Measurement of the Rheological Properties of Polymer Melts with Slit Rheometer. II. Blend Systems

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Synopsis

A slit rheometer described in part I of this series was used for characterizing two blend systems by their viscous and elastic properties in the molten state. The blend systems chosen for study were blends of two high-density polyethylenes having widely different molecular weight distributions and blends of polystyrene and polypropylene which are incompatible in the molten state. The present study shows that blends of two high-density polyethylenes and blends of polystyrene with polypropylene exhibit a minimum in melt viscosity and a maximum and minimum in melt elasticity (in terms of "exit pressure") at certain blending ratios. These results confirm the author's earlier findings, which were obtained with a capillary rheometer.

INTRODUCTION

In recent years, quite an intensive study seems to have been made of formulating polymer blends, in particular by polymer-processing industries. Such attempts appear to have been motivated by both economic and scientific necessities. In other words, it may be economical to blend polymers having different molecular weights and molecular weight distributions, so that the blend gives rise to certain desired physical properties of the finished product, instead of manufacturing a new polymer for the same purpose.

In order to accomplish such objectives, however, it would be quite helpful to have some blend laws that can be used for predicting the rheological properties of the blends in the molten state from information on the blending ratios and the rheological properties of individual components. Some efforts[1-3] have been spent in the past, with limited success, to obtain blend laws. It is to be noted, however, that the studies referred to above were concerned with blends of two polymers having the same molecular structure but different molecular weights and molecular weight distributions, (e.g., blends of polyethylenes and blends of polystyrenes).

Another type which would be of practical interest is a blend of two polymers having different molecular structures. This type of blend system is interesting in itself because two chemically dissimilar polymers are in general incompatible in the molten state. Recent studies by Hill and Maxwell[4] and Han and Yu[5] show unusual rheological behavior in blends of

polystyrene and polypropylene and blends of polystyrene and polyethylene in the molten state.

In addition, there is an important class of polymer systems of commercial importance that, in fact, contains two phases in the molten state. Examples of this class are high-impact polystyrenes and ABS resins.

The purpose of this paper, the second in this series, is to present some new experimental observations on both viscous and elastic properties of two blend systems, namely blends of two high-density polyethylenes having widely different molecular weight distributions and blends of polystyrene and polypropylene. The rheological properties reported here were determined using the slit rheometer described in part I of this series.[6]

EXPERIMENTAL

Materials

The first set of blends was prepared from two high-density polyethylenes, one having a polydispersity of 16 (Union Carbide Corp., DGNB 3825), and the other having a polydispersity of 84 (Union Carbide Corp., DMDJ 4309). Molecular characteristics of these polymer samples were given in an earlier paper.[7] The second set of blends was general-purpose polystyrene (Dow Chemical Co., Styron 686) with polypropylene (Enjay Chemical Co., Resin E115). The blending ratios and sample codes for the polyethylene blends and for the two-phase systems of polystyrene and polypropylene are given in Table I.

TABLE I
Blending Ratios and Sample Codes of Polyethylene Blends
and Polystyrene–Polypropylene Blends

Sample code	Blending ratio
A	100 wt-% DMDJ 4309
B	100 wt-% DGNB 3825
A/B = 20/80	20 wt-% DMDJ 4309 and 80 wt-% DGNB 3825
A/B = 50/50	50 wt-% DMDJ 4309 and 50 wt-% DGNB 3825
A/B = 80/20	80 wt-% DMDJ 4309 and 20 wt-% DGNB 3825
PS	100 wt-% polystyrene
PP	100 wt-% polypropylene
PS/PP = 20/80	20 wt-% polystyrene and 80 wt-% polypropylene
PS/PP = 50/50	50 wt-% polystyrene and 50 wt-% polypropylene
PS/PP = 80/20	80 wt-% polystyrene and 20 wt-% polypropylene

Polymer blends were prepared by mixing two polymers, in the form of pellets, in a tumbling operation. Fortunately, the pellet sizes of the polymers were almost identical (about $1/8$ in.) and hence no particle segregation was observed when the blends were fed to the extruder.

Apparatus and Experimental Procedure

The apparatus used for the present study is the same as that described in part I of this series.[6] However, in the present study, only one slit die,

having an aspect ratio of 20 (referred to as Slit Die 2 in part I of this series[6]), was used throughout the whole experimental runs. The operating temperature was 200°C.

The experimental procedure was also the same as that described in part I of this series.[6]

RESULTS AND DISCUSSION

Rheological Properties of Polyethylene Blends

Figure 1 shows representative axial pressure profiles for a blend of 50 wt-% DMDJ 4309 and 50 wt-% DGNB 3825 (A/B = 50/50). Similar plots were obtained for other blends. In all cases the pressure profiles were found to lie on straight lines, which then permitted one to determine viscous properties from their slopes and elastic properties from the "exit pressures."

Using the method described in part I of this series,[6] flow curves were constructed for three blends and two pure components, as shown in Figure 2. It is to be noted that each blend follows a power law over the range of shear rates encountered. One can further plot melt viscosity against shear rate, as shown in Figure 3. In order to see the effect of blending ratio on melt flow viscosity, cross plots of Figure 3 are prepared in Figure 4. This result
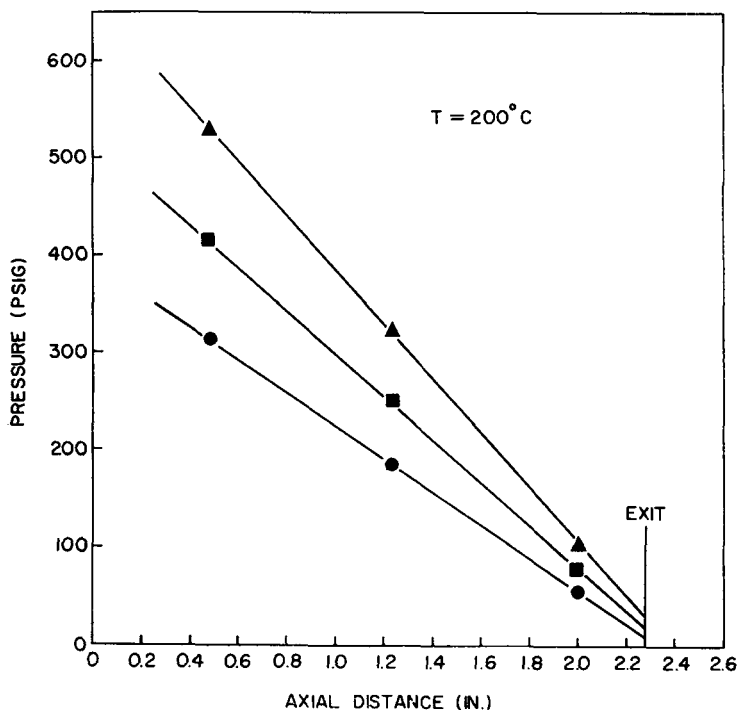

Fig. 1. Representative axial pressure profiles for A/B = 50/50 at 200° C: (▲) $\dot{\gamma}$ = 266 sec^{-1}; (■) $\dot{\gamma}$ = 147 sec^{-1}; (●) $\dot{\gamma}$ = 77 sec^{-1}.

is in accord with the findings by Horio et al.,[3] who reported that the dynamic viscosities of the polyethylene blends change systematically with blending ratio.

Note, however, that blends of two high-density polyethylenes studied earlier by the author[7] gave rise to a slight maximum in melt viscosity at a blending ratio of 20 wt-% DMDJ 4309 to 80 wt-% DMDJ 5140. It is to be
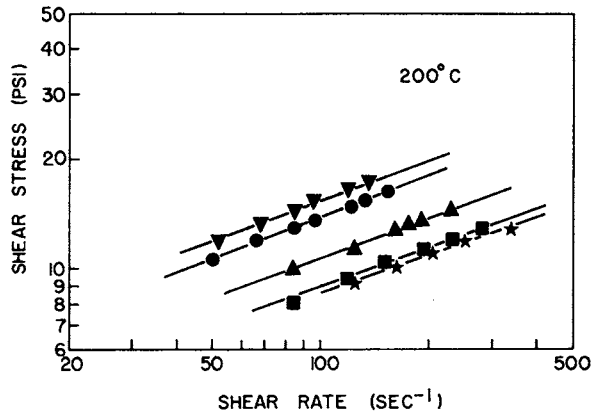

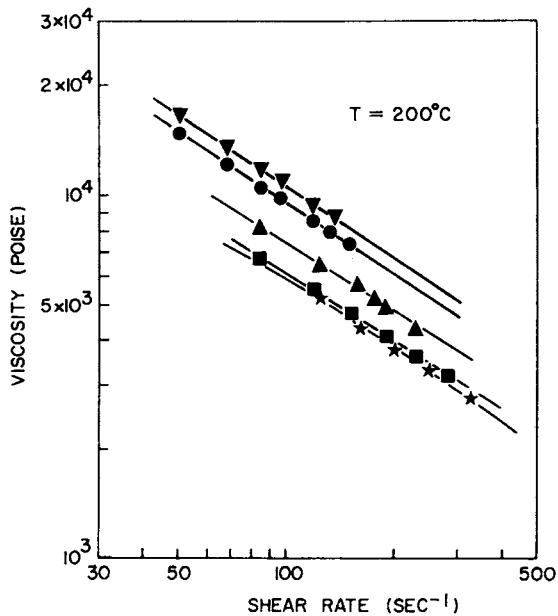Fig. 2. Flow curves of polyethylene blends at 200°C: (★) A; (●) A/B = 20/80; (▲) A/B = 50/50; (■) A/B = 80/20; (▼) B.

Fig. 3. Melt viscosity vs. shear rate for polyethylene blends at 200°C. Symbols same as Fig. 2.
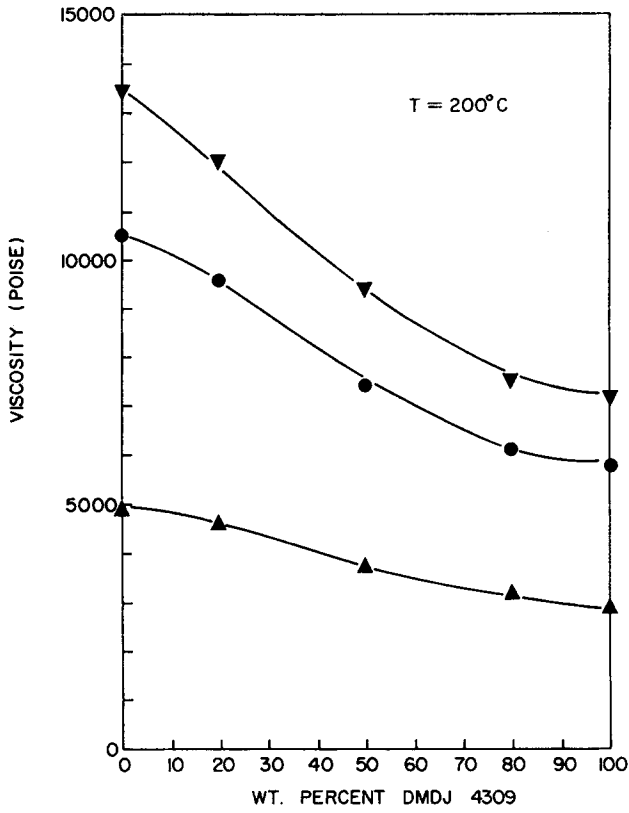
Fig. 4. Melt viscosity vs. blending ratio for polyethylene blends at 200° C: (▼) $\dot{\gamma} = 70$ sec^{-1}; (●) $\dot{\gamma} = 100$ sec^{-1}; (▲) $\dot{\gamma} = 300$ sec^{-1}.
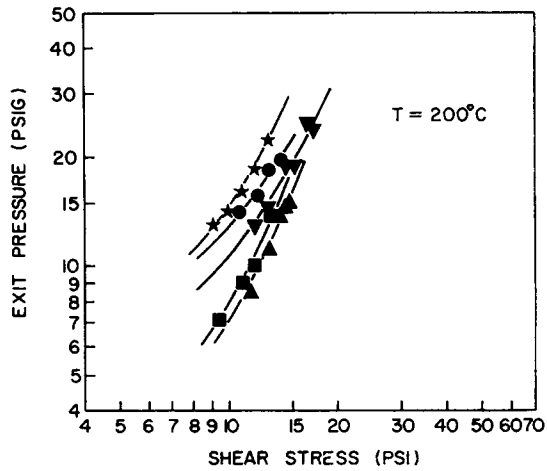

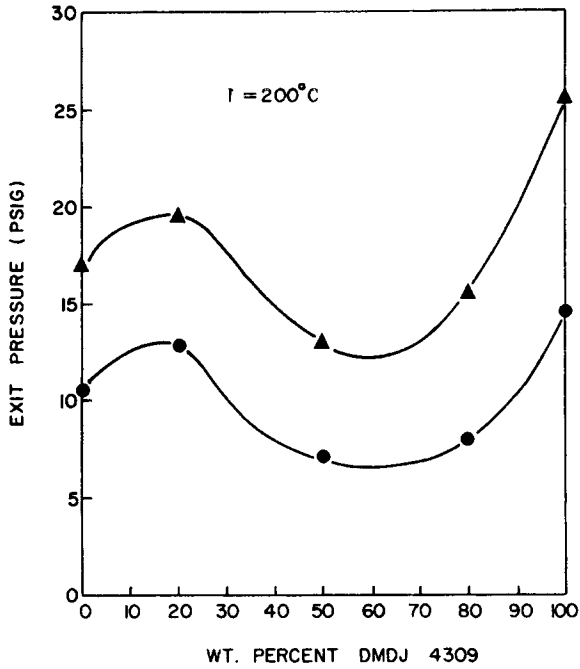Fig. 5. Exit pressure vs. shear stress for polyethylene blends at 200° C. Symbols same as in Fig. 2.

Fig. 6. Exit pressure vs. blending ratio for polyethylene blends at 200°C: (▲) $\tau_w = 14$ psi; (●) $\tau_w = 10$ psi.

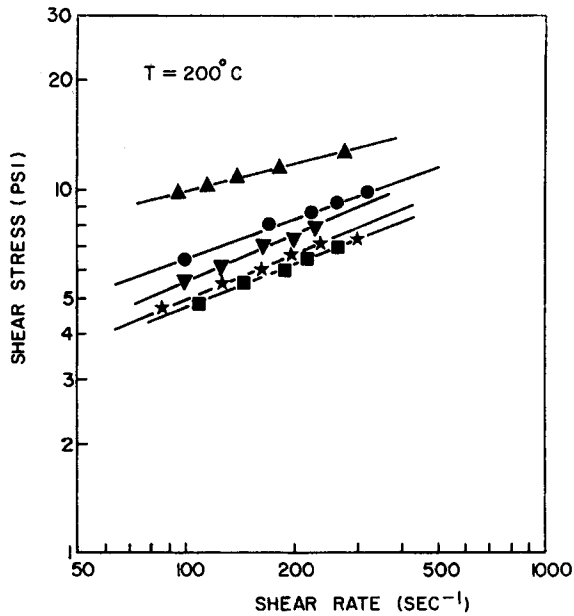Fig. 7. Flow curves for polystyrene–polypropylene blends at 200°C: (▲) PS; (★) PS/PP $= 20/80$; (■) PS/PP $= 50/50$; (▼) PS/PP $= 80/20$; (●) PP.

noted that DMDJ 5140 has a polydispersity of 8, which is slightly lower than that of DGNB 3825 used in the present study (see Table II of ref. 7 for molecular characteristics). Note that Horio et al.[3] prepared the blends by using a nonvent-type extruder, while the blends used in this and earlier studies by the author were prepared in a tumbling operation. These observations then seem to point out that the blending method is an important factor which should be incorporated in the prediction of the rheological properties of a blend system. Recently, Iino et al.[8] reported that blending methods affect the rheological properties of blends. At present, however, there seems to be no theory available that takes into account the effect of blending method on the rheological properties of polymer blends in the molten state.

The elastic properties of the polyethylene blends are given in Figure 5, in which the exit pressures are plotted against shear stress, instead of against shear rate, for the reasons described in part I of this series.[6] The cross plots of Figure 5 are shown in Figure 6, in order to examine the effect of blending ratio on the melt elasticity of the blends. It is seen from Figure 6 that the exit pressure (hence, melt elasticity) goes through a maximum and minimum at certain blending ratios. It is to be noted that a previous study[7] of a polyethylene blend system showed a maximum melt elasticity in terms of exit pressure at a blending ratio of 80 wt-% DMDJ 4309 to 20 wt-% DMDJ 5140. Again, it appears that the blending method is an important factor in predicting the melt elasticity of blend systems.
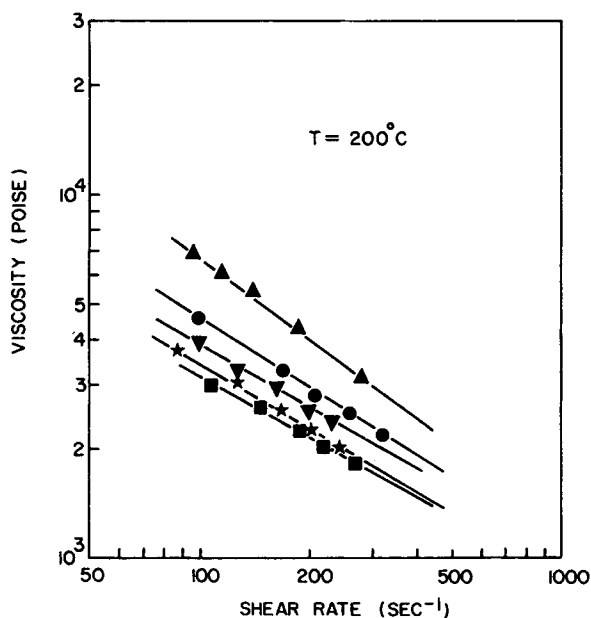

Fig. 8. Melt viscosity vs. shear rate for polystyrene–polypropylene blends at 200°C. Symbols same as in Fig. 7.

Rheological Properties of Polystyrene–Polypropylene Blends

Figure 7 shows flow curves for three blends of polystyrene and polypropylene and for pure components, indicating that each sample follows a power law over the range of shear rates investigated.   Figure 8 shows plots of melt viscosity versus shear rate, and Figure 9 gives cross plots of Figure 8.   It is interesting to observe from Figure 9 that melt viscosity goes through a minimum at a blending ratio for 50 wt-% polystyrene to 50 wt-% polypropylene.

A close look at Figure 9 inicates further that the addition of a relatively small amount of one component to the other results in a reduction in melt viscosity of the blend, independent of the viscosities of the individual components.   However, plausible explanations may be given for the drop in viscosity of the polystyrene–polypropylene blend system from a structural point of view because this blend system forms two incompatible phases in the molten state.   Clear evidence has recently been presented at the forma-
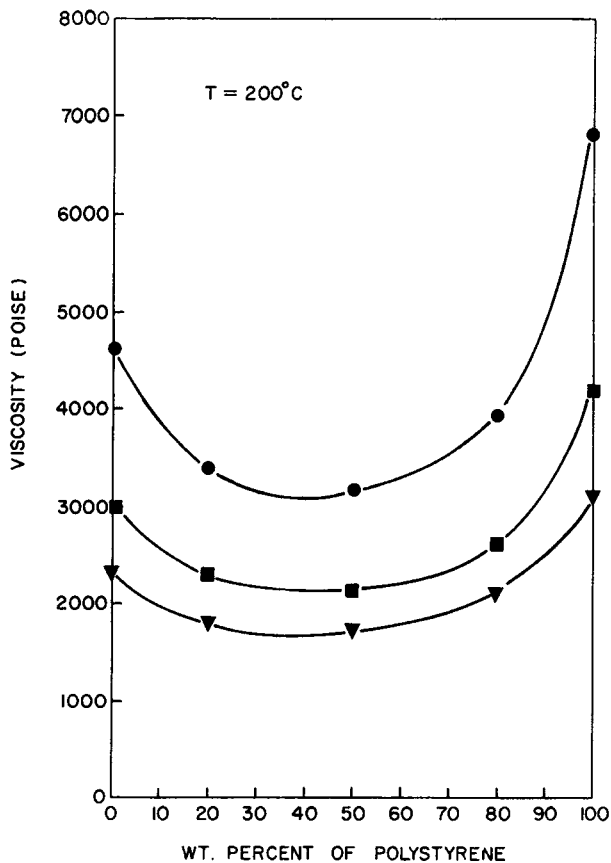

Fig. 9.   Melt viscosity vs. blending ratio for polystyrene–polypropylene blends at 200°C: (▼) $\dot{\gamma} = 300$ sec^{-1};   (■) $\dot{\gamma} = 200$ sec^{-1};   (●) $\dot{\gamma} = 100$ sec^{-1}.
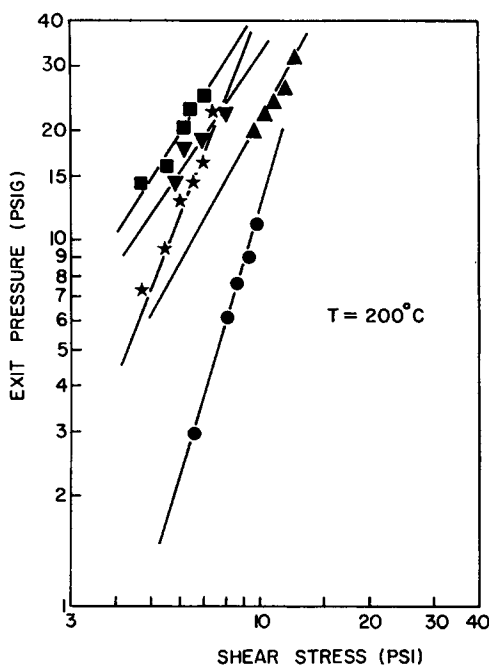
Fig. 10. Exit pressure vs. shear stress for polystyrene–polypropylene blends at 200°C. Symbols same as in Fig. 7.

tion of two phases in this blend system from a study of the microstructures of extrudate samples by Van Oene[9] and Han and Yu.[5]   Since the two components, polystyrene and polypropylene, are incompatible, the presence of a relatively small amount of one component may be considered to act as a lubricant for the other.   Natov and Djagarowa[10,11] made some interesting studies, reporting that a small amount of a low molecular weight material, which was incompatible with polymer melts, reduced the melt flow viscosity considerably.   It should be noted, however, that the blending method also could play an important role in determining the viscous properties of incompatible systems.

Figure 10 shows plots of exit pressure versus shear stress for blends of polystyrene and polypropylene, and Figure 11 gives cross plots of Figure 10.   Note from Figure 10 that the blends of the two-phase system exhibit the same rheological behavior as pure components (homopolymers) do, and further note from Figure 11 that the exit pressure (hence, melt elasticity) goes through a maximum at a blending ratio of 50 wt-% polystyrene to 50 wt-% polypropylene.   A recent study by Hill and Maxwell[4] reported a maximum elastic property (in terms of shear modulus) at a certain blending ratio for the polystyrene–polypropylene system.   They used a rotational type of rheometer, whereas a slit rheometer was used in the present study.   Considering that two entirely different experimental techniques have generated very similar results in melt elasticity, the author tends to be-
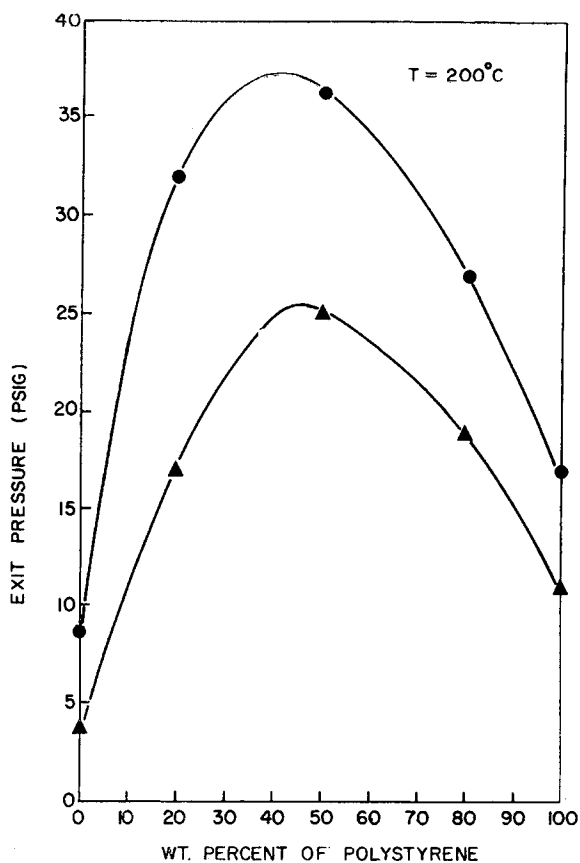
Fig. 11. Exit pressure vs. blending ratio for polystyrene–polypropylene blends at 200°C: (▲) $\tau_w = 7$ psi; (●) $\tau_w = 9$ psi.

lieve that the exhibition of either a maximum or minimum, or both, at a certain blending ratio is generally characteristic of the rheological properties of blend systems. Again, it should be noted that the blending method appears to play an important role in determining the elastic properties of incompatible systems.

Unfortunately, there appears to be no theory available at the present time which could explain the experimental results presented above. The author hopes that the results presented in this paper will stimulate future research in this rather interesting and important area.

CONCLUSIONS

The rheological properties of two blend systems have been determined by using a slit rheometer described in part I of this series.[6] The measurements were discussed by comparison with the results available in the literature.

The present study yielded results very similar to those obtained earlier by the author, using a capillary rheometer. The apparently anomalous rheological properties of blend systems presented in this paper seem to be characteristic of blend systems. However, it was pointed out that the blending method could play an important role in determining the rheological properties.

Future study will be directed to investigating in detail the effect of blending methods and to explaining the unusual rheological behavior of blend systems from the standpoints of molecular behavior.

References

1. K. Ninomiya, *J. Colloid Sci.*, **14**, 49 (1959).
2. K. Ninomiya, *J. Colloid Sci.*, **17**, 759 (1962).
3. M. Horio, T. Fujii, and S. Onogi, *J. Phys. Chem.*, **68**, 778 (1964).
4. A. S. Hill and B. Maxwell, *Polym. Eng. Sci.*, **10**, 289 (1970).
5. C. D. Han and T. C. Yu, *J. Appl. Polym. Sci.*, **15**, 1163 (1971).
6. C. D. Han, *J. Appl. Polym. Sci.*, **15**, 2567 (1971).
7. C. D. Han, T. C. Yu, and K. U. Kim, *J. Appl. Polym. Sci.*, **15**, 1149 (1971).
8. H. Iino, M. Tsukasa, T. Nagafune, K. K. Sekaicho, and Y. Minoura, *Nippon Gomu Kyokaishi*, **40**, 726 (1967).
9. H. Van Oene and Y. F. Chang, paper presented at the 40th Annual Meeting of the Society of Rheology, St. Paul, Minn., October, 1969.
10. M. A. Natov and Y. K. Djagarowa, *Polym. Sci. U.S.S.R.*, **8**, 2032 (1966).
11. M. A. Natov and Y. K. Djagarowa, *Makromol. Chem.*, **100**, 126 (1967).