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Measurement of the Rheological Properties of Polymer Melts with Slit Rheometer. I. Homopolymer Systems

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Synopsis

Two slit dies have been designed, having aspect ratios of 10 and 20. Three melt pressure transducers were flush-mounted on the long side of the rectangular slot, along the longitudinal centerline of each die. The dies were then used to measure wall normal stresses along the longitudinal direction of polymer melts flowing through the thin slit. The polymeric materials investigated were high-density polyethylene, low-density polyethylene, polypropylene, and polystyrene. The measurement of wall normal stresses were used to determine the rheological properties of melts, namely, the melt viscosity from the slope of axial pressure profiles and the melt elasticity from exit pressures. The present study shows that the rheological properties determined from the slit rheometer are in good agreement with those from the capillary rheometer reported in the author's earlier papers. Therefore it may be concluded that a slit die also may be used as a means of characterizing polymeric materials by their viscous and elastic properties in the molten state.

INTRODUCTION

Extensive use has been made of the capillary rheometer to determine the rheological properties of viscoelastic fluids, for instance, polymer melts. One of the advantages of using the capillary rheometer is the facility of analyzing its experimental data, because the theoretical development of the flow problems associated with a circular tube has been well advanced.

Another geometry which is considered to be equally as simple as the capillary rheometer is the system of two parallel plates of infinite width. Since plates of infinite width are not obtainable in practice, the geometry of a rectangular cross section having a large aspect ratio (the ratio of long side to short side) can be considered as a substitute. The flow can then be treated as one-dimensional instead of two-dimensional. To illustrate this, Figure 1 shows isovels, contour lines connecting points having the same velocity, in a thin slit having a large aspect ratio. It is seen from the figure that the isovels are parallel to the long sides over most of the width of the rectangle and that for all practical purposes one can treat the flow as one-dimensional. Therefore the analysis of the flow data obtained from the geometry of a thin slit becomes very much simplified. Use of this concept was made by

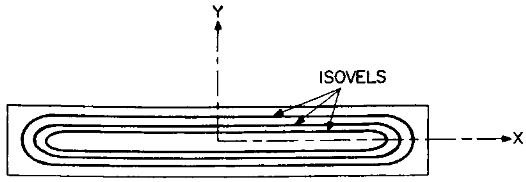

Fig. 1. Schematic representation of isolvels in a thin slot.

Eswaran et al.[1] and Wales et al.[2] for the measurement of the rheological properties of polymer melts.

It is to be noted, however, that as the aspect ratio becomes small, say less than 10, the flow in a rectangular duct must be treated as two-dimensional, which makes the analysis much more complicated. The analysis becomes even more complicated when one attempts to use viscoelastic models. This is a main reason why very little theoretical work has been done on two-dimensional flow problems of viscoelastic fluids.

Recently, Han[3,4] has studied the flow of polymer melts in rectangular ducts of small aspect ratio. Han's objective was primarily to prove the existence of the "exit pressure" in rectangular ducts from the measurements of wall normal stress distributions along the axis of the duct. He then proceeded to give rheological interpretations to the "exit pressure" with additional measurements of extrudate swelling.

It is the purpose of this paper, the first of this series, to present a method for determining the rheological properties of polymer melts by using a newly constructed slit rheometer. Slit rheometer data have been found to be in good agreement with capillary rheometer data.

EXPERIMENTAL

Two slit dies are constructed, made of aluminum. Each of these dies has three pressure tap holes along the axis of longitudinal direction. The

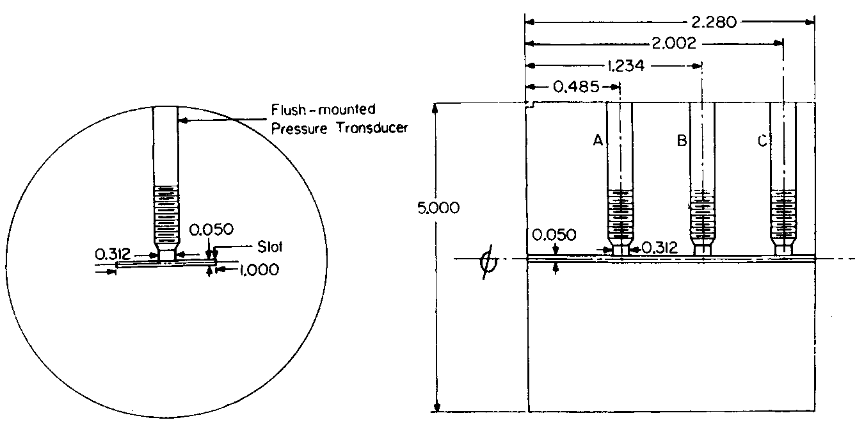

Fig. 2. Detailed design of slit die 2.

dimensions of the slot and the positions of pressure transducers in each slit die are given in Table I. The melt pressure transducers are *mounted flush* with the slot wall, as shown in Figure 2.

TABLE I
Dimensions of Slit Dies and Locations of Pressure Transducers

	Slit die 1	Slit die 2
Length of die L, in.	3.280	2.280
Slit thickness h, in.	0.100	0.050
Slit width w, in.	1.000	1.000
Aspect ratio w/h	10	20
Location of pressure transducer from die inlet, in.		
A	0.999	0.485
B	1.999	1.234
C	2.999	2.002

The slit die section is attached to a reservoir section which has a flow channel 1.125 in. in diameter and 10 in. long. The reservoir channel is connected to the outlet of the extruder. Both the reservoir and die sections are electrically heated and heavily insulated to prevent heat loss. Other

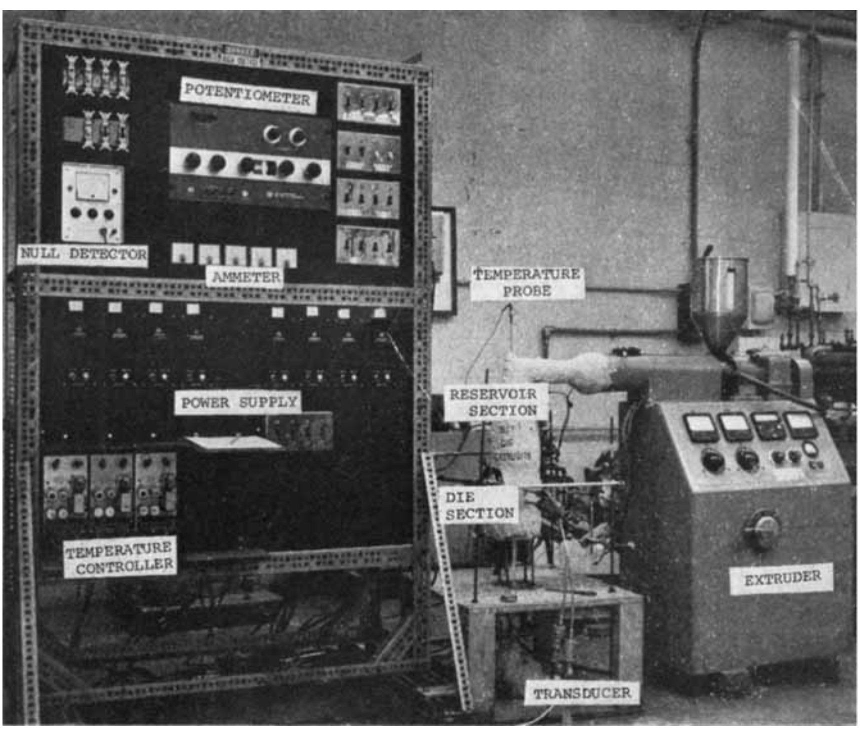

Fig. 3. Experimental apparatus.

auxiliary equipment are shown in Figure 3, and details of the operating procedures are as described in the author's earlier publications.[5,6]

The materials used for the present study were: two high-density polyethylenes (Union Carbide Corp., DMDJ 4309 and DGNB 3825), polypropylene (Enjay Chemical Company, Resin E115) with melt index 5.0, low-density polyethylene (Union Carbide Corp., PEP211) with melt index 3.5, and general-purpose polystyrene (Dow Chemical Company Styron 686).

RESULTS AND DISCUSSION

Pressure Profiles

Representative plots of the axial pressure profiles are given in Figure 4 for DMDJ 4309 at 200°C, with the shear rate as a parameter. Similar plots were obtained for four other polymer melts investigated. The following observations can be made from these plots: (a) The pressure gras dient becomes constant within the length of the die in which measurementwere taken, showing that fully developed flow is achieved. (b) The pressure gradients are clearly dependent upon the flow rate and hence dependent upon shear rate. (c) Nonzero "exit pressures" are obtained, which are de-

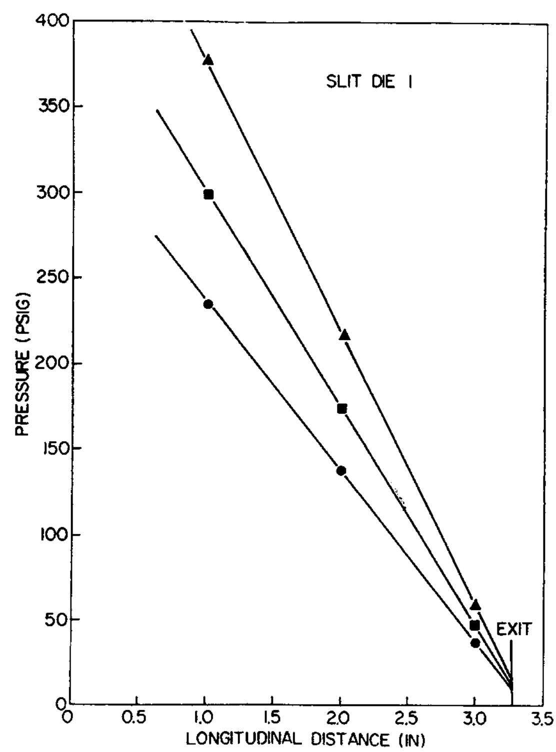

Fig. 4. Representative axial pressure profiles for high-density polyethylene (DMDJ 4309) at 200°C: (▲) $\dot{\gamma}$ = 74.74 sec^{-1}; (■) $\dot{\gamma}$ = 40.36 sec^{-1}; (●) $\dot{\gamma}$ = 21.67 sec^{-1}.

pendent upon shear rate. The "exit pressure" here is defined as the pressure obtained by extrapolating pressure readings to the exit of the duct. Note that the above observations are consistent with the author's previous results obtained from a capillary rheometer.[5–7]

At this point, it seems proper to make some comments on the work of Eswaran et al.[1] and Wales et al.,[2] who several years ago made pressure profile measurements with slit dies. The authors assumed that there should be no "exit pressures" when the melt is discharged into the open air. In fact, Eswaran et al.[1] took only two pressure measurements in the axial direction, one near the entrance of the duct and another near the end of the duct. These authors discarded their measurements near the end of the duct because of some uncertainties involved in their measurements and used only a single measurement taken near the entrance of the duct to obtain flow curves. Wales et al.[2] essentially repeated the work of Eswaran et al.[1] with an additional pressure measurement in the middle of the longitudinal axis of the slit die.

It is important to note, however, that the previous work by Han has shown the existence of the "exit pressure" in flow through a circular tube[5–7] and in flow through a rectangular duct of small aspect ratio.[3,4] In view of the work referred to above and the results of the present study, the assumption regarding the "exit pressure" made by Eswaran et al.[1] and Wales et al.[2] is believed to be unjustified.

Viscous Properties of Melts

The wall shear stress τ_w in a slit die may be given by

$$\tau_w = -\frac{\partial p}{\partial x}\frac{h}{2} \tag{1}$$

where $-\partial p/\partial x$ is the pressure gradient along the axis (in the region where flow is fully developed) and h is the slit thickness (short side of rectangle). The apparent shear rate $\dot{\gamma}_w$ may be defined by

$$\dot{\gamma}_w = \frac{6Q}{wh^2}, \tag{2}$$

and the true wall shear rate $\dot{\gamma}$ with Rabinowitch correction may be written as

$$\dot{\gamma} = \dot{\gamma}_w\left[\frac{2}{3} + \frac{1}{3}\frac{d\ln\dot{\gamma}_w}{d\ln\tau_w}\right]. \tag{3}$$

One can then construct flow curves (plots of shear stress versus shear rate) from the measurements of the pressure gradient $-\partial p/\partial x$ and the volumetric flow rate Q.

Figure 5 shows flow curves of five polymer melts at 200°C. It is seen that the materials can be described by a power law relation over the range of shear rates studied:

$$\tau_w = K\dot{\gamma}^n. \tag{4}$$

One can then plot the melt viscosity against shear rate, as shown in Figure 6. It is seen from Figure 6 that the materials investigated are in the non-Newtonian flow regime over the range of shear rates studied.

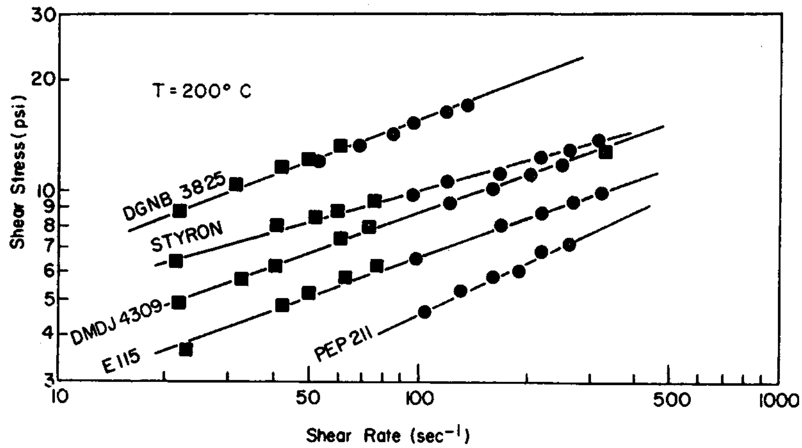

Fig. 5. Shear stress vs. shear rate: (■) slit die 1; (●) slit die 2.

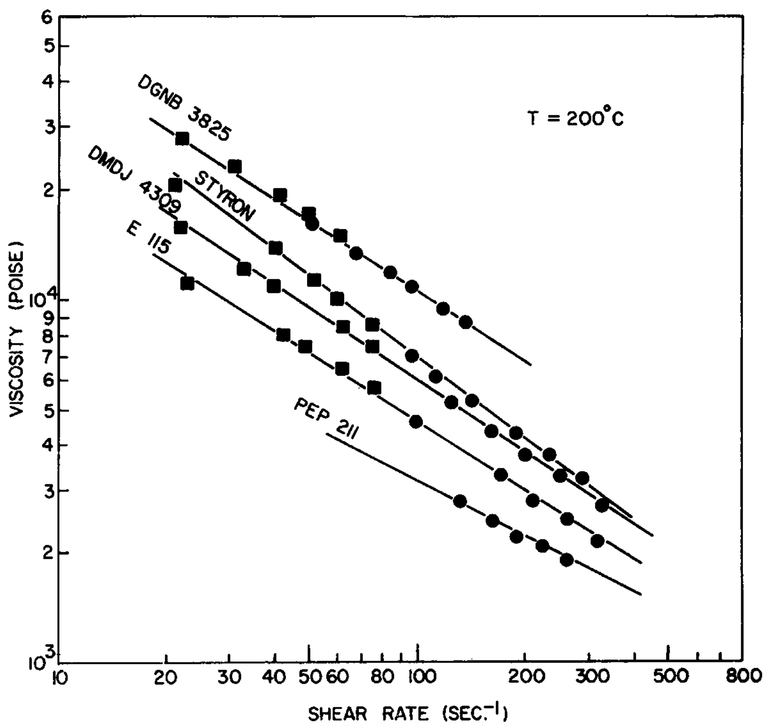

Fig. 6. Melt viscosity vs. shear rate: (■) slit die 1; (●) slit die 2.

It is to be noted that the same materials have already been studied[6] with a capillary rheometer, in which a power law relation was also found to hold.

Elastic Properties of Melts

As may be seen from Figure 4, the exit pressures increase as shear rate is increased. It may be best seen from Figure 7, in which plots of the exit pressure versus shear rate are shown for the materials investigated. From the plots, one can see that a power law relation holds:

$$P_{\text{exit}} = \alpha \dot{\gamma}^{\beta} \quad (5)$$

in which P_{exit} denotes the exit pressure and α and β are constants characteristic of the material.

According to Han,[5–7] the exit pressure is approximately equal to the normal stress difference, $(P_{11} - P_{22})$, for polymer melts, that is,

$$(P_{11} - P_{22})_L = P_{\text{exit}}. \quad (6)$$

Equation (5) may then be rewritten as

$$(P_{11} - P_{22})_L = \alpha \dot{\gamma}^{\beta}. \quad (7)$$

It may be seen easily from Figure 7 that the materials give rise to the value of β much less than 2.0, indicating that the polymer melts do not obey the second-order approximate constituitive equations over the range of shear rate studied.

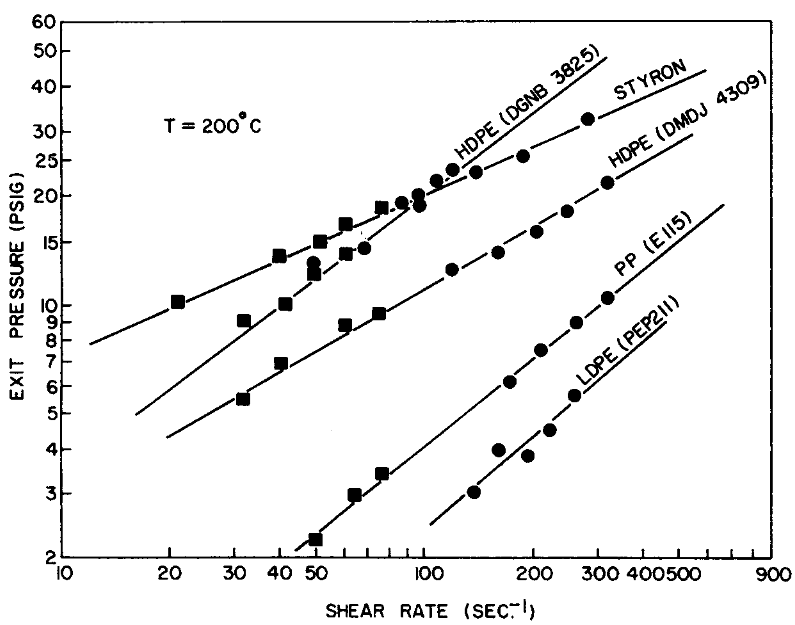

Fig. 7. Exit pressure vs. shear rate: (■) slit die 1; (●) slit die 2.

It is very important to realize the significance of the correlation given by eq. (7), because one now has a method for determining the elastic properties of polymer melts, as well as the viscous properties, from measurements of pressure profiles alone in a slit rheometer.

Comparison of Slit with Capillary Rheometer Data

Having presented the experimental data of slit rheometer, we shall compare these data with the capillary rheometer data obtained earlier by the author.[6] This comparison will serve two important purposes. First, one can see if indeeded the flow in a slit die with a large aspect ratio can reasonably be approximated as one-dimensional flow. Secondly, one can see if there is any significant "pressure hole" effect.[8,9] Note that all the measurements with circular dies[5-7] were obtained with pressure tap holes 0.039 in. in diameter and 0.25 in. long, connecting the capillary wall with the tip of the pressure transducer.

In Figures 8 and 9 are shown capillary rheometer data together with slit rheometer data. It is seen that the agreement is remarkably good, serving two purposes referred to above. In other words, the agreement of the data obtained from two sources, which have entirely different features of die design, indicates that the slit die used for the present study can be con-

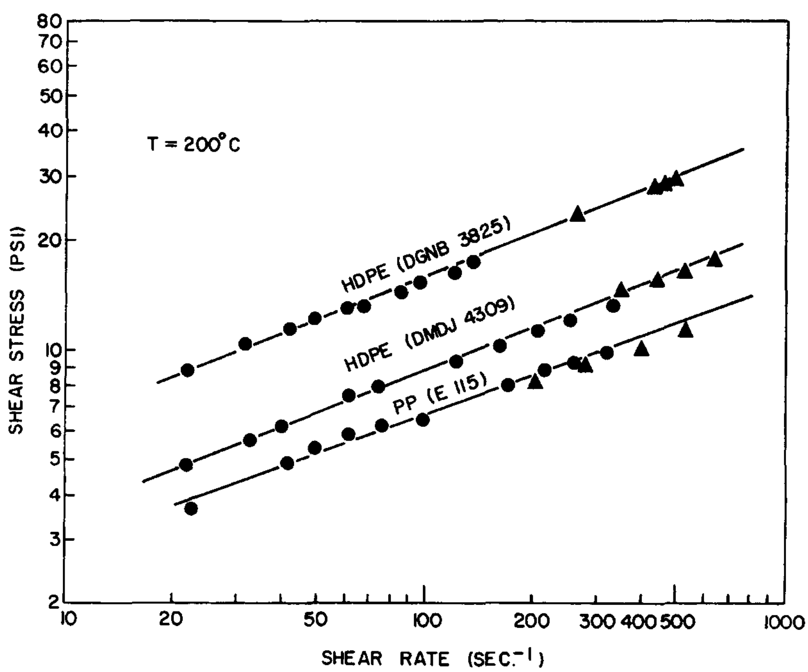

Fig. 8. Shear stress vs. shear rate: (●) slit rheometer data; (▲) capillary rheometer data (Han et al.[6]).

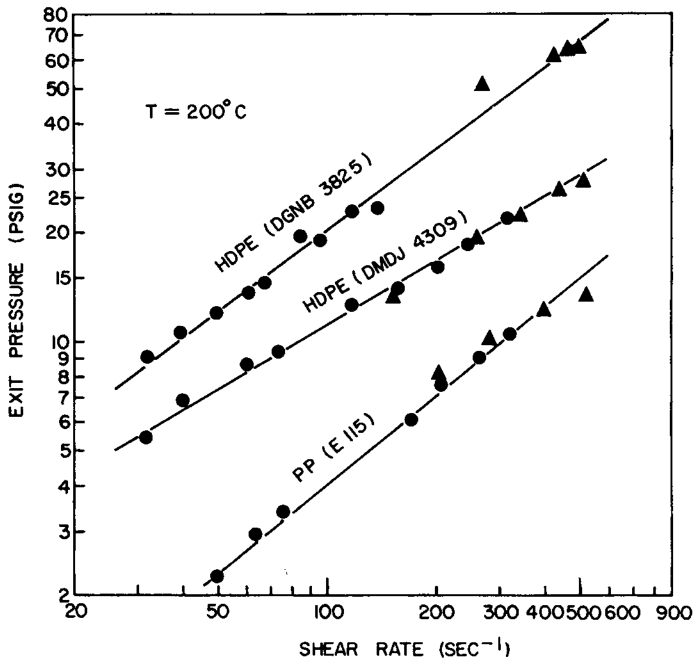

Fig. 9. Exit pressure vs. shear rate: (●) slit rheometer data; (▲) capillary rheometer data (Han et al.[6]).

sidered as equivalent to a circular die so far as flow regime is concerned and that there is no "pressure hole" effect, at least for the materials studied.

A Criterion for Evaluating the Relative Elasticity of the Materials

It is well known that both viscous and elastic properties depend on melt temperature. Figure 10 shows plots of exit pressure versus shear rate for two high-density polyethylenes at 200°C and 240°C. Note that DMDJ 4309 has a polydispersity of 84, whereas DGNB 3825 has a polydispersity of 16 (see Table II of ref. 6 for molecular characteristics). One may note from Figure 10 that the exit pressure, hence the melt elasticity, decreases as the melt temperature is increased and that the magnitudes of the exit pressures of DGNB 3825 are higher than those of DMDJ 4309 over the range of shear rate investigated at 200°C and 240°C. One might be therefore tempted to draw the conclusion that DGNB 3825 is more elastic than DMDJ 4309. However, such a conclusion may be drawn properly only if a plot can be prepared that is independent of melt temperature.

Earlier, Han[10] has suggested to plot exit pressure against shear stress, as shown in Figure 11. The plots are free of temperature dependence, and it can be seen that the magnitude of the exit pressure of DMDJ 4309 is higher than that of DGNB 3825 over the range of shear stress investigated.

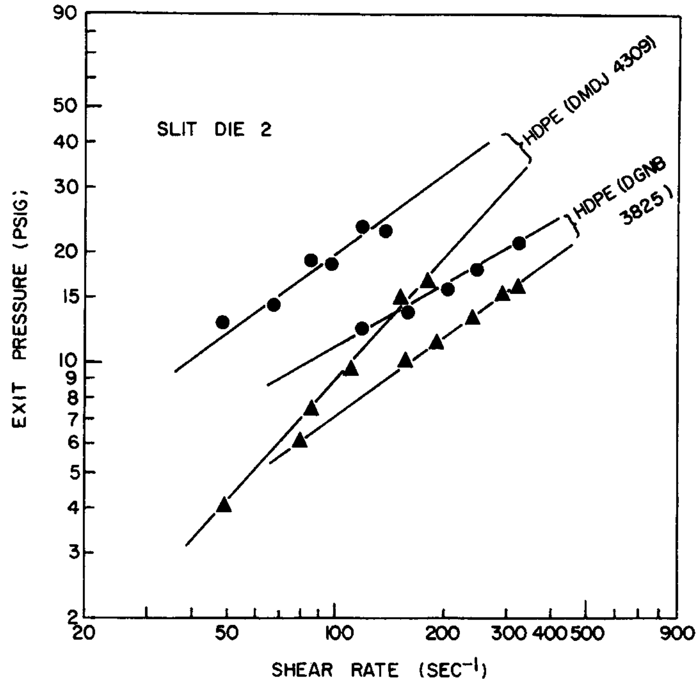

Fig. 10. Plots of exit pressure vs. shear rate: (●) 200°C; (▲) 240°C.

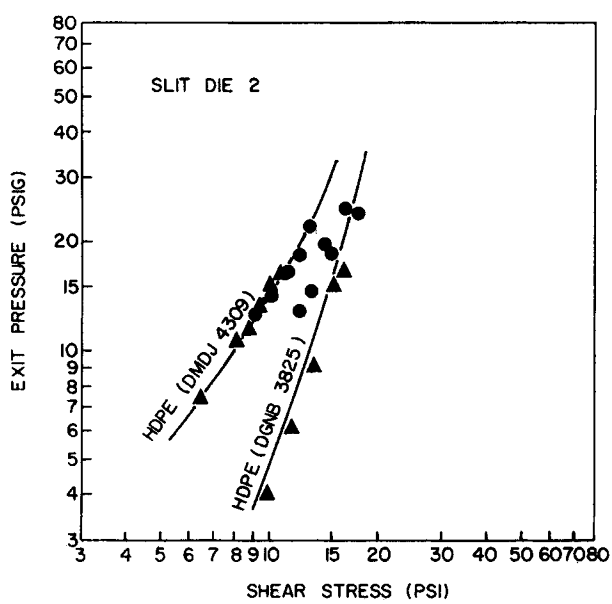

Fig. 11. Plots of exit pressure vs. shear stress: (●) 200°C; (▲) 240°C.

Since the exit pressure represents the elastic property of the materials, it can thus confidently be said the DMDJ 4309 is more elastic than DGNB 3825. Furthermore, from a standpoint of molecular structure, Figure 11 appears to indicate that the broader the molecular weight distribution of the material, the more elastic the material is. This conclusion is in conformity with that given by Guillet et al.[11] and Combs et al.,[12] who made the study of melt recovery of samples of widely different molecular weight distribution. A similar conclusion has been drawn in the author's earlier work[6] based on capillary rheometer data. Hence the plots of exit pressure versus shear stress are very useful for evaluating the relative melt elasticity of various polymeric materials.

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