

## **Rheological Properties of Molten Polymers. II. Two-Phase Systems**

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### **Synopsis**

A study is carried out for characterizing two-phase systems of molten polymers by their viscous and elastic properties. The two-phase systems chosen for study are blends of polystyrene and polypropylene, and blends of polystyrene and high-density polyethylene. For the study, measurements of wall normal stresses are made by use of a capillary melt rheometer described in part I of this series. The concept of the "exit pressure" is used to determine the elastic properties of the two-phase polymer systems. The present study shows anomalous viscous and elastic properties of two-phase systems, which are difficult to predict from knowing the viscous and elastic properties of their individual components. A detailed discussion is given on the state of dispersion of two incompatible polymer systems in the molten state, by presenting pictures of the microstructure of the extrudate samples. The state of dispersion appears to vary depending on the blending ratio, extrusion temperature, melt viscosities of individual components, and blending method.

### **INTRODUCTION**

In recent years, an increasing number of commercial products have appeared on the market, made of more than one polymeric material. To name two, composite fibers and films are typical examples. By virtue of the development of these products, considerable interest has been aroused in understanding the fundamental nature of the flow properties of polymer blend systems. In particular, a better understanding of the rheological properties of two-phase polymer systems, which are incompatible in the molten state, is of great importance to a successful operation of the various items of processing equipment.

An advantage of having composite materials lies in the improved physical properties of the finished product. For instance, bicomponent fibers yield improved tensile properties as well as resistance to abrasion. A most important property which composite fibers, in particular, possess is their ability to form crimps, which simulate natural wool fibers.<sup>1,2</sup> Therefore, bicomponent fibers are made to form crimps by properly choosing two components having different thermal shrinkage on heating, for instance.

However, little has been published in the literature dealing with the rheological properties of incompatible two-phase molten polymers. Heit-miller et al.<sup>3</sup> made a study of two-component polymer systems and suggested the use of an empirical relationship between the composition and the viscosity of a mixture. It should be pointed out, however, that these authors treated the polymer systems as Newtonian fluids in the molten state, which does not apply to many processing conditions. Very recently, VanOene and Chang<sup>4</sup> made an interesting experimental study on the flow of polystyrene/polyethylene mixtures. However, none of these authors has mentioned the elastic properties of the mixtures of two-component systems in the molten state.

It is the purpose of this paper, the second of the series, to present some new experimental data on both the viscous and elastic properties of two-phase polymer systems in the molten state.

## EXPERIMENTAL

### Materials

Two different blend systems were prepared from three polymers. These were: high-density polyethylene (Union Carbide DMDJ 4309), polystyrene (Dow Chemical Styron 686), and polypropylene (Enjay Chemical

TABLE I  
Blending Ratios and Sample Codes of Two-Component Systems

Sample code	Blending ratio, wt-%/wt-%
PS/PP = 10/90	10% polystyrene/90% polypropylene
PS/PP = 20/80	20% polystyrene/80% polypropylene
PS/PP = 50/50	50% polystyrene/50% polypropylene
PS/PP = 80/20	80% polystyrene/20% polypropylene
PS/PP = 90/10	90% polystyrene/10% polypropylene
PS/PE = 10/90	10% polystyrene/90% polyethylene
PS/PE = 20/80	20% polystyrene/80% polyethylene
PS/PE = 50/50	50% polystyrene/50% polyethylene
PS/PE = 80/20	80% polystyrene/20% polyethylene
PS/PE = 90/10	90% polystyrene/10% polyethylene

E115 Resin). The blend systems prepared were polystyrene/polyethylene and polystyrene/polypropylene of different blending ratios. The blending ratios and sample codes are given in Table I.

### Apparatus and Experimental Procedure

The apparatus and experimental procedure used were described in part I of this series.<sup>5</sup>

Polymer blends were prepared by mixing two polymers, available in the form of pellets, through tumbling operation.

**RESULTS AND DISCUSSION**

In the present study, the viscous and elastic properties of two homopolymers, the general-purpose polystyrene Styron 686 and polypropylene

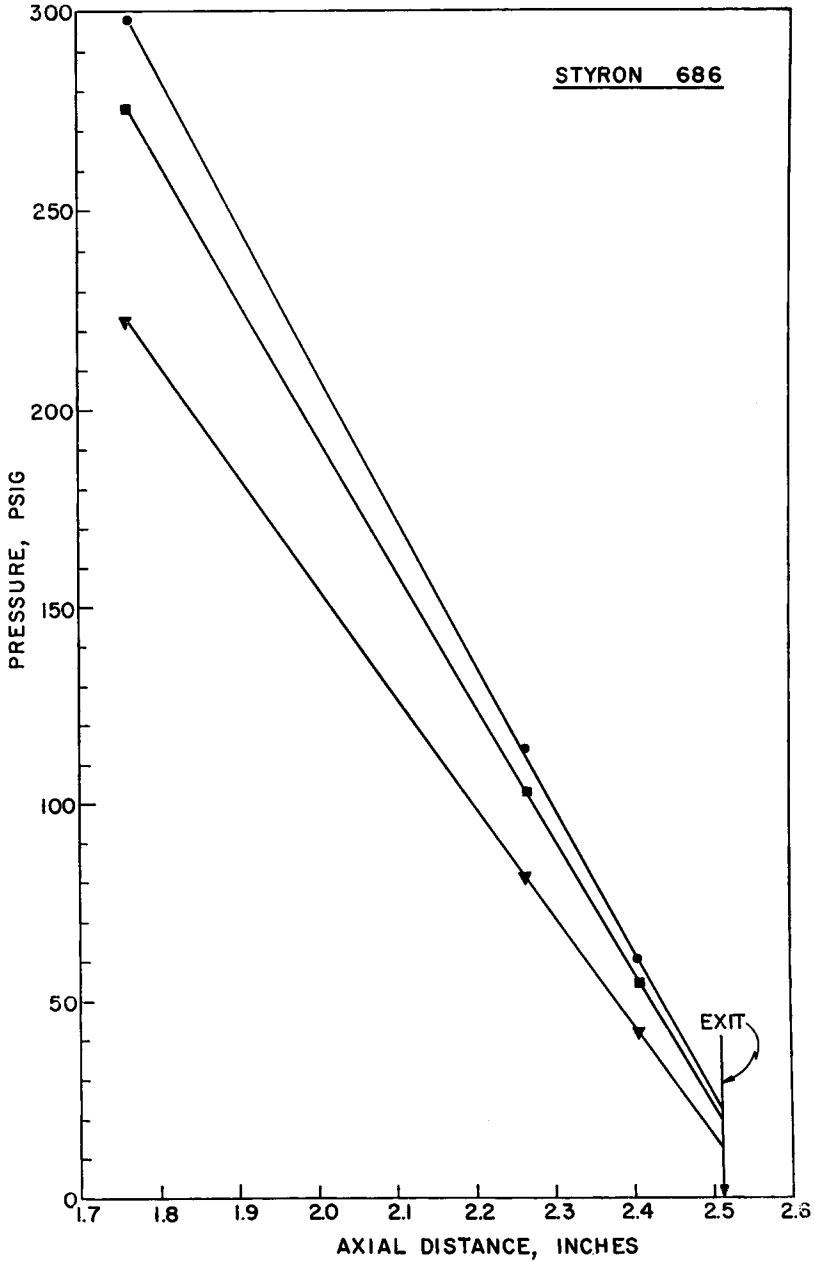


Fig. 1. Axial pressure profiles of Styron 686 melts ( $L/D=20$ ,  $T=200^\circ\text{C}$ ): (●)  $\dot{\gamma} = 533.4 \text{ sec}^{-1}$ ; (■)  $\dot{\gamma} = 390.2 \text{ sec}^{-1}$ ; (▼)  $\dot{\gamma} = 176.3 \text{ sec}^{-1}$ .

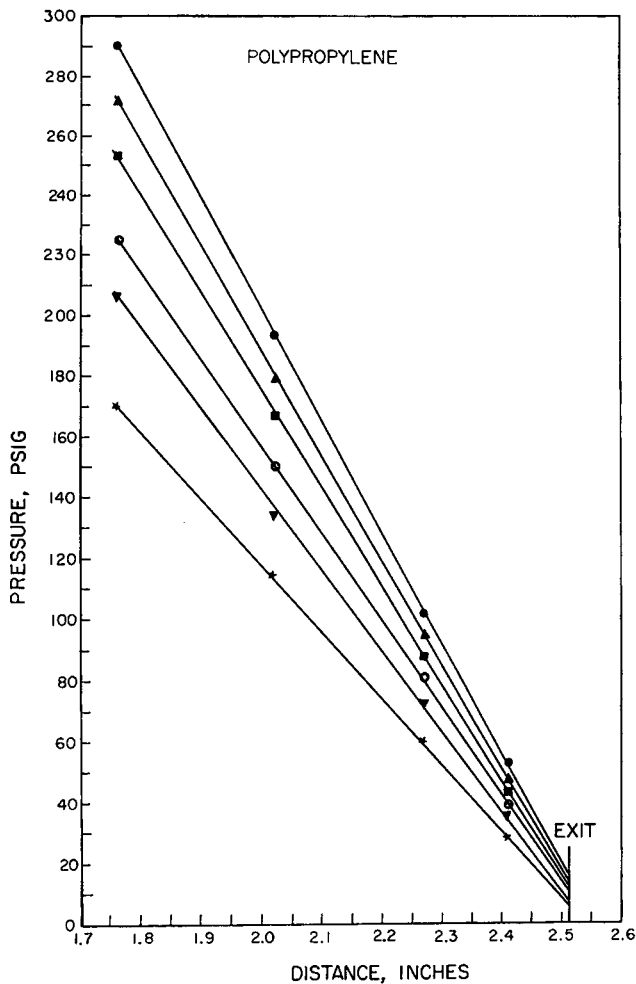


Fig. 2. Axial pressure profiles of polypropylene melts ( $L/D = 20$ ,  $T = 200^\circ\text{C}$ ): (●)  $532.2 \text{ sec}^{-1}$ ; (▲)  $488.2 \text{ sec}^{-1}$ ; (■)  $363.9 \text{ sec}^{-1}$ ; (⊙)  $283.1 \text{ sec}^{-1}$ ; (▼)  $206.3 \text{ sec}^{-1}$ ; (★)  $132.5 \text{ sec}^{-1}$ .

(E115 Resin) melts, were first determined before measurements of two-phase systems were taken. Note that the rheological properties of the third homopolymer, a high-density polyethylene (DMDJ 4309), had already been determined and presented in part I of the series. Also in part I, we described the method of analyzing the experimental data, which only requires the axial pressure profiles of each material concerned as a function of the volumetric flow rate. Typical axial profiles are shown in Figure 1 for polystyrene melts and in Figure 2 for polypropylene melts. It is to be noted that all two-phase systems tested generated similar pressure profiles. It is to be noted further that measurements of all two-phase systems were taken with a capillary length-to-diameter ratio of 20,

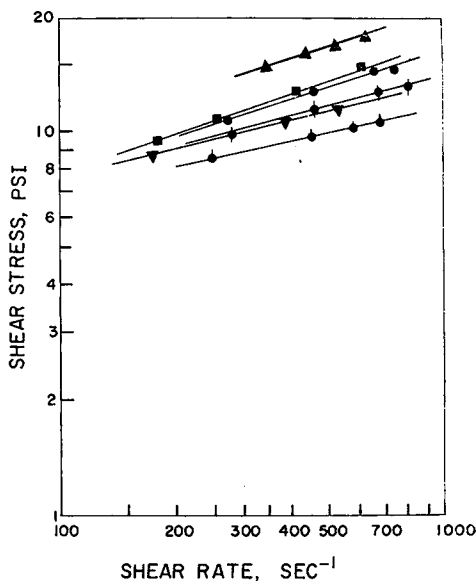


Fig. 3. Shear stress vs. shear rate for polystyrene/polyethylene systems ( $T = 200^{\circ}\text{C}$ ): ( $\nabla$ ) PS; ( $\blacksquare$ ) PS/PE = 10/90; ( $\bullet$ ) PS/PE = 20/80; ( $\blacklozenge$ ) PS/PE = 50/50; ( $\bullet$ ) PS/PE = 90/10; ( $\blacktriangle$ ) PE.

### Effect of Blending Ratio on the Melt Viscosity of Two-Phase Systems

Plots of the shear stress versus shear rate are shown for polystyrene/polyethylene systems in Figure 3 and for polystyrene/polypropylene systems in Figure 4. Note that these plots were prepared by use of the slope of the axial pressure profiles of each material concerned. It is clearly seen from Figures 3 and 4 that all two-phase systems follow a power law, in the same way that homopolymers do.

In addition, plots of viscosity versus shear rate are shown in Figure 5 for polystyrene/polyethylene systems and in Figure 6 for polystyrene/polypropylene systems. It is seen from these figures that some two-phase systems have lower values of viscosity than homopolymers (pure components). The effect of blending ratio on the melt viscosity of two-phase systems can best be seen from the cross plots of each of the two figures. These are shown in Figure 7 for polystyrene/polyethylene systems and in Figure 8 for polystyrene/polypropylene systems.

It is interesting to observe from Figures 7 and 8 that a certain blending ratio gives rise to a minimum value of viscosity of a two-phase system. Note further that addition of a relatively small amount of one component to another component (say, 10% of PS to 90% of PE, and 10% of PE to 90% of PS) gives rise to a rather large drop in viscosity of the two-phase system concerned. This may be attributable to a lubricating role of the small quantity of a component present in the two-phase system. At this

point, the work of Natov and Djagarowa<sup>6,7</sup> may be worth noting. Investigating the role of low molecular weight organic materials in the flow of polymer melts, these authors reported that when a very small quantity of a low molecular weight material, which was incompatible with polymer

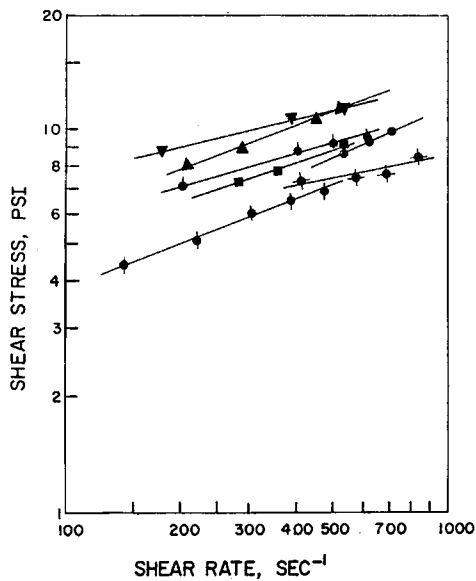


Fig. 4. Shear stress vs. shear rate for polystyrene/polypropylene systems ( $T = 200^{\circ}\text{C}$ ): ( $\nabla$ ) PS; ( $\blacksquare$ ) PS/PP = 10/90; ( $\bullet$ ) PS/PP = 20/80; ( $\blacklozenge$ ) PS/PP = 50/50; ( $\blacklozenge$ ) PS/PP = 80/20; ( $\bullet$ ) PS/PP = 90/10; ( $\blacktriangle$ ) PP.

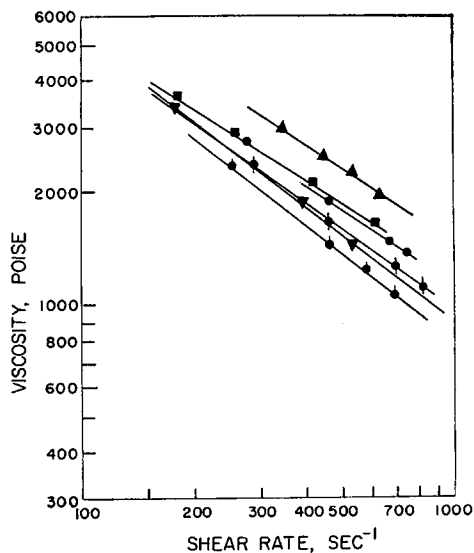


Fig. 5. Viscosity vs. shear rate for polystyrene/polyethylene systems ( $T = 200^{\circ}\text{C}$ ). Symbols same as in Fig. 3.

melts, was added to polymer melts, it reduced the melt flow viscosity considerably.

However, in the two-phase systems studied here, both the average molecular weight and the melt flow viscosity of each individual homopoly-

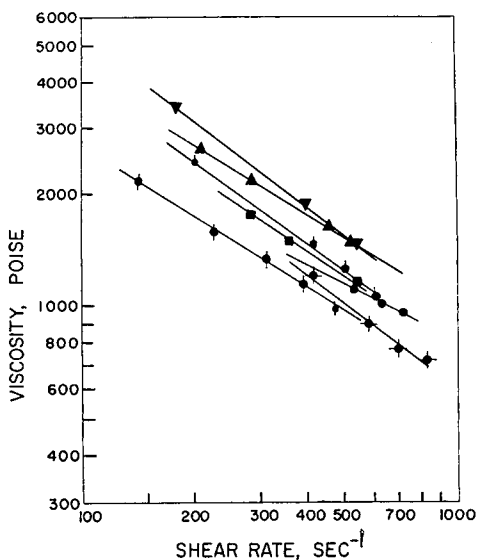


Fig. 6. Viscosity vs. shear rate for polystyrene/polypropylene systems ( $T = 200^{\circ}\text{C}$ )  
 Symbols same as in Fig. 4.

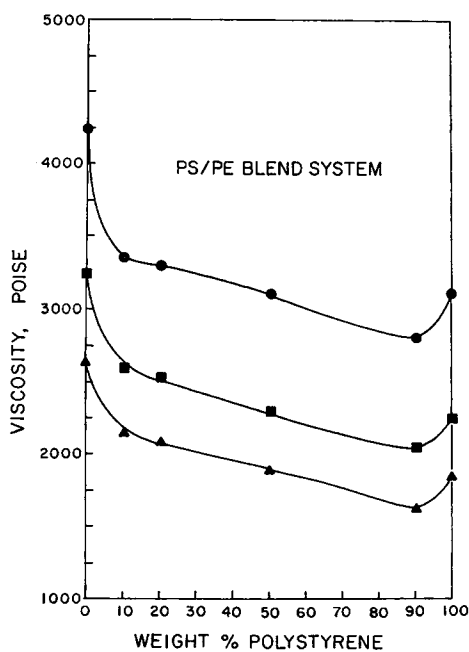


Fig. 7. Viscosity vs. blending ratio for polystyrene/polyethylene systems ( $T = 200^{\circ}\text{C}$ ):  
 (●)  $\dot{\gamma} = 200 \text{ sec}^{-1}$ ; (■)  $\dot{\gamma} = 300 \text{ sec}^{-1}$ ; (▲)  $\dot{\gamma} = 400 \text{ sec}^{-1}$ .

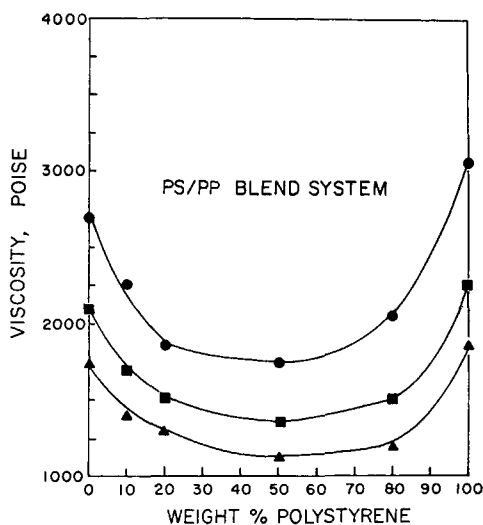


Fig. 8. Viscosity vs. blending ratio for polystyrene/polypropylene systems ( $T = 200^\circ\text{C}$ ): (●)  $\dot{\gamma} = 200 \text{ sec}^{-1}$ ; (■)  $\dot{\gamma} = 300 \text{ sec}^{-1}$ ; (▲)  $\dot{\gamma} = 400 \text{ sec}^{-1}$ .

mer are of the same order of magnitude. Yet the melt flow viscosities of the two-phase systems appear to suggest a kind of lubricating effect of a component present in a small quantity. For example, in the polystyrene/polyethylene system, it is interesting to see that the addition of 10 wt-% polyethylene (more viscous) to 90 wt-% polystyrene (less viscous) reduces the viscosity of the two-phase system considerably, in fact, to a value lower than that of polystyrene alone.

### Effect of Blending Ratio on the Melt Elasticity of Two-Phase Systems

The elastic behavior of the two-phase systems was examined, as in the case of homopolymer systems, in terms of the exit pressure (see part I of this series for details).

Plots of exit pressure versus shear stress are shown for polystyrene/polyethylene systems in Figure 9, and for polystyrene/polypropylene systems in Figure 10. It is seen that all two-phase systems follow a power law, as in the case of homopolymer systems, at least in the range of the shear rate tested. In order to see the effect of blending ratio on the elastic behavior of two-phase systems, cross plots of Figure 9 are prepared in Figure 11 for polystyrene/polyethylene systems and in Figure 12 for polystyrene/polypropylene systems. Note that the plots shown in Figures 11 and 12 are for fixed values of shear stress, instead of shear rate. The reason is that plots of exit pressure versus shear stress, instead of exit pressure versus shear rate, are believed to be more useful for evaluating the melt elasticity of different materials in a relative sense.

Now it is interesting to observe from Figure 11 that in the polystyrene/-



polyethylene system, there is a minimum value for melt elasticity at the blending ratio of 10 wt-% polystyrene/90 wt-% polyethylene, and a maximum value for melt elasticity at the blending ratio of 90 wt-% polystyrene/-10 wt-% polyethylene. On the other hand, for the two-phase system of

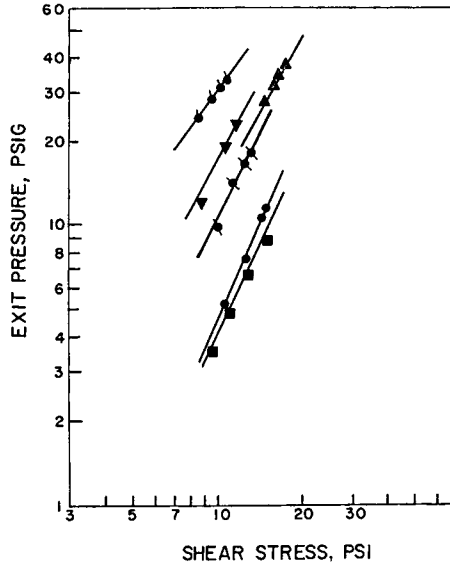


Fig. 9. Exit pressure vs. shear stress for polystyrene/polyethylene systems ( $T = 200^{\circ}\text{C}$ ). Symbols same as in Fig. 3.

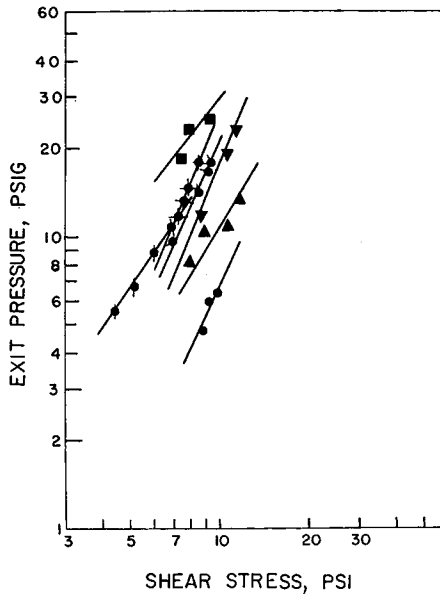


Fig. 10. Exit pressure vs. shear stress for polystyrene/polypropylene systems ( $T = 200^{\circ}\text{C}$ ). Symbols same as in Fig. 4.

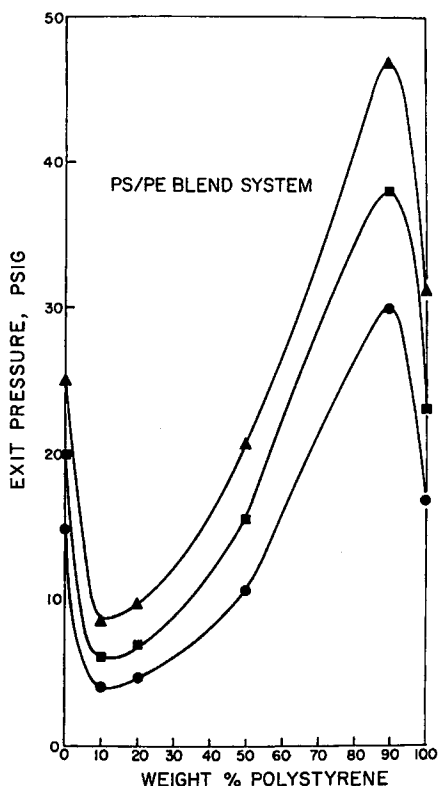


Fig. 11. Exit pressure vs. blending ratio for polystyrene/polyethylene systems ( $T = 200^\circ\text{C}$ ): (●)  $\tau_w = 10$  psi; (■)  $\tau_w = 12$  psi; (▲)  $\tau_w = 14$  psi.

polystyrene/polypropylene, Figure 12 shows two maxima in its melt elasticity at the blending ratio of 10 wt-% polyethylene/90 wt-% polypropylene and 80 wt-% polystyrene/20 wt-% polypropylene, respectively, and a minimum value for melt elasticity at the blending ratio of 20 wt-% polystyrene/80 wt-% polypropylene. This rather unexpected behavior in melt elasticity of two-phase systems has recently been reported by Hill and Maxwell,<sup>8</sup> who used a rotational type of rheometer. Considering that two entirely different experimental techniques have yielded a very similar result in melt elasticity of two-phase systems, the authors believe that the results shown in Figures 11 and 12 are characteristic of the two-phase systems concerned.

In passing, it is also worth noting that the authors have observed anomalous behavior in die swell of the two-phase system investigated at certain blending ratios. In other words, the die swell ratio of the two-phase system studied seems to be consistent with the measurements of exit pressures, although measurements of die swell were not taken in the study reported here. Note that one of the authors (Han<sup>9</sup>) reported earlier that a clear correlation exists between die swell ratio and the exit pressure for homo-

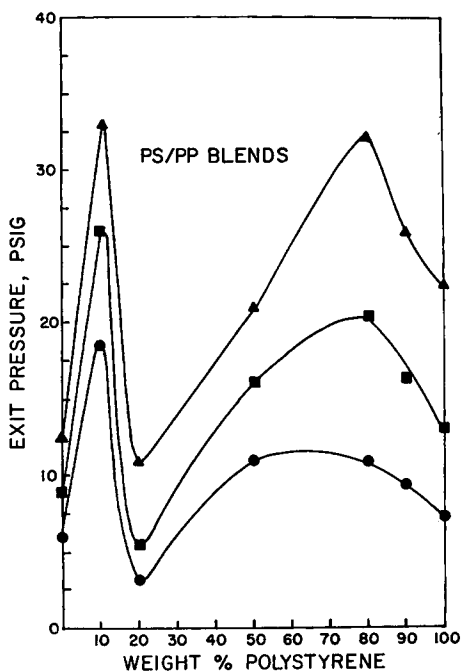


Fig. 12. Exit pressure vs. blending ratio for polystyrene/polypropylene systems ( $T = 200^\circ\text{C}$ ): (●)  $\tau_w = 7$  psi; (■)  $\tau_w = 9$  psi; (▲)  $\tau_w = 11$  psi.

polymer systems. At present, the authors have taken steps to make measurements of die swell and exit pressure under wide ranges of operating conditions (such as temperature and throughput rate) in order to investigate if such a correlation as observed in homopolymer systems exists for two-phase systems.

### State of Dispersion of Two-Phase Systems

It is generally believed that incompatibility prevails for two chemically dissimilar polymers in the molten state. Hence, the two systems considered in this paper are easily conceivable as incompatible (polystyrene/polyethylene and polystyrene/polypropylene), because the structure of polystyrene (containing benzene rings) belongs to the aromatic group, while both polyethylene and polypropylene contain straight carbon chains belonging to the aliphatic group. Besides incompatibility of the two-phase systems chosen for study, it is worth noting that one component in each system (polystyrene) is an amorphous polymer, while the other component (polyethylene and polypropylene) is a crystalline polymer. In other words, a choice of a two-phase system consisting of an amorphous polymer and a crystalline polymer is of particular interest to us from the standpoint of studying polymer morphology.

In the present study, extrudate samples were collected from each experimental run, and later microstructures of extrudate samples were examined

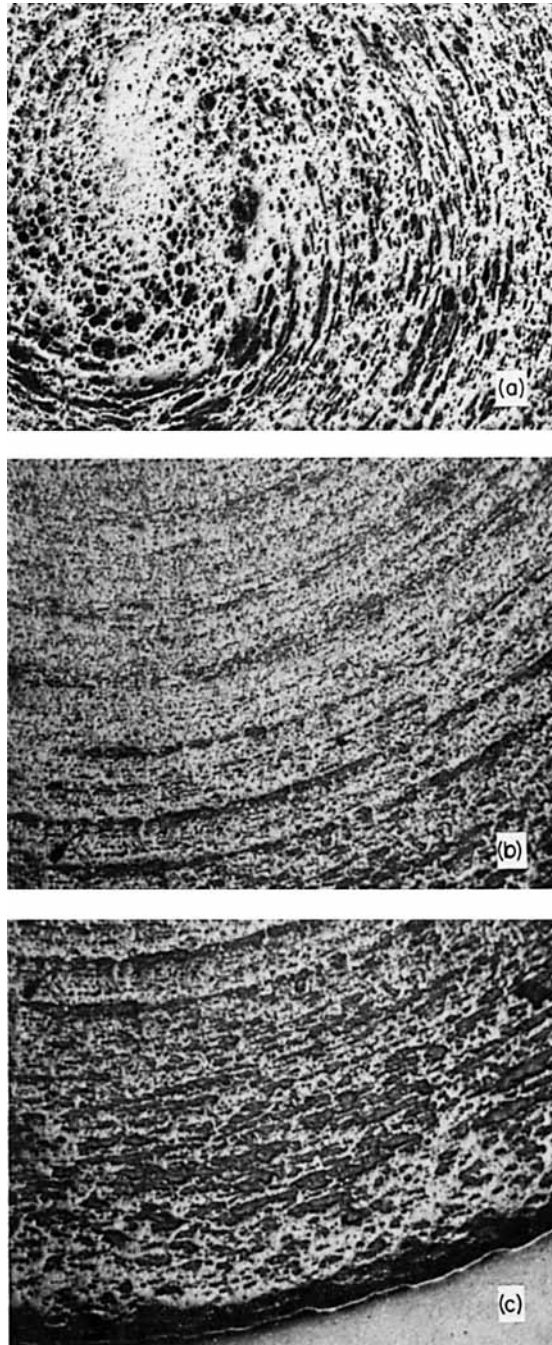


Fig. 13. Pictures ( $100\times$ ) of extrudate cross section for 20% polystyrene/80% polyethylene system: (a) center portion; (b) middle portion; (c) edge portion. Shear rate:  $664 \text{ sec}^{-1}$ ;  $T = 200^\circ\text{C}$ .

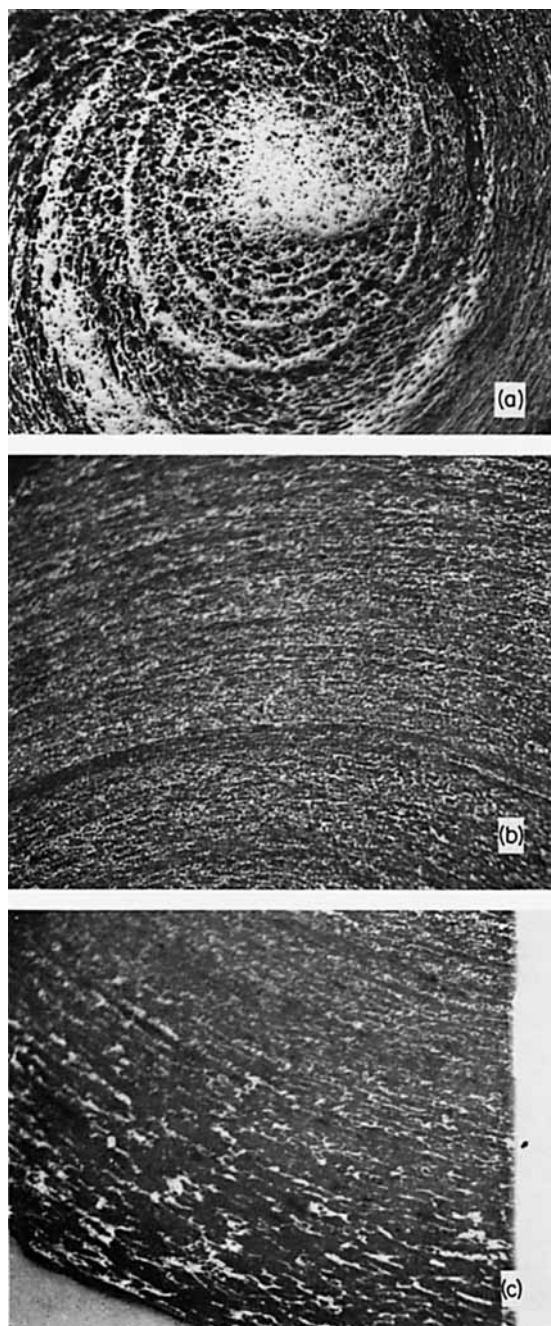


Fig. 14. Pictures ( $100\times$ ) of extrudate cross section for 50% polystyrene/50% polyethylene system: (a) center portion; (b) middle portion; (c) edge portion. Shear rate:  $684 \text{ sec}^{-1}$ ;  $T = 200^\circ\text{C}$ .

by taking pictures of the extrudate cross section. Figure 13 shows pictures of the extrudate cross section of a 20 wt-% polystyrene/80 wt-% polyethylene system at a shear rate of  $664 \text{ sec}^{-1}$  and at  $200^\circ\text{C}$ . Figure 13a shows the center portion, Figure 13b the middle portion, and Figure 13c the edge of the cross section. In order to take pictures, samples were mounted in epoxy (room temperature cure) and subsequently ground and polished to a  $0.3\text{-}\mu$  finish. Samples were then photographed in reflection in order to obtain the in situ distribution of the components. The polystyrene phase was then dissolved with xylene in an ultrasonic cleaning bath (1 min). In this way the polyethylene phase remains to provide positive identification of the two phases. It is seen from these pictures that polystyrene forms the discrete phase and polyethylene, the continuous phase. Figure 14 shows pictures of the extrudate cross section of a 50 wt-% polystyrene/50 wt-% polyethylene system at a shear rate of  $684 \text{ sec}^{-1}$  and at  $200^\circ\text{C}$ . Note that all these pictures were taken under  $100\times$  magnification.

Two interesting observations can be made in reference to the extrudate pictures shown in Figures 13 and 14. First, at the center portion of the extrudate cross section is seen the clear vortex. Note that the white portions of Figures 13a and 14a are the areas where polystyrene is removed by being dissolved with xylene. Hence, it can be said that polyethylene forms the vortex in these instances. However, which component of the polystyrene/polyethylene system forms the vortex appears to depend on the melt temperature, and hence on the melt viscosity, of the individual component. Secondly, it is seen from Figures 13 and 14 that a finer dispersion appears to occur near the center than near the edge. This seems to be attributable to the fact that the velocity of the melt is higher near the center.

It would also be interesting to see the length of the center vortex in a longitudinal direction. Figure 15 shows the center portion of the vortex of the 50 wt-% polystyrene/50 wt-% polyethylene system at shear rate  $684 \text{ sec}^{-1}$  and at  $200^\circ\text{C}$ . It appears from this picture that some material fractionation is occurring. One can further say that the extrudate structure appears to have broken down somewhat during cooling, because one can see many droplets in a row in the longitudinal direction.

It must be pointed out that the present study reported here was directed mainly to the measurement of wall normal stress distributions rather than to the state of dispersion of two-phase systems. VanOene<sup>4,10</sup> has recently carried out an extensive study on the dispersion of two-phase molten polymer systems and has attempted to explain the two different types of dispersion, i.e., fiber formation and stratification, by the use of such thermodynamic variables as free energy.

We have taken pictures of polystyrene/polypropylene systems of five blending ratios. However, because of the limited space available here,

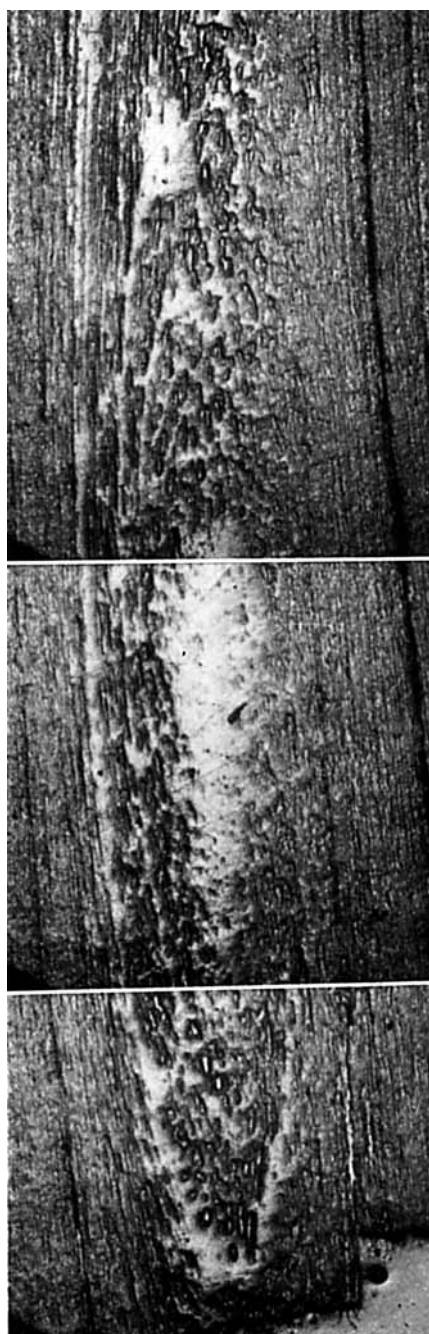
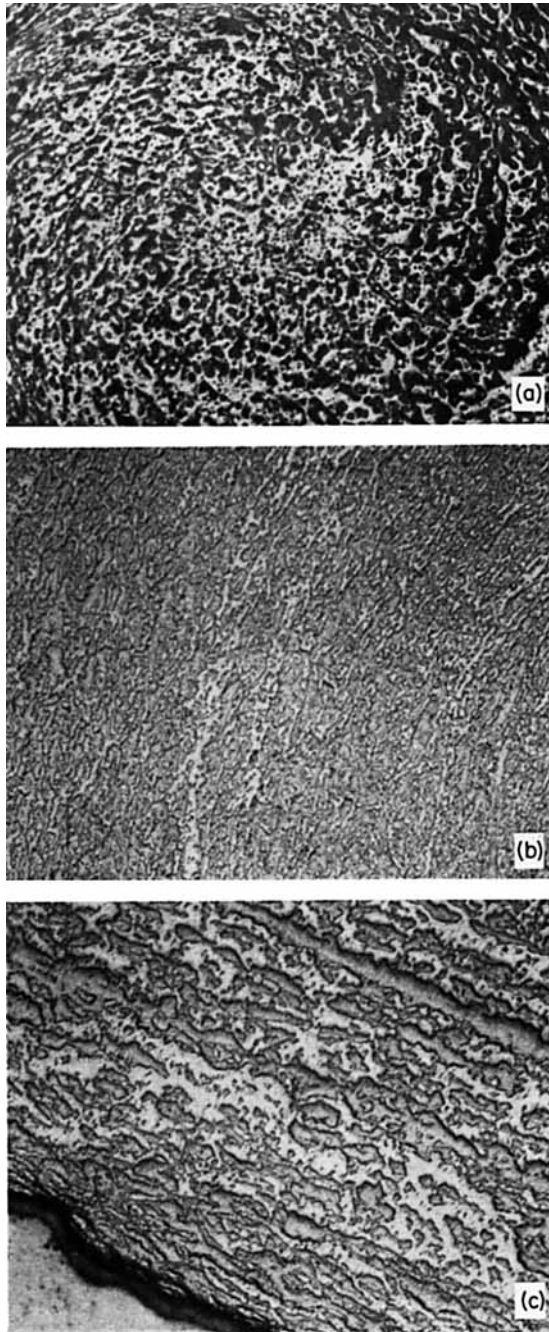


Fig. 15. Pictures (100 $\times$ ) of extrudate sample in the longitudinal direction for 50% polystyrene/50% polyethylene system. Shear rate 684 sec<sup>-1</sup>;  $T = 200^{\circ}\text{C}$ .



**Fig. 16.** Pictures ( $200\times$ ) of extrudate samples of 50% polystyrene/50% polypropylene system: (a) center portion of the cross section; (b) middle portion of the cross section; (c) edge portion in the longitudinal direction. Shear rate:  $589\text{ sec}^{-1}$ ;  $T = 200^\circ\text{C}$ .



only pictures of the 50 wt-% polystyrene/50 wt-% polypropylene system are shown in Figure 16. The extrudate sample was collected at a shear rate of  $589 \text{ sec}^{-1}$  and at a melt temperature of  $200^\circ\text{C}$ . The pictures shown are magnified  $200\times$ . It is interesting to see here that there is a very mild vortex at the center portion (Fig. 16a) in this case, compared to that of the same blending ratio of polystyrene/polyethylene shown in Figure 14. Note that polystyrene forms the discrete phase and polypropylene forms the continuous phase. The middle portion of the extrudate cross section (Fig. 16b) shows a finer dispersion, and the edge portion (Fig. 16c) shows some kind of droplet formation which appears to be due to the breakdown of the extrudate structure during cooling.

Now the difference in the dispersion state between the polystyrene/polyethylene system and the polystyrene/polypropylene system (particularly with reference to the center portion of the extrudate cross section, see Figs. 14a and 16a) appears to depend on the melt viscosities of individual components at a given temperature. For instance, in the polystyrene/polyethylene system at  $200^\circ\text{C}$ , polyethylene melt is much more viscous than polystyrene melt, as may be seen from Figure 7. Therefore, at a 50/50 blending ratio, the two-phase system has one component (polyethylene) much more viscous than the other component (polystyrene). On the other hand, in the polystyrene/polypropylene system at  $200^\circ\text{C}$ , the

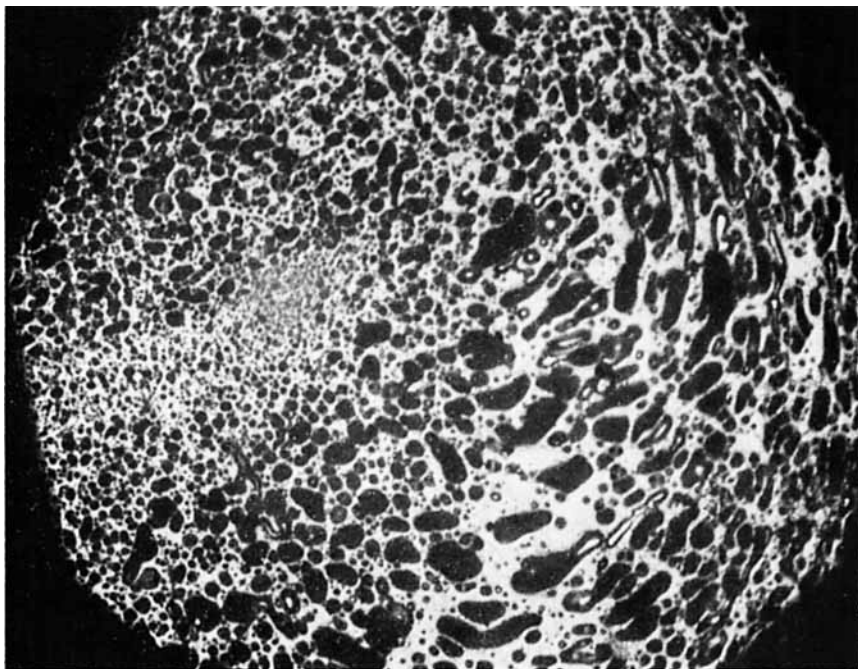


Fig. 17. Picture ( $200\times$ ) of the extrudate cross section (center portion) for 50% polystyrene/50% polyethylene system. Shear rate:  $640 \text{ sec}^{-1}$ ;  $T = 220^\circ\text{C}$ .

viscosities of individual components are not much different from each other, and, in fact, at a 50/50 blending ratio the two-phase system shows a minimum viscosity value (lower than the viscosities of individual components), as shown in Figure 8.

Perhaps a more interesting picture might be the one shown in Figure 17, which is the center portion of the extrudate cross section for the 50 wt-% polystyrene/50 wt-% polyethylene system at 220°C melt temperature. This picture shows no vortex, while the sample at 200°C shows a conspicuous vortex at the center of the extrudate cross section, as can be seen in Figure 14a. Furthermore, at 220°C, the two-phase system has polystyrene as continuous phase (white portion in the picture) and polyethylene as discrete phase (black portion of the picture), which is quite opposite to the situation at 200°C.

One should note, however, that the state of dispersion of extrudate samples in any blending system depends on the method of blending and also on the pellet size of the individual components. As may be surmised, the use of powder instead of pellets is believed to give a much finer dispersion in the extrudate of two-phase systems. However, VanOene<sup>4,10</sup> has found that, even using powder, and however fine a dispersion one may get, the extrudates have vortices, just as if pellets were used.

In summary, there is still very much to be learned about the complicated flow behavior of two-phase systems of molten polymers. It is believed that a better understanding of two-phase systems will be of considerable help to industry in the development of new products and the improvement of product quality.

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