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Rheological Properties of Molten Polymers. I. Homopolymer Systems

CHANG DAE HAN, THOMAS C. YU, and KWANG UNG KIM,
Department of Chemical Engineering,
Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

Synopsis

Experimental work has been carried out to investigate the influence of molecular weight distribution and long chain branching on both viscous and elastic properties of molten polymers, using a capillary rheometer, as described in a recent paper by Han. The materials used for the study are three high-density polyethylene samples of widely different molecular weight distributions and a low-density polyethylene containing much long-chain branching. For the analysis of the experimental data, and to obtain the information on the melt elasticity, the concept of the exit pressure recently advanced by Han is used. The study shows that the sample containing long-chain branching is much more elastic than the samples containing little or no long-chain branching, and that the broader the molecular weight distribution of the material, the more elastic the material is. These findings are in conformity with those reported in the literature. Also studied were blends of two high-density polyethylenes having widely different molecular weight distributions. The results of the blend systems show a maximum in melt viscosity as well as in elasticity for a certain blending ratio. The results of the present study may be of considerable interest to those who are concerned with modifying the structure of polymer and also with determining optimum processing conditions.

INTRODUCTION

It is generally understood that the rheological properties of molten polymers are influenced by the molecular weight, molecular weight distribution, and the degree of long-chain branching. A better understanding of the relationships between molecular structure and rheological properties is very important from the standpoints of both polymer preparation and polymer processing. However, the theoretical development of this aspect of the problem is far from complete, though some progress has been made in recent years.[1-4]

Some experimental studies[5-10] have been reported in which the effect of chain branching on the rheological properties was investigated. Bagley[5,6] found that branched polyethylene has much higher values of end correction compared to those for linear polyethylene and that branched polyethylene exhibits a more pronounced melt elasticity than linear polyethylene. Guillet et al.[7] reported that fractions with a high degree of long-chain branching have high die swell, while linear polyethylene fractions have a

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relatively low die swell, which is independent of molecular weight over the wide range tested. However, very few quantitative measurements of melt elasticity for branched polymers have been reported in the literature. Some experimental studies[9-12] have also been reported on the effects of molecular weight and molecular weight distribution on the melt elasticity. Guillet et al.[11] and Combs et al.[12] reported that melt recovery (which essentially means die swell) increases as the molecular weight distribution broadens. These authors also found that the flow index n in the power law model decreases as the molecular weight distribution broadens. It should be noted, however, that the experimental technique adopted by these authors yields qualitative, but not quantitative, information.

In the present series of papers, we shall present a systematic investigation of the rheological properties of various polymeric systems, such as homopolymer systems, two-phase (incompatible) systems, plasticized polymer systems, etc., with particular emphasis on the melt elasticity. Throughout the series, the concept of the "exit pressure" will be used for analyzing the experimental data so far as the melt elasticity is concerned. The purpose of the present paper, the first of the series, is to present some new experimental data on the rheological properties of three high-density polyethylenes, a low-density polyethylene, and three blends of two high-density polyethylenes.

EXPERIMENTAL

Apparatus and Experimental Procedure

The apparatus used in the present study is essentially the same, except for a few changes, as that described in a previous paper.[13] In Figure 1 are shown the detailed layouts of the four basic dies, A1, A2, A3 and A4, with axial positions of pressure tap holes located. For each die, pressure tap holes are on 60° centers. Table I gives the dimensions of the dies and the combinations which provide the L/D ratios, 4, 8, 12, 16, 20, and 24. It is to be noted that dies A2 and A4 are extension sections (see Fig. 1b and 1d)

TABLE I
Dimensions of Capillary Dies

Die[a]	Diameter, in.	Length, in.	L/D ratio
A1	0.125	0.500	4
A2	0.125	2.000	16
A3	0.125	1.000	8
A4	0.125	1.000	8
A1 + A4	0.125	1.500	12
A3 + A4	0.125	2.000	16
A1 + A2	0.125	2.500	20
A3 + A2	0.125	3.000	24

[a] Dies A1 and A3 are the head die sections which contain a part of the reservoir section. Dies A2 and A4 are the extension sections which have to be used with either dies A1 or A3, depending on the desired L/D ratio.

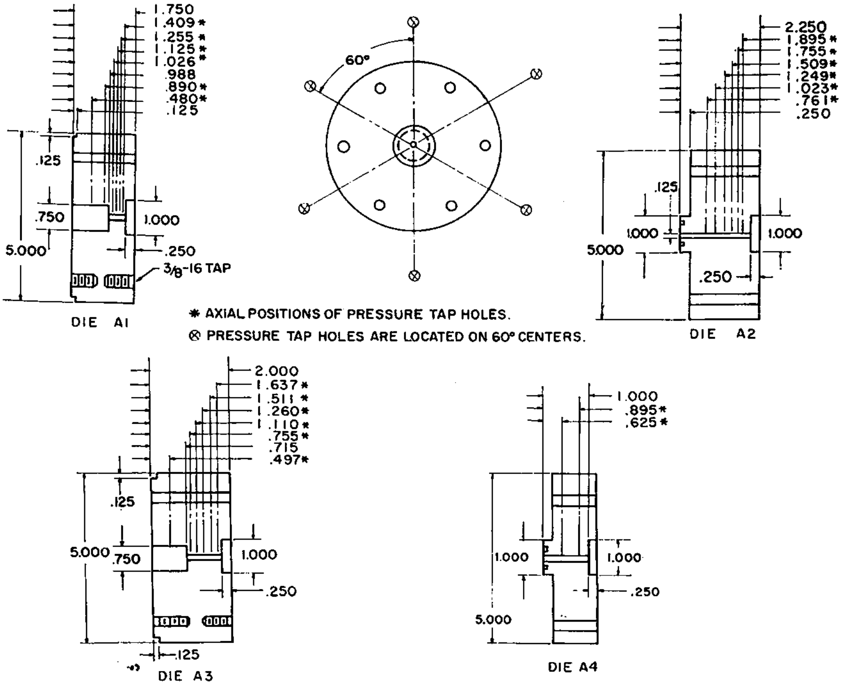

Fig. 1. Detailed layouts of die design.

and therefore have to be used together with either die A1 or A3. The entrance to the capillary is flat (180°).

The pressures at the wall (i.e., the total radial normal stresses) were measured with Dynisco melt pressure transducers. Their electrical outputs, in millivolts, were read on a potentiometer which was balanced with the aid of a d.c. null detector. The transducers were calibrated against a dead weight tester and were found to give outputs repeatable to within $\pm 1\%$ of the measured value at pressures of 100 psig and greater. The temperature was monitored at various positions in the reservoir and die sections with the aid of iron-Constantan thermocouples, and the temperature was controlled to within $\pm 0.5°$F by Thermistor-operated thermal regulators. The heating system itself consists of resistance wire wound on aluminum jackets for even heat distribution, and the entire system was well insulated.

The volumetric flow rate is determined by collecting the extrudate sample for a certain time interval. This was later used to calculate apparent shear rate.

Materials

The polymers used for the present study were three high-density polyethylene (commercial products of Union Carbide Corp.) of different molecular weight distributions and a low-density polyethylene. Molecular char-

TABLE II
Molecular Characteristics of Polyethylene Samples[a]

Sample code	Density	Melt index	M_n	M_w	M_w/M_n
DMDJ 4309	0.958 (high density)	0.2	2×10^3	1.68×10^5	84
DGNB 3825	0.961 (high density)	0.2	1.4×10^4	2.20×10^5	16
DMDJ 5140	0.961 (high density)	0.8	2.0×10^4	1.66×10^5	8
PEP 211[b]	0.918 (low density)	3.5	2.0×10^4	4.00×10^5	20

[a] Samples were supplied by the Union Carbide Corp. Number-average (M_n) and weight-average (M_w) molecular weights were determined by means of gel permeation chromatography.

[b] Molecular weight results for PEP-211 are approximate, being interpolated among results for other resins of the same family. There is much long-chain branching in PEP-211 according to rather qualitative measurements. Such branching is essentially absent from the three high-density samples.

acteristics of these polymer samples, which were supplied to us by the manufacturer,[14] are as given in Table II.

Also measured were the rheological properties of three blend systems of DMDJ 4309 and DMDJ 5140, the blending ratios being (a) 20 wt-% DMDJ 4309 + 80 wt-% DMDJ 5140; (b) 50 wt-% DMDJ 4309 + 50 wt-% DMDJ 5140; (c) 80 wt-% DMDJ 4309 + 20 wt-% DMDJ 5140.

RESULTS AND DISCUSSION

Effect of Molecular Weight and Molecular Weight Distribution on Melt Viscosity

All results to be presented below are obtained for an L/D ratio of 20 and at melt temperature of 200°C.

Figure 2 shows typical axial pressure distributions for DMDJ 4309 at three 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 tube exit gives rise to a positive nonzero gauge pressure, which has been called the "exit pressure."[13] The constancy of the pressure gradient, $-\Delta P/L$, permits one to calculate the true wall shear stress τ_w by

$$\tau_w = \left(\frac{-\Delta P}{L}\right)\frac{D}{4} \tag{1}$$

in which D is the capillary diameter. It can then be seen from eq. (1) that for a given shear rate the larger the value of $-\Delta P/L$, the higher the shear stress and hence the more viscous the material is. It is to be noted from eq. (1) that no end correction is necessary in this approach.

Figure 3 shows plots of shear stress versus shear rate, so-called flow curves, for four homopolymer samples. It is seen from Figure 3 that the materials used for the study follow a power law,

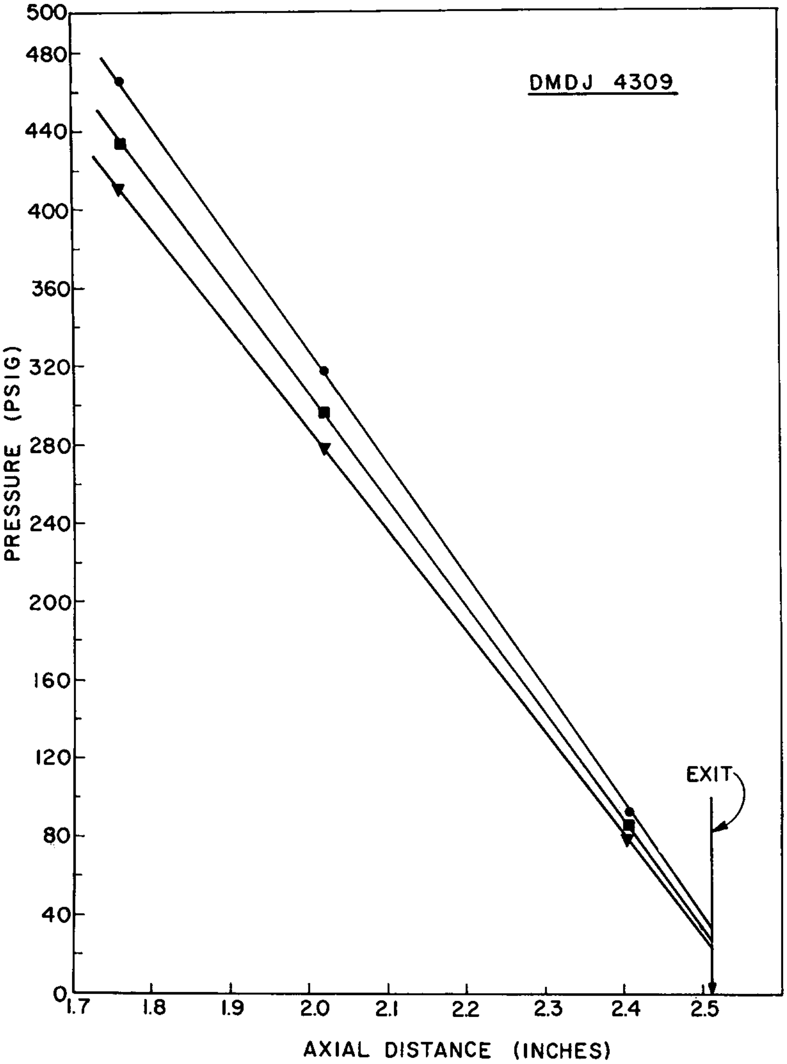

Fig. 2. Typical axial pressure profiles of DMDJ 4309 melts ($L/D = 20$, $T = 200°C$): (●) $\nu = 639.5\ \text{sec}^{-1}$; (■) $\dot{\nu} = 531.6\ \text{sec}^{-1}$; (▼) $\dot{\nu} = 443.1\ \text{sec}^{-1}$.

$$\tau_w = K\dot{\gamma}^n, \tag{2}$$

for the range of shear rate used, in which $\dot{\gamma}$ is the true shear rate evaluated by use of the Rabinowitsch-Mooney equation, K is material consistency, and n is flow index. From the definition of viscosity,

$$\eta = \tau_w/\dot{\gamma}, \tag{3}$$

one has

$$\eta = K\dot{\gamma}^{n-1} \tag{4}$$

in which η is the flow viscosity.

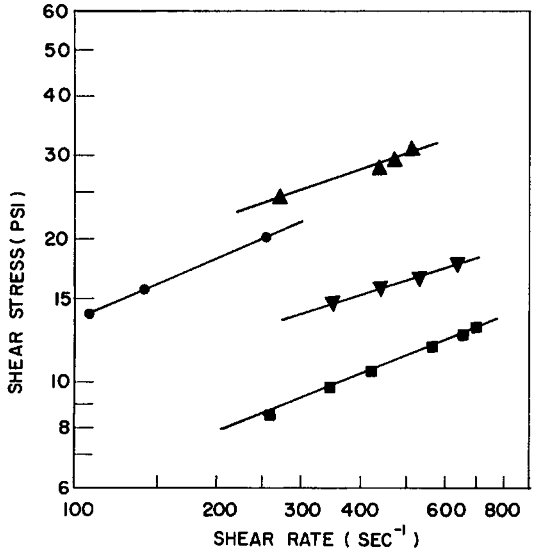

Fig. 3. Shear stress vs. shear rate for four polyethylene samples (T = 200°C): (▲) DGNB 3825; (●) DMDJ 5140; (▼) DMDJ 4309; (■) PEP 211.

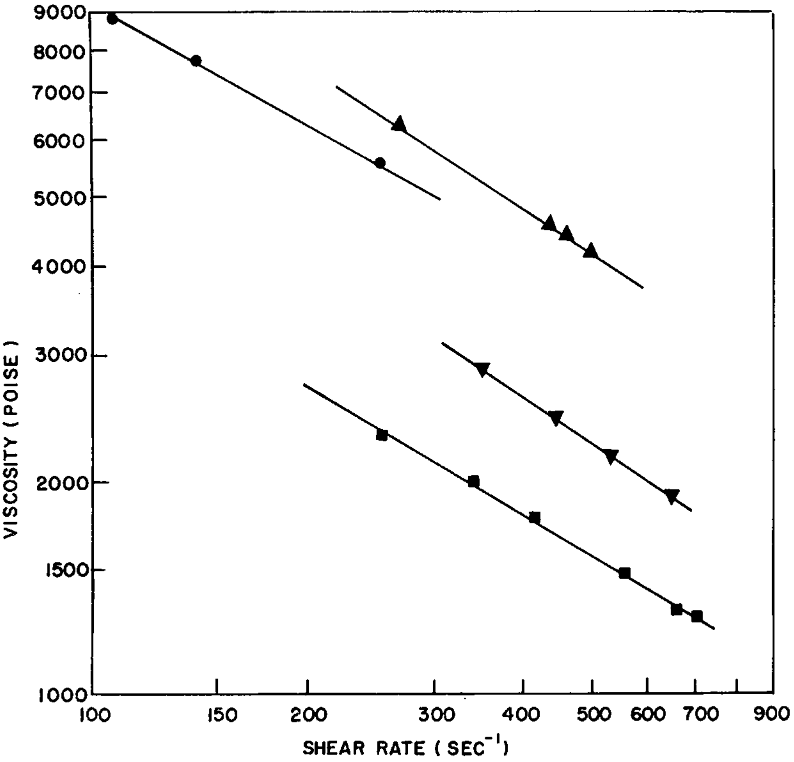

Fig. 4. Melt viscosity vs. shear rate for four polyethylene samples (T = 200°C): (▲) DGNB 3825; (●) DMDJ 5140; (▼) DMDJ 4309; (■) PEP 211.

TABLE III
Material Constants in Eqs. (2) and (5)

Sample code	K	n	α	β
DMDJ 4309 (HDPE)	2.387	0.310	1.661	0.494
DGNB 3825 (HDPE)	4.151	0.318	0.898	0.301
DMDJ 5140 (HDPE)	1.890	0.427	4.056	0.408
PEP 211 (LDPE)	0.965	0.398	0.689	0.293

In Figure 4 are shown plots of flow viscosity versus shear rate, indicating that the materials tested were in the non-Newtonian flow regime. Table III gives the values of K and n for the materials tested.

We can see that, as far as high-density polyethylenes are concerned, the value of flow index n in the power law model decreases as the molecular weight distribution broadens. A similar result was reported by Guillet et al.[11] In other words, the melt viscosity is less for samples having broad molecular weight distribution than for samples having narrow molecular weight distribution. This has been attributed, according to Guillet et al.,[11] to the greater degree of chain entanglement that occurs with a broad distribution of molecular weights.

Secondly, it is seen from Table II that the three high-density polyethylene samples show little difference in weight-average molecular weight but a big difference in number-average molecular weight, which indicates the wide spread in molecular weight distribution of the samples. One can therefore conclude from Figure 4 that the viscosity of the sample having a narrow molecular weight distribution is higher than that of the sample with a broad molecular weight distribution. In the present case, this is attributed to the difference in number-average molecular weight. Two previous studies,[10,15] support the results of the present study. Ballman and Simon[10] concluded from their study with polydisperse polystyrene that the melt viscosity depends on the weight-average molecular weight at low shear rates and on the number-average molecular weight at high shear rates. More recently, Adames et al.[15] reported from their study with polypropylene melts that the melt viscosity of the sample having a narrow molecular weight distribution was higher by a factor of 2 than that of the broad molecular weight distribution sample at high shear rate (at about 400 sec^{-1}).

Effect of Molecular Weight and Molecular Weight Distribution on Melt Elasticity

Figure 5 shows plots of the exit pressure versus shear rate for four samples, three being high-density polyethylenes and one a low density-polyethylene. It is seen from this figure that all samples follow a power law,

$$P_{\text{exit}} = \alpha\dot{\gamma}^{\beta}, \tag{5}$$

where P_{exit} denotes the exit pressure and α and β are constants characteristic of the materials. The values of α and β for the materials tested are also given in Table III. According to Han,[13] the exit pressure is equal to the

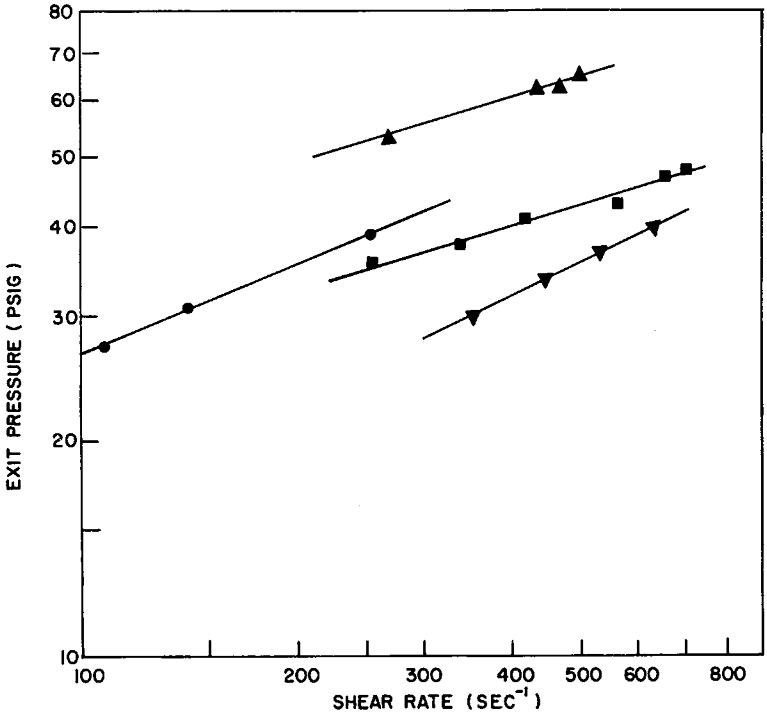

Fig. 5. Exit pressure vs. shear rate for four polyethylene samples (T = 200°C): (▲) DGNB 3825; (●) DMDJ 5140; (▼) DMDJ 4309; (■) PEP 211.

normal stress difference $P_{11} - P_{22}$ in fully developed flow for polymer melts. Therefore, eq. (5) may be written as

$$P_{11} - P_{22} = \alpha\dot{\gamma}^{\beta}. \tag{6}$$

In view of eq. (6), the plots of the exit pressure versus shear rate in Figure 5 may appear to indicate, at a first glance, that the sample having a narrow molecular weight distribution is more elastic than that having a broad molecular weight distribution, which is certainly contradictory to information reported in the literature. This casts doubt on the use of the plots of the exit pressure versus shear rate for determining the relative values of melt elasticity of different materials. For this purpose, very recently Han[16] has suggested the use of the plot of exit pressure against shear stress, instead of against shear rate.

Figure 6 gives plots of exit pressure versus shear stress for the four samples, showing what is to be expected. This result is in conformity with that of previous work.[7,11,12,15] Guillet et al.[11] reported from their die swell measurement that die swell increases as the molecular weight distribution broadens. More recently, Adams et al.[15] reported their measurements of the elasticity of polypropylene melts by means of the Weissenberg rheogoniometer and by the use of the phenomenon of flow birefringence, show-

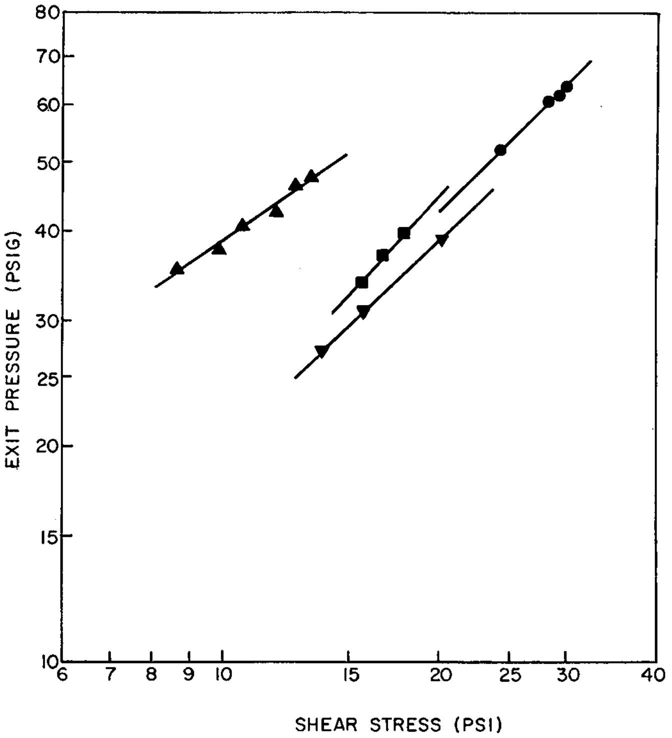

Fig. 6. Exit pressure vs. shear stress for four polyethylene samples ($T = 200°C$): (▲) PEP 211; (■) DMDJ 4309; (●) DGNB 3825; (▼) DMDJ 5140.

ing that the normal stress differences of the sample having a broad molecular weight distribution were much higher than those of narrower molecular weight distribution.

Effect of Long-Chain Branching on Melt Viscosity and Elasticity

We have seen from Figure 4 that the melt viscosity of the low-density polyethylene sample is lower than that of the three high-density polyethylene samples. This result is in accord with that of previous work.[8,12,17] In general, high-density polyethylene is considered to contain little or no long-chain branching, while low-density polyethylene contains much long-chain branching. Conceivably, high-density polyethylene contains some short-chain branchings. It is worth pointing out, however, that Peticolas[17] concluded from his study that polymers containing short-chain branching have only a very slightly lower melt viscosity than linear high-density polyethylenes of the same weight-average molecular weight. So, considering the molecular weight and molecular weight distribution of the four samples as shown in Table II, we can conclude from Figure 4 that the much lower melt viscosity of low-density polyethylene (PEP 211) is attributable to long-chain branching.

We have also seen from Figure 6 that low-density polyethylene is much more elastic than high-density polyethylenes, which is again to be expected from the consideration of already published literature.[5,6,11,12] It is worth noting the work of Busse,[8] who reported that die swell was increased considerably by adding a small fraction of a per cent of very long, flexible fibrils to linear polyethylene and polystyrene. Busse also reported that adding such materials as glass or asbestos to the polymers did not increase the die swell. Then he proceeded to speculate that long, thin fibrils might penetrate through and entangle many random coil polymer molecules and act as an elastic coupling between them, thus exerting a large effect on elasticity. Thus, one can conclude that the results presented in Figures 4 and 6 are in accord with the currently held views on the role of long-chain branching in the viscoelastic properties of molten bulk polymers.

Melt Viscosity and Elasticity of Blend Systems

In Figure 7 are shown flow curves of two pure components (DMDJ 4309 and DMDJ 5140) and three blend systems. It is clearly seen that the blend systems also follow a power law as given by eq. (2). Figure 8 shows plots of melt viscosity versus shear rate, constructed by the use of eq. (3) and flow curves in Figure 7. In order to see the effect of blending ratio on melt viscosity, cross plots of Figure 8 are prepared in Figure 9. It is interesting to note from Figure 9 that there exists a maximum value of melt viscosity at a blending ratio of 20 wt-% DMDJ 4309 to 80 wt-% DMDJ 5140.

Figure 10 shows plots of the exit pressure versus shear stress for two pure components (DMDJ 4309 and DMDJ 5140) and three blend systems, indicating that the power law as given by eq. (5) also holds true for blend systems. The cross plots of Figure 10 are shown in Figure 11, indicating that

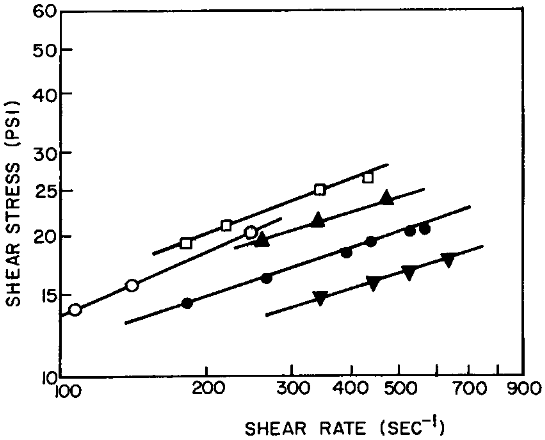

Fig. 7. Shear stress vs. shear rate for blend systems (T = 200°C): (▼) DMDJ 4309; (□) DMDJ 4309/DMDJ 5140 = 20/80; (▲) DMDJ 4309/DMDJ 5140 = 50/50; (●) DMDJ 4309/DMDJ 5140 = 80/20; (O) DMDJ 5140.

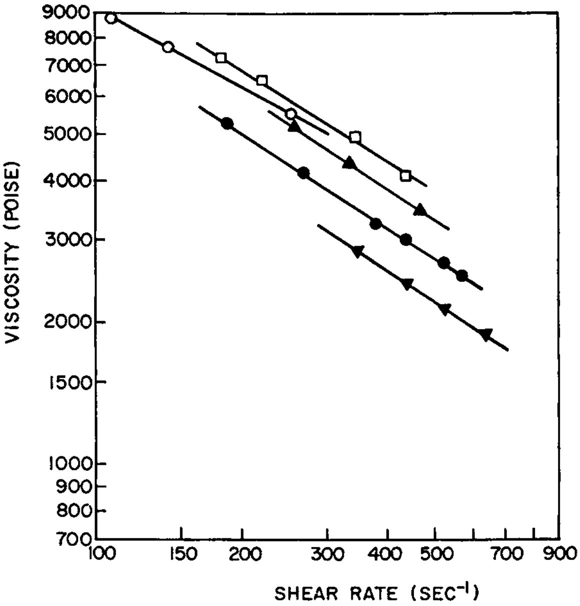

Fig. 8. Melt viscosity vs. shear rate for blend systems (T = 200°C): (▼) DMDJ 4309; (□) DMDJ 4309/DMDJ 5140 = 20/80; (▲) DMDJ 4309/DMDJ 5140 = 50/50; (●) DMDJ 4309/DMDJ 5140 = 80/20; (○) DMDJ 5140.

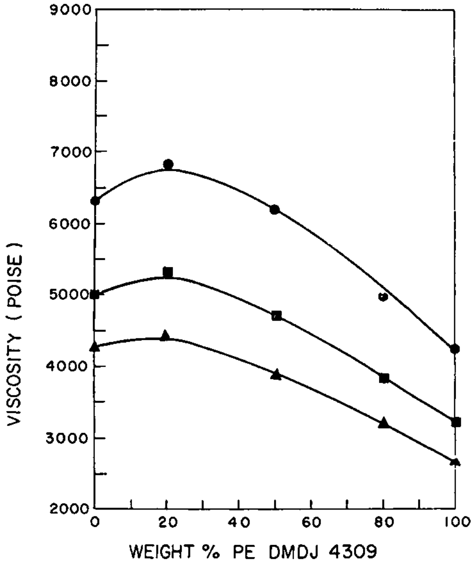

Fig. 9. Melt viscosity vs. blending ratio (T = 200°C): (●) $\dot{\nu}$ = 200 sec^{-1}; (■) $\dot{\nu}$ = 300 sec^{-1}; (▲) $\dot{\nu}$ = 400 sec^{-1}.

there exists a maximum value of melt elasticity at a blending ratio of 80 wt-% DMDJ 4309 to 20 wt-% DMDJ 5140.

The observation of the maximum values of melt viscosity and elasticity,

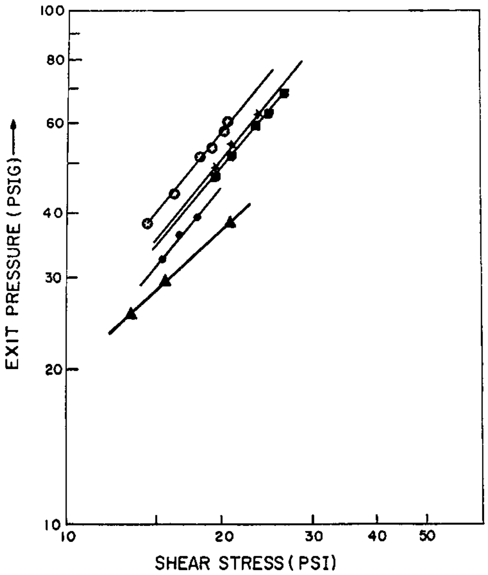

Fig. 10. Exit pressure vs. shear stress for blend systems (T = 200°C): (●) DMDJ 4309; (■) DMDJ 4309/DMDJ 5140 = 20/80; (★) DMDJ 4309/DMDJ 5140 = 50/50; (○) DMDJ 4309/DMDJ 5140 = 80/20; (▲) DMDJ 5140.

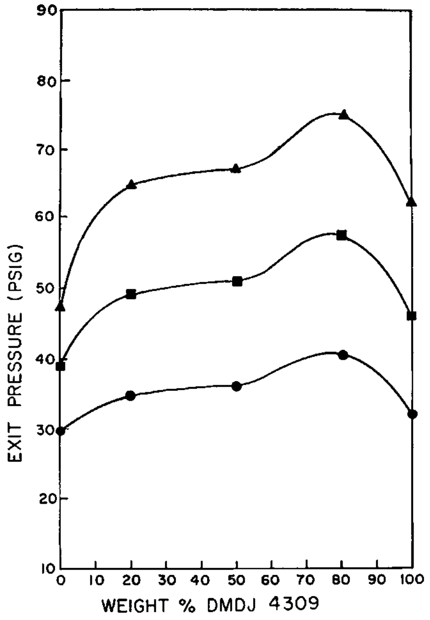

Fig. 11. Exit pressure vs. blending ratio (T = 200°C): (●) τ_w = 15 psi; (■) τ_w = 20 psi; (▲) τ_w = 25 psi.

though it appears strange, has recently been reported by Iino et al.,[18] who investigated the effect of blending method on the elastic shear modulus of the extrudate. However, there seems to be no satisfactory theory available at present which could explain how the blending method might be incorporated into a procedure for predicting the rheological properties of a blend system.

CONCLUSIONS

The following conclusions may be drawn from the results of the present study:

1. The breadth of the molecular weight distribution of polymers influences the flow viscosity and elasticity of melts as follows. Polymers of broad molecular weight distribution are less viscous but more elastic than those of narrow molecular weight disrribution. This result is in accord with the findings of previous work.[7,10,11,12,15]

2. The presence of long-chain branching in a polymer gives rise to lower melt viscosity yet higher melt elasticity compared to linear polymers which do not contain long-chain branching. This result is also as found by previous workers.[5,6,11,12,17]

3. In view of the above two conclusions, one can say, then, that the capillary rheometer described in previous papers[13] has been proved once again to be a very useful, practical instrument that will permit one to characterize molten polymers by their viscous and elastic properties, in particular in the range of shear rates commonly occurring in processing various polymeric materials.

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