

## Morphology and Mechanical Properties of Injection-Molded Specimens of Two-Phase Polymer Blends

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### Synopsis

An experimental study was carried out to investigate the moldability of polymer blends which form two phases in the molten state and the effect of mixing on the morphology and mechanical properties of molded specimens. Blends of polystyrene with polypropylene and blends of polystyrene with high-density polyethylene were used for this study. A plunger-type injection molding machine (Van Dorn) was employed for molding specimens. To improve the mixing performance of the plunger machine, a Static Mixer (Kenics Corp., Super Nozzle) was installed between the heating cylinder and the sprue. A number of different molding conditions (injection pressure, temperature, injection time, cooling time) were varied, and molded specimens were collected under each molding condition. The specimens were used for studying the degree of dispersion in the blends and for determining the mechanical properties. A differential thermal analysis (DTA) experiment was also carried out to determine the degree of dispersion of the blends in molded specimens. It was found that a linear correlation exists between the blend composition and thermal spectra area of the blends tested.

### INTRODUCTION

In recent years, there has been a growing interest in the polymer processing industry with injection molding of blends of two or more polymers or a polymer containing an additive (or additives) as a processing aid.

Injection molding of two thermoplastic polymers, for instance, brings about an interesting processing problem; namely, it is difficult to achieve good dispersion of one polymer in another. It is essential to have good mixing to obtain a product with uniform mechanical/physical properties. Therefore, as may be surmised, the use of an effective mixing device is very important in producing a product of acceptable quality. During the past decade, a number of researchers<sup>1-5</sup> have made attempts to better understand the effect of injection molding conditions on the morphology and mechanical/physical properties of injection molded specimens of homopolymers. But, relatively little has been published dealing with the morphology and mechanical properties of two-phase polymeric systems.

Injection molding of thermoplastic polymers involves applying heat to melt the material in the heating cylinder and removing this heat while the molded specimen is in the mold. Hence, the rate of heat transfer is very important in determining the cycle time. It should be noted that the important thermal properties of polymers in injection molding are melting and softening points,

specific heats, heat of fusion, and thermal conductivity. In mixing two molten polymers, the thermal properties of the individual polymers have a profound influence on the moldability of the resulting blend.

When a material is melted (or is heated above its glass transition temperature), it will flow under pressure from the heating cylinder (or torpedo section) into the mold cavity through the gate. In the case of polymer blends, it is necessary for the blend to be well mixed before it is injected into the mold cavity because no additional mixing is expected to take place within the mold cavity. Good mixing is essential, particularly when two (or more) polymers in a blend are incompatible in the molten state. To achieve good mixing and dispersion, the screw-plunger machine is expected to do far more satisfactory work than the plunger machine.

Very recently, the authors undertook a study of injection molding blends of two thermoplastics, namely, blends of polystyrene with polypropylene over a wide range of molding conditions. The primary objectives of the study were (i) to find the optimal molding conditions of the polymer blends chosen for study, (ii) to study the effect of various mixing devices on the state of dispersion of one polymer in another and on the mechanical properties of the molded specimens, and (iii) to study the effect of the blend composition on the mechanical properties.

It was found that the use of a Static Mixer in the plunger machine improved the mixing of two incompatible polymers considerably, compared to the use of the plunger machine alone. In order to simulate the screw-plunger machine, a 1-in. single-screw extruder was used to extrude flat films of the polymer blends. The extruded films were chopped into small pieces and were subsequently fed to the plunger machine with and without a Static Mixer. A twin-screw compounding machine was also employed to prepare polymer blends which were then injection molded using the plunger machine. In this way, it was possible to investigate the effect of various mixing devices on the morphology and mechanical properties of the injection-molded specimens. For the polymer blends investigated, it was found that the use of a Static Mixer with the plunger machine is as effective as the use of the screw-plunger machine. In this paper, we shall present some representative results of the study.

## EXPERIMENTAL

### Apparatus and Mixing Devices

The machine used for this study is a plunger injection molding machine (Van Dorn). A commercially available nonmoving-part mixing device, a Static Mixer (Kenics Corp., Super Nozzle), was installed between the heating cylinder and the sprue section to improve the extent of mixing. Figure 1 shows a schematic of the layout of the major parts of the machine, and Figure 2 shows a photograph of the cross section of the Static Mixer. Details of the design of the Static Mixer are described elsewhere.<sup>6</sup>

Injection molding experiments were carried out over a wide range of injection pressure, cylinder temperature, injection time, and cooling time, as shown in Table I.

The mold used was rectangular, being 2.5 in. long, 0.5 in. wide, and 0.1 in. deep,

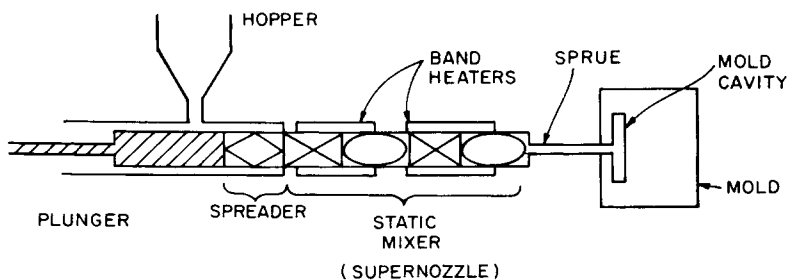


Fig. 1. Schematic of the heating cylinder section modified with a Static Mixer.

and was kept at constant temperature by circulating cold water through the channels surrounding it. The cylinder section, inline mixing device, and sprue section were heated by automatically controlled band heaters. During the experiment, residence time was well controlled. Ten specimens were collected during each run for determining the mechanical/physical properties and for studying morphology of the blends.

In order to simulate a screw-plunger injection molding machine, which was not available at the time of experiment, blends of polystyrene and polypropylene were first extruded through a film die with the aid of a single-screw extruder. The extruded films were then chopped into flakes and injection molded using the plunger machine with and without a Static Mixer. In this way, we were able to investigate the effect of additional mixing on the morphology and mechanical properties of specimens. We also prepared blends of polypropylene and polystyrene using a twin-screw compounding machine (Werner Pfleiderer Corp., ZSK/53L) and then injection-molded specimens using the plunger machine. Figure 3 summarizes the five different mixing devices which were used in preparing injection-molded specimens.

### Materials and Their Rheological Properties

The materials used were blends of polystyrene (Dow Chemical Co., Styron 686) with polypropylene (Exxon Chemical Co., E115) and blends of polystyrene with high-density polyethylene (Union Carbide Corp., DMDJ 4309). Blends of various weight percentages were prepared by tumbling the materials in the form of pellets. Table II gives the molecular characteristics of the homopolymers.

The rheological properties of the homopolymers and blends were determined by use of the slit rheometer developed earlier by Han.<sup>7</sup> Figures 4 and 5 give plots of melt viscosity versus blending ratio for polypropylene/polystyrene blends and high-density polyethylene/polystyrene blends, respectively.

### Measurement of Mechanical/Physical Properties

All specimens for physical testing were aged for a minimum of one week at laboratory conditions prior to testing. For determining stress-strain properties, the ASTM-D-638-68 was followed.<sup>8</sup> The Instron testing machine was used at the following conditions: room temperature at  $23^\circ \pm 1^\circ\text{C}$ ; relative humidity at  $55\% \pm 5\%$ ; speed of testing, 0.4 in./min; distance between grips, 1 in.

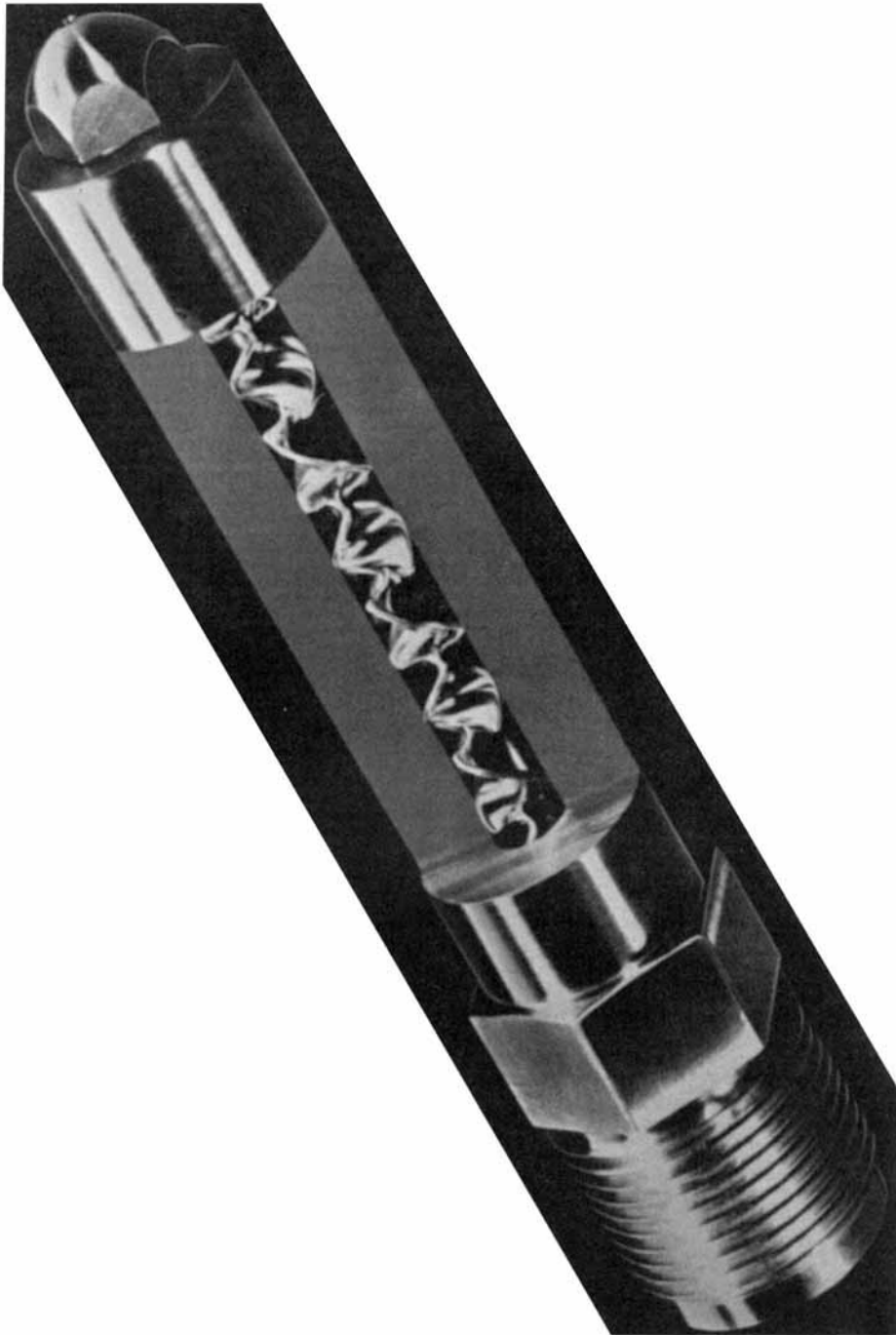


Fig. 2. Schematic describing the flow patterns in a Static Mixer supernozzle.

Since the tensile properties of a specimen depend upon the molding conditions,<sup>2,4</sup> specimens molded under the following conditions were used for measurements of tensile properties: cylinder temperature, 450°F; injection pressure, 100 psi; injection time, 5 sec for PP/PS blends and 10 sec for HDPE/PS blends;

TABLE I  
Injection Molding Conditions Employed

Molding variable	Range
Cylinder temperature	300–500 °F
Injection pressure	500–1500 psi
Injection time	1–40 sec
Cooling time	1–60 sec

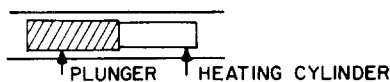
TABLE II  
Molecular Characteristics of Polymers Used

Polymer	Sample code	Melt index	$\bar{M}_n$	$\bar{M}_w$	Manufacturer
Polystyrene (PS)	Styron 686	2.5	$1.02 \times 10^5$	$2.38 \times 10^5$	Dow Chemical
High-density polyethylene (HDPE)	DMDJ 4309	0.2	$2.0 \times 10^3$	$1.68 \times 10^5$	Union Carbide
Polypropylene (PP)	E115	5.0	$4.08 \times 10^4$	$4.44 \times 10^5$	Exxon Chemical

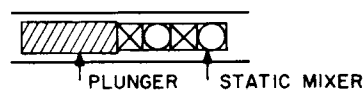
cooling time, 12 sec for PP/PS blends and 16 sec for HDPE/PS blends. The specimens were tested with the stress applied parallel to flow direction.

For shrinkage measurement, the ASTM-D-955-51 was followed,<sup>8</sup> and for

(a) PLUNGER MACHINE



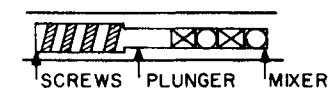
(b) PLUNGER/MIXER



(c) SCREW-PLUNGER MACHINE



(d) SCREW-PLUNGER/MIXER



(e) TWIN-SCREW MACHINE

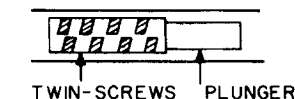


Fig. 3. Schematic of different types of mixing device used.

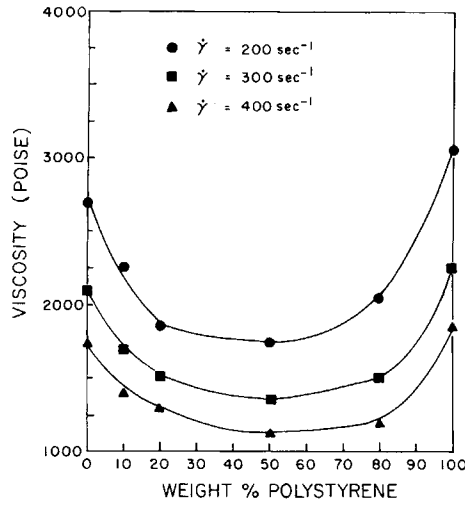


Fig. 4. Viscosity vs. blending ratio for the blends of polypropylene and polystyrene at 200°C.

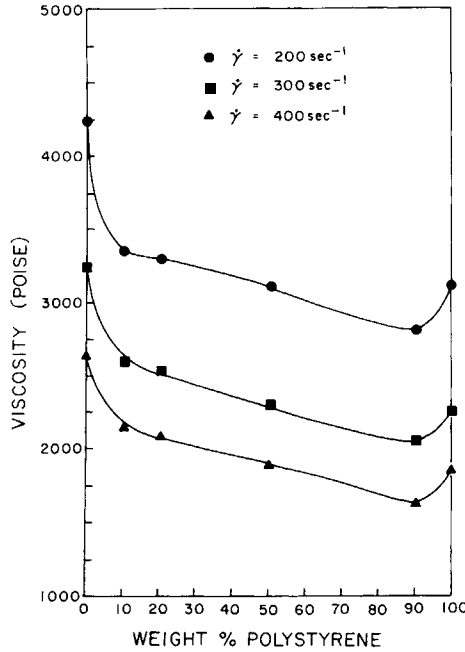


Fig. 5. Viscosity vs. blending ratio for the blends of high-density polyethylene and polystyrene at 200°C.

hardness measurement, the ASTM-D-2240-68 was used.<sup>8</sup> The measurements were made on the same specimens as those used for tensile measurements.

### Solvent Leaching and Microscopy

Micrographs were taken after specimens were first mounted in epoxy (room temperature cure) and then ground and polished. The polystyrene phase was

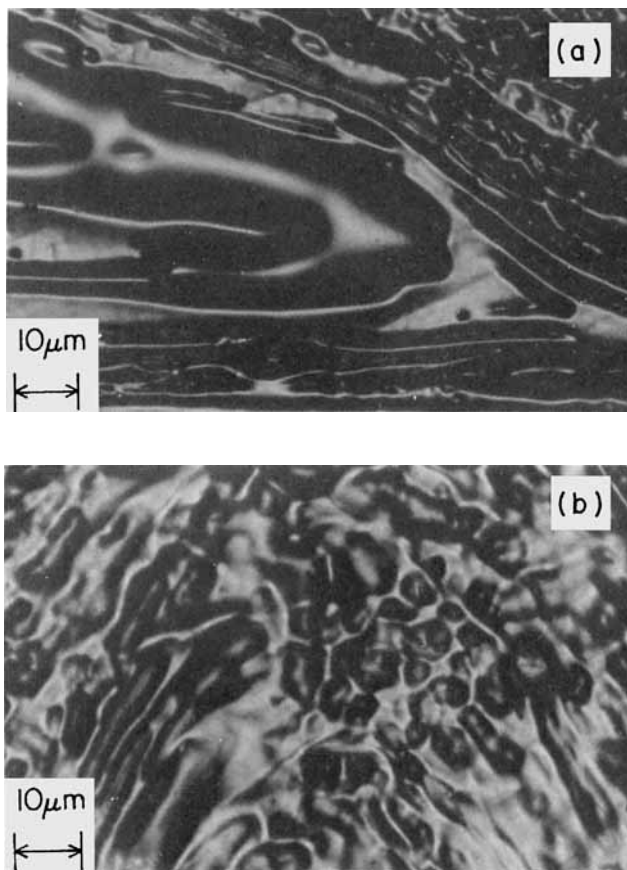


Fig. 6. Photomicrographs of the cross section of the specimens of PS/PP = 60/40: (a) plunger; (b) plunger/Static Mixer.

then dissolved with toluene. In this method, the polypropylene phase remains to provide positive identification (white area) of the two phases. Note that the dark area represents the polystyrene phase and the white area represents the polypropylene phase. Similarly, in the specimens of the polyethylene/polystyrene blend, the polystyrene phase was dissolved with toluene, giving rise to the dark area, whereas the polyethylene phase was seen as the white area when viewed under the microscope. Photomicrographs were then taken using incident light to observe the in situ distribution of the components, with the aid of an optical microscope.<sup>9-11</sup>

### Differential Thermal Analysis

Differential thermal analysis (DTA) was carried out to examine the degree of dispersion, using a du Pont instrument. The DTA instrument was heated at a rate of 10°C/min in nitrogen atmosphere. The range of temperature tested was 25° through 300°C. Test samples of polystyrene/polypropylene blends were prepared by means of the ice-grinding technique. Each sample weighed approximately 0.1 mg.

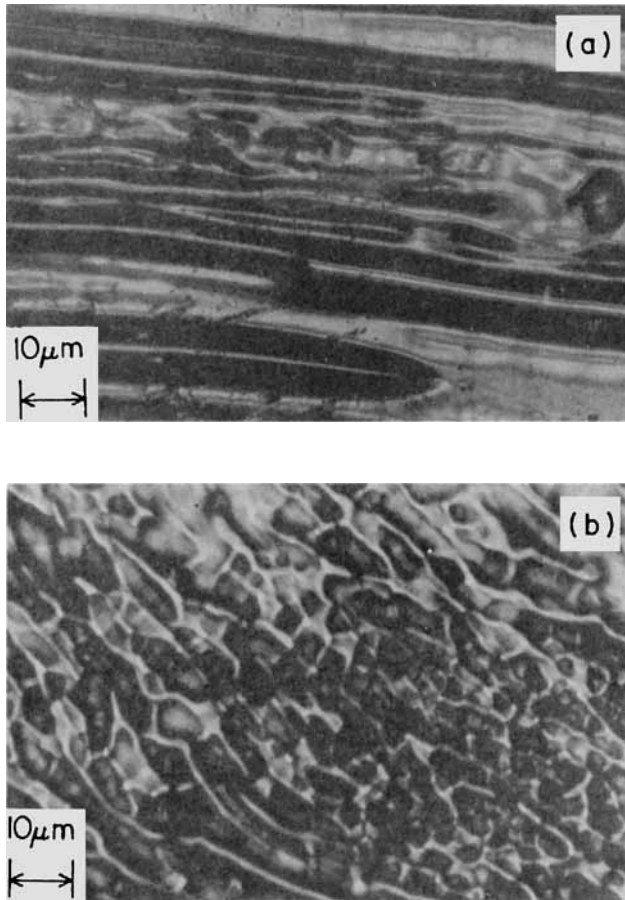


Fig. 7. Photomicrographs of the cross section of the specimens of PS/HDPE = 60/40: (a) plunger; (b) plunger/Static Mixer.

## RESULTS AND DISCUSSION

### Molding Characteristics of Polymer Blends

The criteria used for determining the optimal molding conditions were as follows: the condition at which melt flows easily without being frozen at the sprue; and the condition at which there is little flushing of the resin, easy ejection, little distortion, good surface, and minimum warpage of the molded article.

Considering the pseudoplastic flow behavior of thermoplastic polymers, we expect that, over the range of shear rates encountered in the sprue, the melt viscosity will be decreased by increasing the injection pressure. Consequently, as the melt viscosity decreases, the filling time will be decreased. This is of particular interest to injection molding polymer blends that give rise to viscosities lower than the viscosity of individual homopolymers. Note in Figure 4, for instance, that blends of polypropylene and polystyrene give rise to viscosities lower than the viscosities of polypropylene and polystyrene.<sup>9-11</sup> In such a situation,



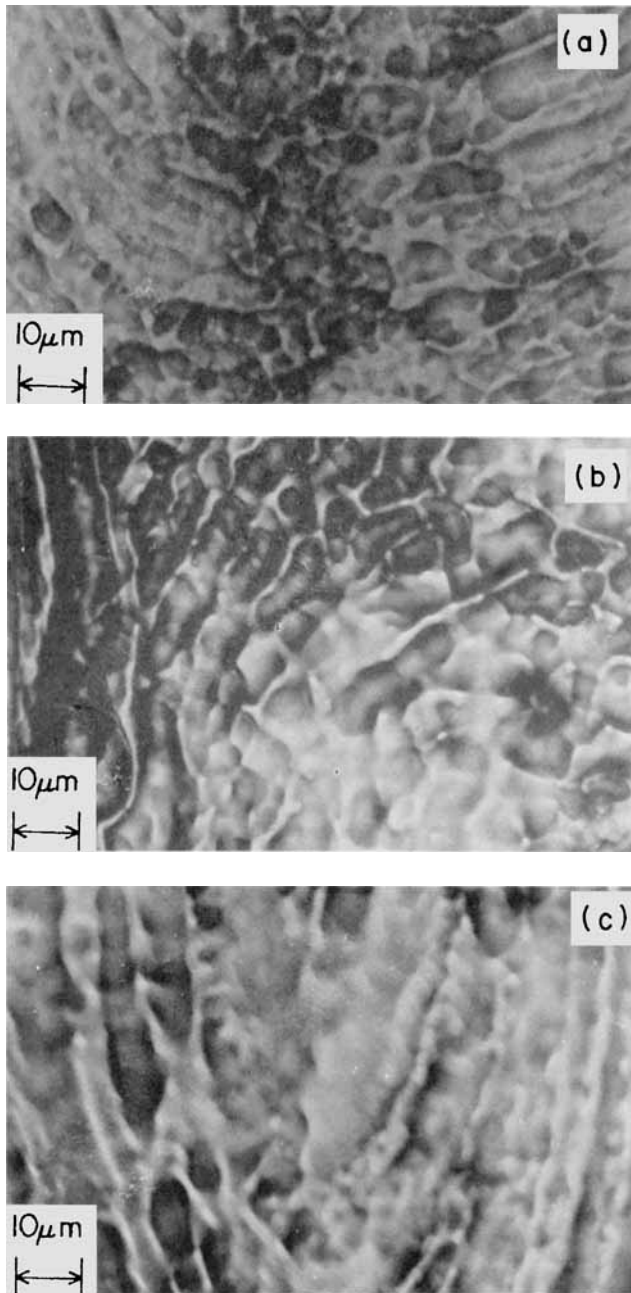


Fig. 8. Photomicrographs of the cross section of the specimens of PS/PP = 75/25: (a) screw/plunger; (b) screw/plunger/Static Mixer; (c) twin screw.

one may be able to use an injection pressure for the blends much lower than that for either polypropylene or polystyrene, without necessarily lowering the molding temperature. Therefore, measurements of the flow properties of polymers will help to choose optimal molding conditions.

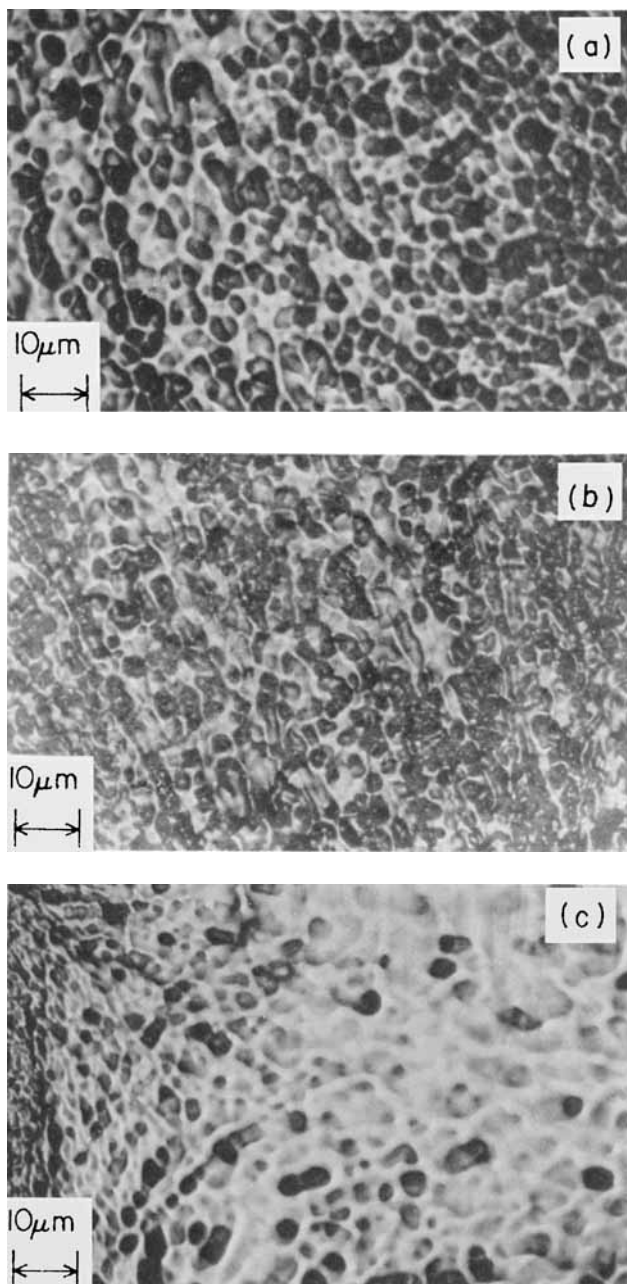


Fig. 9. Photomicrographs of the cross section of the specimens of PS/PP = 50/50: (a) screw/plunger; (b) screw/plunger/Static Mixer; (c) twin screw.

### Morphology of Polymer Blend Specimens

Figure 6 illustrates the microstructure observed in cross section of injection-molded specimens of a blend of 60 wt % polystyrene/40 wt % polypropylene. Similar observation can also be made in Figure 7, which gives similar photomicrographs for a blend of 60 wt % polystyrene/40 wt % high-density polyethylene.

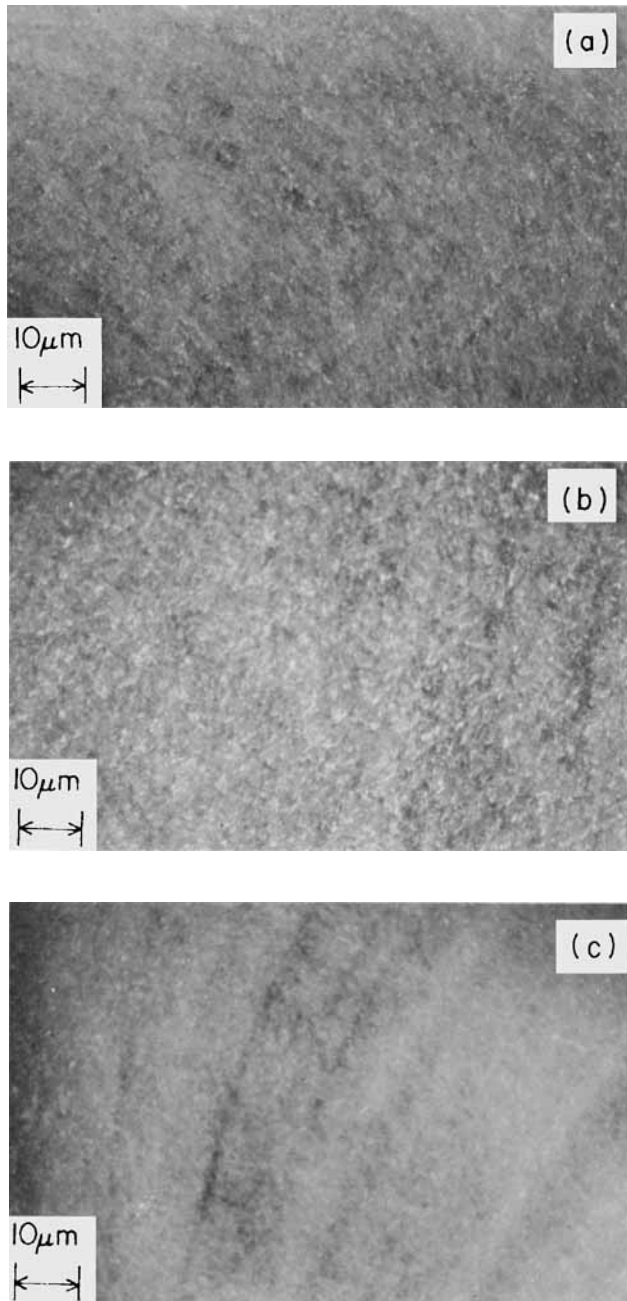


Fig. 10. Photomicrographs of the cross section of the specimens of PS/PP = 25/75: (a) screw/plunger; (b) screw-plunger/Static Mixer; (c) twin-screw.

It is to be noted that the polystyrene phase (dark area) is dispersed in the high-density polyethylene phase (white area). It is clearly seen in Figures 6 and 7 that the use of a Static Mixer improves mixing considerably.

Similar photomicrographs for a blend of 75 wt % polystyrene/25 wt % polypropylene are given in Figure 8, for a blend of 50 wt % polystyrene/50 wt %

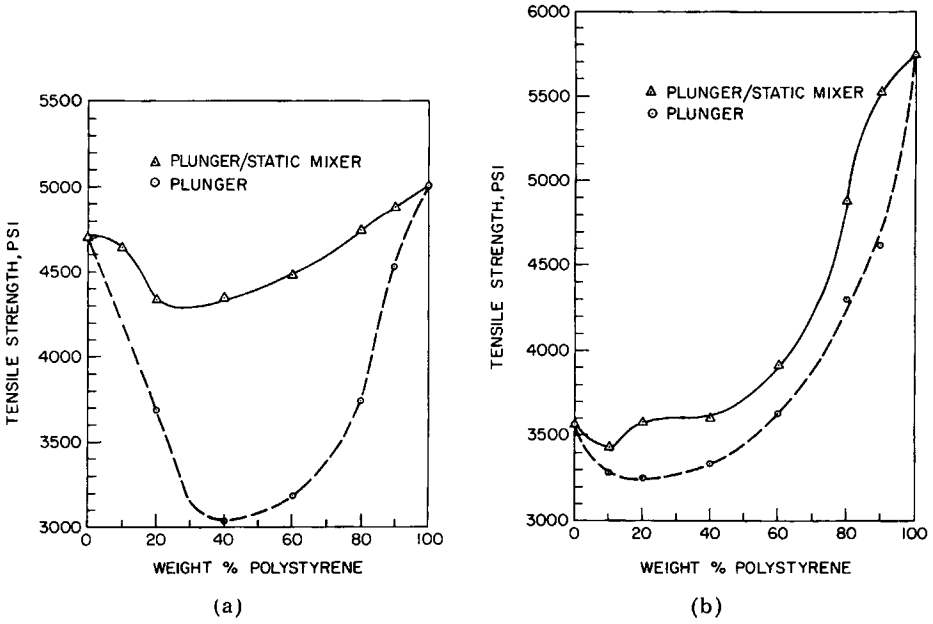


Fig. 11. Tensile strength vs. blending ratio: (a) PP/PS blend; (b) HDPE/PS blend.

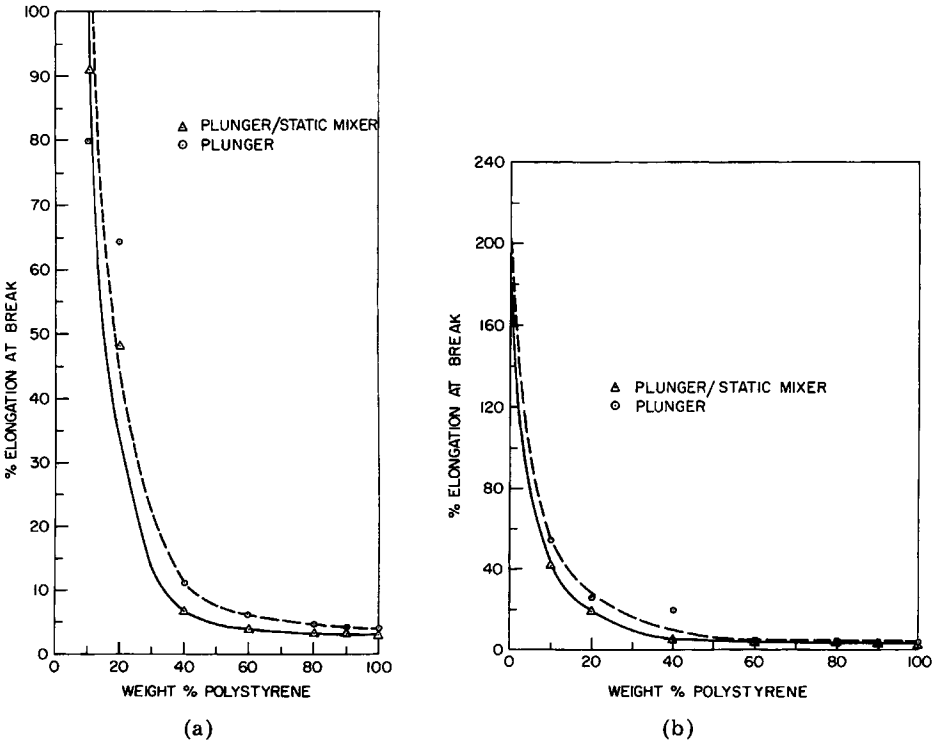
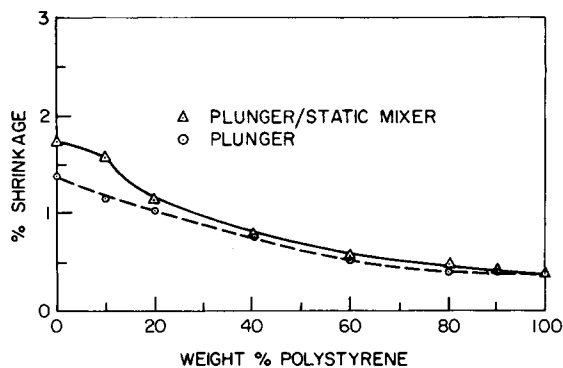
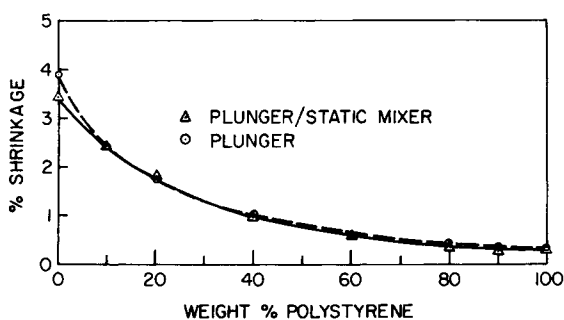


Fig. 12. Percent elongation at break vs. blending ratio: (a) PP/PS blend; (b) HDPE/PS blend.



(a)



(b)

Fig. 13. Shrinkage (per cent) vs. blending ratio: (a) PP/PS blend; (b) HDPE/PS blend.

polypropylene in Figure 9, and for a blend of 25 wt % polystyrene/75 wt % polypropylene in Figure 10. For a given composition of the blends, three mixing devices were used. They are: single-screw/plunger, single-screw/plunger/Static Mixer, and twin-screw/plunger. Comparison of Figures 6b and 8 indicates that the use of a Static Mixer with the plunger machine is as effective as the use of the screw-plunger machine. It is seen that different blending ratios give rise to greatly different degrees of dispersion. These differences are illustrated in Figures 8–10. In the blends of 75 wt % polystyrene/25 wt % polypropylene and 50 wt % polystyrene/50 wt % polypropylene, the polystyrene phase forms the dispersed phase (black area) in the polypropylene phase (white area); however, in the blend of 25 wt % polystyrene/75 wt % polypropylene, it is not clear which of the two components forms the dispersed phase. Thus, the blending ratio is of far greater importance than the mixing device in controlling the mode and degree of dispersion in a blend of two incompatible polymers.

It appears from Figures 8–10 that the state of dispersion obtained with the twin-screw compounding machine is not much different from that obtained with the static mixer, for the particular blends investigated. It is quite possible, however, that the twin-screw compounding machine will do an effective job when there is a large difference in viscosities of individual components to be blended, for instance, in the compounding of a polymer with low-viscosity additives or with solid particles as fillers.

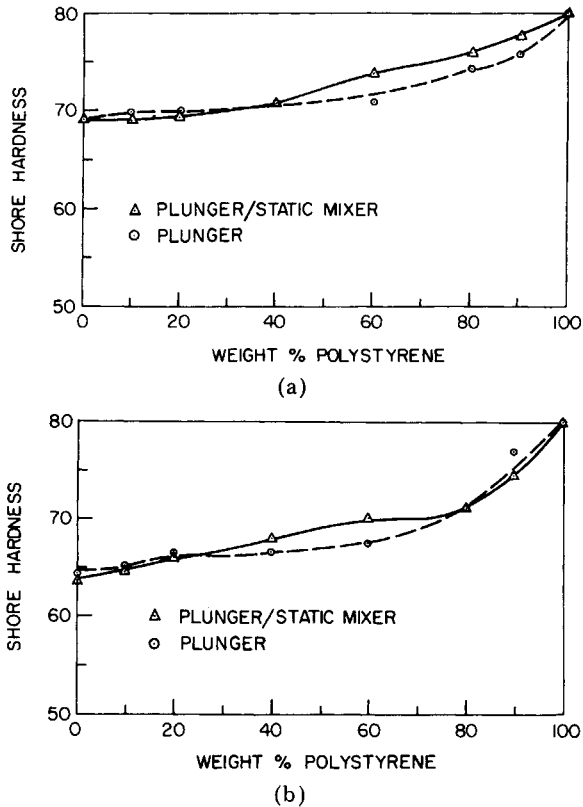


Fig. 14. Shore hardness vs. blending ratio: (a) PP/PS blend; (b) HDPE/PS blend.

### Effect of Mixing on Mechanical Properties of Molded Specimens

In order to observe the degree to which the different mixing devices affected mechanical properties, plots were prepared of various properties measured against blending ratio. First, we compared the effect of a Static Mixer when used together with the plunger machine on the tensile strength, per cent elongation at break, per cent shrinkage, and shore hardness. These results are shown in Figures 11–14.

Figure 11a shows that the tensile strength of PS/PP blends goes through a minimum at approximately 40 wt % polystyrene, indicating that the blends give rise to a tensile strength less than that of individual components (i.e., both polystyrene and polypropylene). However, the plunger machine, when used together with a Static Mixer, gives rise to a tensile strength greater than that obtained by the plunger machine alone. It should be noted that the minimum is still observed, but the transition from PP behavior to PS behavior is smoother. Figure 11b shows that the tensile strength of HDPE/PS blends also goes through a minimum, and that the use of a Static Mixer gives rise to slightly higher tensile strength over the composition range compared to that obtained by use of the plunger machine alone. However, it is seen in Figures 12–14 that other properties tested (per cent elongation at break, per cent shrinkage, and shore hardness) are not much affected by whether or not a Static Mixer is used with the plunger machine.

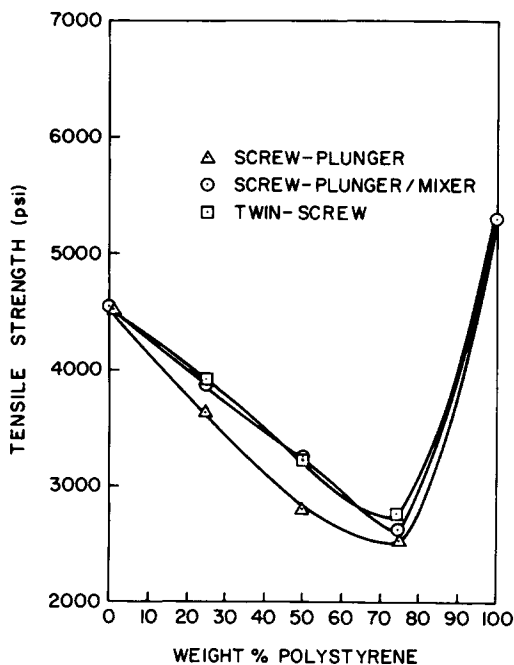


Fig. 15. Tensile strength vs. blending ratio for PP/PS blends.

We now examine the tensile strength of injection-molded specimens obtained by use of the screw/plunger machine with and without a Static Mixer and the twin-screw compounding machine. Figure 15 shows plots of tensile strength versus blending ratio for PP/PS blends. Note that the specimens tested were obtained at molding conditions different from those used in obtaining the specimens for Figure 11. Therefore, it is not possible to make a direct comparison of Figure 11a and Figure 15. This points out that molding conditions influence the mechanical properties of injection-molded specimens considerably, which is consistent with the results of others reported in the literature.<sup>2-4</sup> It is seen in Figure 15 that both the screw/plunger machine with a Static Mixer and the twin-screw machine give rise to a slightly improved tensile strength compared to that obtained by the screw/plunger machine without a Static Mixer. Note also that the use of a Static Mixer together with the screw/plunger machine gives rise to a tensile strength almost identical to that obtained by the twin-screw compounding machine. It is of interest to note in Figure 16 that the per cent elongation at break is fairly insensitive to three different types of mixing devices employed. This is consistent with the data presented above for the plunger machine.

The fact that the tensile strength of the blends is poor compared to the tensile strength of individual homopolymers (see Figs. 11 and 15) may be explained with the aid of photomicrographs. It is seen in Figures 6-10 that the particular blends investigated form two phases in which one component is dispersed in the other component. In view of the fact that polystyrene is incompatible with either polypropylene or polyethylene, there would be no effective molecular bonding between the two components in a blend, and hence the mechanical properties

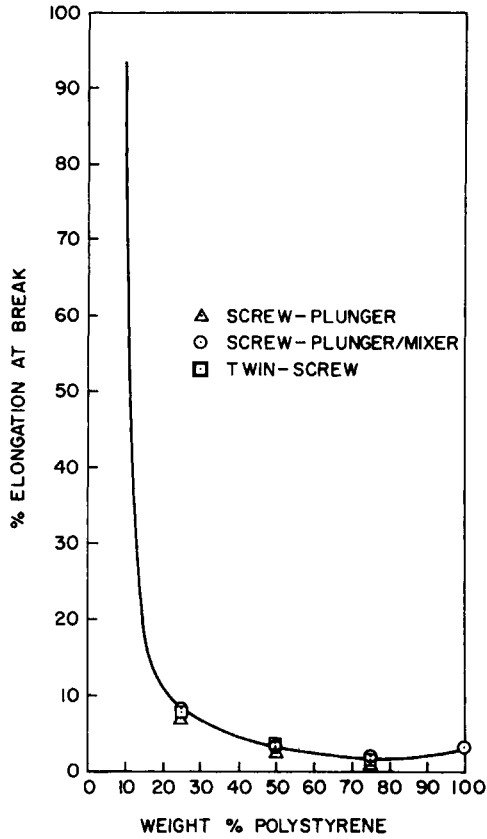


Fig. 16. Per cent elongation at break vs. blending ratio for PP/PS blends.

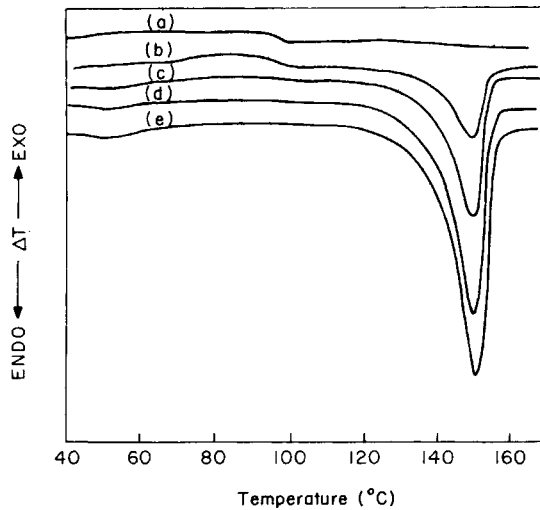


Fig. 17. Differential thermal analysis thermograms of PP/PS blends: (a) 100% PS; (b) PP/PS = 25/75; (c) PP/PS = 50/50; (d) PP/PS = 75/25; (e) 100% PP. Specimens were injection molded using the screw/plunger/Static Mixer system.



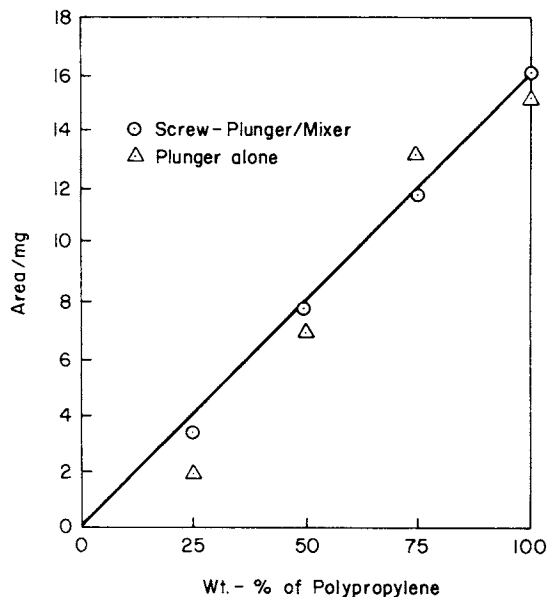


Fig. 18. Peak area in the DTA thermogram vs. blend composition of PP/PS blends.

resulting from such blends would be poorer than those resulting from homopolymers.

### Thermal Analysis of Molded Specimens

Figure 17 shows thermograms of the PP/PS blends. It is seen that the melting point of pure polypropylene shows a very sharp peak; and as the amount of polypropylene in the blend decreases, the peak becomes less sharp. This is as expected from the fact that polystyrene is an amorphous polymer which has no definite melting point.

The weight fraction of the crystalline component (i.e., polypropylene) can be determined from DTA thermograms. Figure 18 summarizes the results. It is of interest to note that the peak area is linearly proportional to the blend composition (i.e., the amount of crystalline polypropylene present in the blend), indicating that a high degree of dispersion was achieved when the PP/PS blends were injection molded by using the screw/plunger/Static Mixer.

For comparison purposes, in Figure 18 we also plot the data of blend samples which was prepared by using the plunger machine alone. As described above, in this case mixing was achieved only by means of the tumbling operation of two homopolymers, polypropylene and polystyrene. In view of the fact that the plunger did a poor job of mixing (see Figs. 6 and 7) while the blend was injection molded, the peak area-composition data deviate from the straight line, indicating that rather poor dispersion was achieved.

In the past, several research groups<sup>12-17</sup> made use of DTA for determining the composition of blends and for characterizing filled polymer systems. The results presented above demonstrate once again that DTA can be used as a rapid and convenient analytical tool to determine the degree of dispersion of polymer blends whose melting points are appreciably different.

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