to h defined in eq. (1) should be sufficiently large. Earlier, Wiley and Pierce¹ reported that $w/h \geq 48.5$ was satisfactory. The ratio of w to h for the annular die used in the present study is 213, which is believed to be sufficiently large for the use of eqs. (2) and (3), with the aid of eq. (1).

Figure 3 shows plots of viscosity versus shear rate for the four homopolymer samples employed, the values plotted being determined from the ratio of eq. (2) to eq. (3), i.e.,

$$\eta = \tau_w / \dot{\gamma}. \quad (5)$$

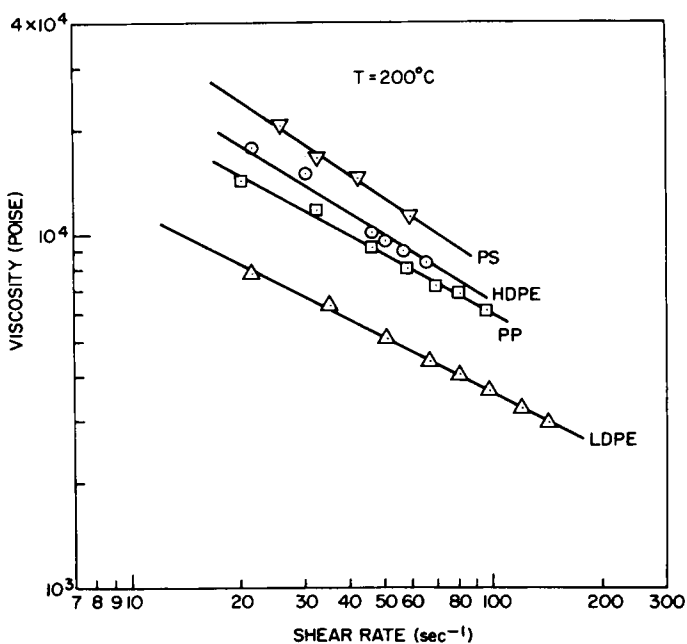


Fig. 3. Viscosity vs. shear rate for homopolymers ($T = 200^{\circ}\text{C}$).

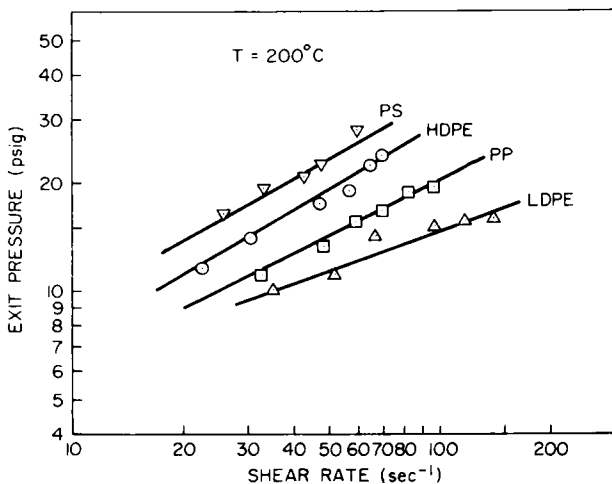


Fig. 4. Exit pressure vs. shear rate for homopolymers ($T = 200^{\circ}\text{C}$).

It is seen that the materials tested were in the power law region, a result which is consistent with the ones reported earlier obtained by the use of slit dies³ and capillary dies.⁶

Figure 4 shows plots of the exit pressure versus shear rate for the four homopolymer samples employed. It is seen that the exit pressure increases with shear rate, consistent with previous results obtained with both slit and

capillary dies.^{3,5,6} At this point readers should be reminded that the exit pressure is a manifestation of elastic behavior and that the exit pressure may be used to determine normal stress differences.⁷

Polymer Blends

Similarly to the homopolymers, axial pressure profiles were also obtained for the two polymer blend systems investigated, namely, polystyrene with polypropylene and polystyrene with high-density polyethylene. Space limitation here does not permit us to present those results. However, we shall discuss below the effects of blending ratio on both the viscous and elastic properties of blend systems.

Figure 5 shows plots of melt viscosity versus wt-% of polystyrene for blends of polystyrene and polypropylene, and Figure 6, plots of melt viscosity versus wt-% of polystyrene for blends of polystyrene and high-density polyethylene. It is interesting to observe in Figures 5 and 6 that melt viscosity goes through a minimum at a certain blending ratio. Similar

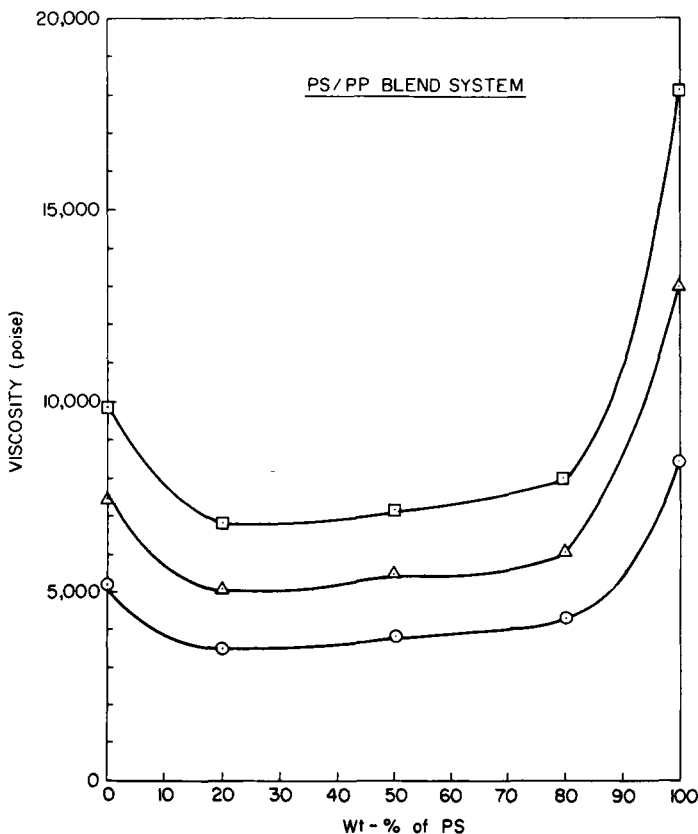


Fig. 5. Viscosity vs. blending ratio for polystyrene/polypropylene blend system: (□) $\dot{\gamma} = 30 \text{ sec}^{-1}$; (△) $\dot{\gamma} = 50 \text{ sec}^{-1}$; (○) $\dot{\gamma} = 100 \text{ sec}^{-1}$.

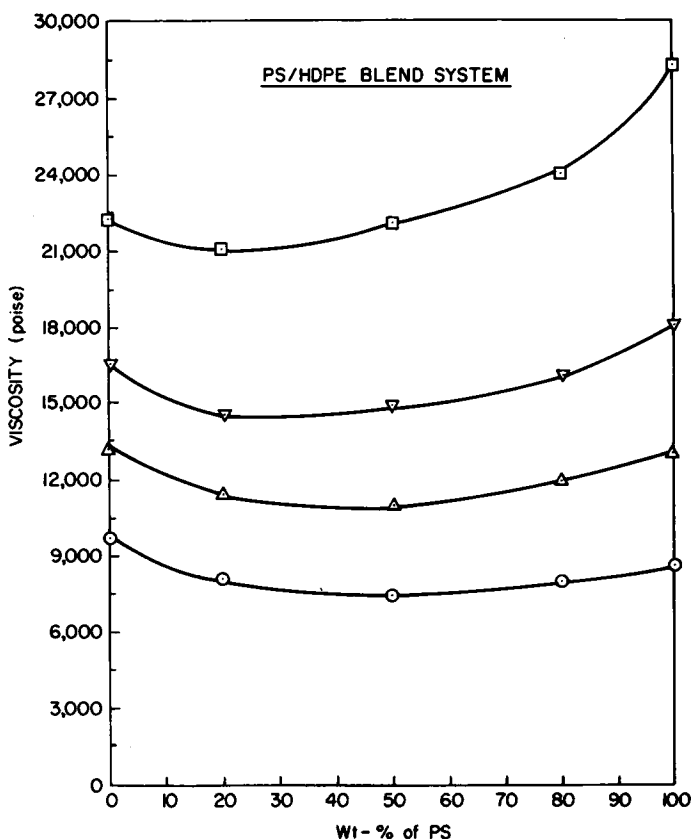


Fig. 6. Viscosity vs. blending ratio for polystyrene/high-density polyethylene blend system: (□) $\dot{\gamma} = 15 \text{ sec}^{-1}$; (▽) $\dot{\gamma} = 30 \text{ sec}^{-1}$; (△) $\dot{\gamma} = 50 \text{ sec}^{-1}$; (○) $\dot{\gamma} = 100 \text{ sec}^{-1}$.

observations were also reported in the author's previous papers which dealt with the same blend systems as those used in the present study, but using slit dies⁸ and capillary dies.^{9,10}

Figure 7 shows plots of exit pressure versus wt-% of polystyrene for blends of polystyrene and polypropylene, and Figure 8, plots of exit pressure versus wt-% of polystyrene for blends of polystyrene and high-density polyethylene. It should be noted that the parameter used in the plots of Figures 7 and 8 is shear stress instead of shear rate, for the reasons given in previous papers of Han.^{9,10} The apparently "anomalous" elastic behavior of the blend systems investigated in the present study has also been reported in previous papers of Han.^{8,9,10} We call the observed behavior anomalous in the sense that the observed viscosity and elasticity of the blends do not appear to obey any simple "law of additivity" in terms of blending ratios and the rheological properties of the individual components involved.

As repeatedly demonstrated in previous papers,^{8,9,10} the blend systems employed in this study form two phases in the molten state. Namely, the more viscous component forms a discrete phase and is suspended in the less viscous component which forms a continuous phase. The discrete phase

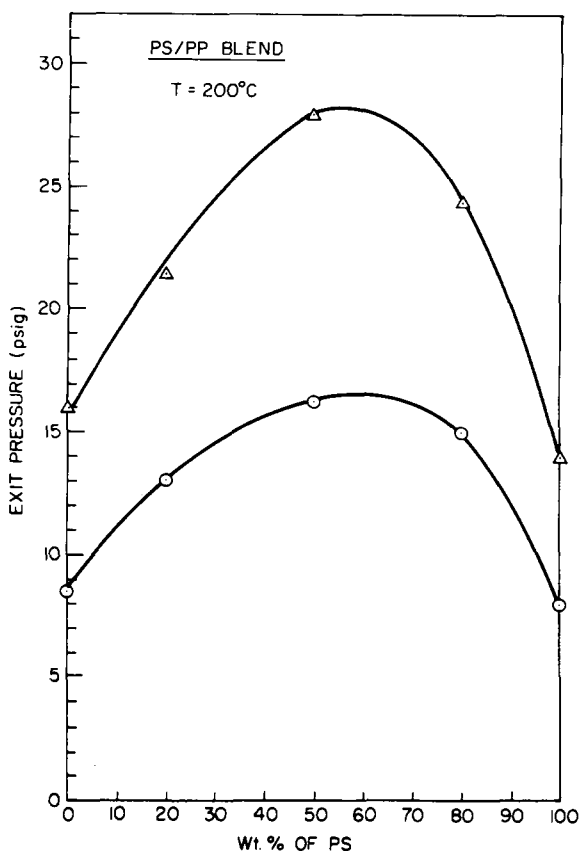


Fig. 7. Exit pressure vs. blending ratio for polystyrene/polypropylene blend system
 (Δ) $\tau_w = 4.83 \times 10^6$ dynes/cm²; (○) $\tau_w = 2.72 \times 10^6$ dynes/cm².

remains as either droplets or long fibrils and is deformable under the flow field concerned. It is therefore quite conceivable that a part of the energy supplied to the bulk of the fluid in motion might have been consumed in deforming the suspended droplets and/or long fibrils. Hence, the overall effective pressure drops experimentally observable could be less in a two-phase system than in a single-phase system. The reduction in effective pressure drops is reflected in Figures 5 and 6, which show that the shear viscosity of the blends is lower than those of the individual components.

Since the individual components of the two-phase systems investigated have an elastic property, they recover a part of the energy which was initially put into the material. Now, it may be the case that the discrete phase (i.e., the suspended medium) can recover a larger fraction of the energy initially put into it than the continuous phase (i.e., the suspending medium). Clearly, the suspended medium needs only to be deformed without actually contacting the die wall, whereas the suspending medium contacts the die well and hence must consume a part of the energy initially

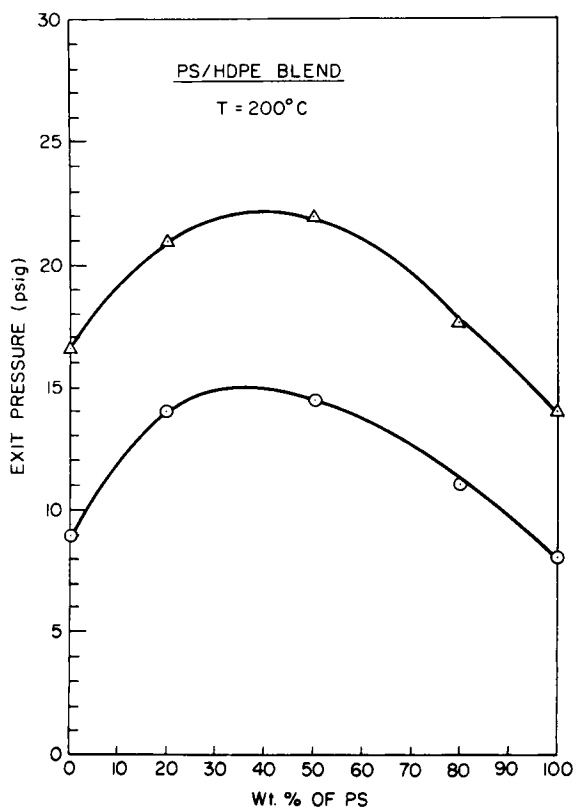


Fig. 8. Exit pressure vs. blending ratio for polystyrene/high-density polyethylene blend system: (Δ) $\tau_w = 4.83 \times 10^6$ dynes/cm²; (\odot) $\tau_w = 2.72 \times 10^6$ dynes/cm².

supplied to it in overcoming the frictional force at the die wall. Based on this concept, the maximum exit pressure at a certain blending ratio shown in Figures 7 and 8 is explainable. In other words, the extent of the recovery of elastic energy would be greater in a two-phase polymer system than in a single-phase system.

It should be noted, however, that the attempt made above at explaining the "anomalous" viscoelastic behavior of two-phase polymer systems is a tentative one, and hence a qualitative one. At present, a study is underway to explain the situation quantitatively and will be reported in a future publication.

Lastly, it should also be mentioned that the blending method is believed to play an important role in determining the viscoelastic properties of incompatible polymer systems. This is because the state of dispersion (e.g., the size and distribution of droplets and/or long fibrils suspended in the continuous phase) is strongly influenced by the method of blending. In the future, we shall report the effect of blending method (and hence of the state of dispersion) on the viscoelastic properties of incompatible polymer systems.

CONCLUSIONS

The rheological properties of four homopolymers and two blend systems have been determined by using a newly constructed annular die having a narrow gap width between the two cylinders. The present study has yielded results very similar to those obtained earlier by the author, using slit and capillary dies. The agreement between the present and earlier studies leads us to believe that the experimental technique employed has a practical value for determining the viscoelastic properties of polymer melts at the range of shear rates that is of industrial importance to many polymer operations.

A qualitative explanation is presented to explain the experimentally observed viscoelastic behavior of two-phase polymer systems. Future study will be directed to investigating quantitatively the effect of the state of dispersion on the rheological properties of incompatible polymers in the molten state.

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