

The Effect of Mixing on the Modes of Dispersion and Rheological Properties of Two-Phase Polymer Blends in Extrusion

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Synopsis

An experimental study was carried out to investigate the effect of mixing on the state of dispersion and rheological properties in the two-phase flow of polymer blends. For the study, blends of polystyrene and polypropylene were used, and two mixing devices were employed: a single-screw extruder combined with a "static mixer," and a twin-screw compounding machine. Materials of various blending ratios were extruded at a constant temperature (200°C) through a capillary die having an L/D ratio of 20 ($D = 0.125$ in.). The state of dispersion in the two-phase system was investigated from pictures taken of the microstructure of the extrudate samples. It was found that different mixing devices have a profound influence on the state of dispersion of one polymer in another. Also determined were the rheological properties of the two-phase system investigated, from wall normal stress measurements. Our results show that, when shear stress is used as a parameter, the melt viscosity goes through a minimum, whereas the melt elasticity goes through a maximum. This is regardless of the type of mixing device employed, although the shapes of the curves are affected by the type employed. It is suggested that shear stress, instead of shear rate, be used in correlating the viscoelastic properties of two-phase polymer systems.

INTRODUCTION

In processing mixtures of two or more polymers, or a polymer containing additives, the polymer processing industry has long been concerned with achieving a good dispersion of one material in another. Because of the highly viscous nature of polymeric materials in the molten state, mixing equipment of special design is needed to obtain good dispersion.

During the past decade, the processing equipment manufacturers have spent much effort on improving the technique of mixing. One device resulting from this effort is an inline mixer with no moving parts, commonly referred to as the "static mixer."¹ It is recommended that such an inline device be installed between the extruder and the die (or mold) to impart improved mixing. Another device is the twin-screw compounding machine,² which, in recent years, has received much attention from the polymer processing industry.

The authors have recently carried out an experimental study for evaluating the mixing performance of both a "static mixer" (Kenics Corp. Thermogenizer) and a "twin-screw compounding machine" (Werner Pfleiderer Corp.), by

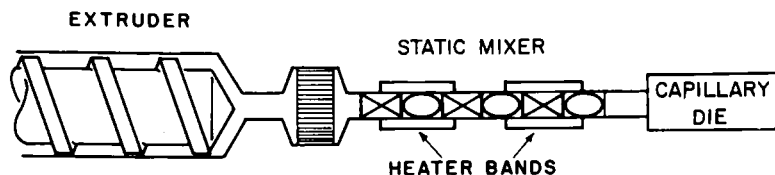


Fig. 1. Schematic of the layout of the apparatus.

extruding blends of polystyrene and polypropylene into a capillary die. Mixing performance of the equipment has been evaluated from the photographs taken of the microstructure of extrudate samples. In this paper, we shall discuss some of the representative results of the study.

EXPERIMENTAL

The main features of the apparatus used are basically the same as those described in previous papers by Han,^{3,4} except for the mixing devices. Two types of equipment, a static mixer and a twin-screw compounding machine, were employed in order to investigate the modes of dispersion of the polymer blend chosen for study.

Figure 1 gives a schematic for the layout of the apparatus, including a "static mixer" (Kenics Corp., Thermogenizer), which is installed between the single-screw extruder (1-in. Killion extruder) and the capillary die. A static mixer having nine mixing elements was used to impart additional mixing to the melt stream leaving the screw extruder. Figure 2 shows a photograph of the mixer, and a paper by Chen⁵ describes the mixing mechanisms and the residence time distribution of the mixer.

In the present study, blends of two polymers, polypropylene (Exxon Chemicals, Resin E115) and general-purpose polystyrene (Dow Chemical, Styron 686), were prepared by a tumbling operation. Three blending ratios (by weight) were used: PS/PP = 25/75, PS/PP = 50/50, and PS/PP = 75/25 (see Table I).

A twin-screw compounding machine (Werner Pfleiderer Corp., ZSK 53L) was also employed to prepare blends. The twin-screw extruder is a convertible design based on the building block principle, and consists of two screw shafts arranged side by side. The homogenizing of the material is achieved by conveying and kneading, and the material is discharged through a die plate and into a water bath. The strands quenched in the water bath are then cut into pellets. Pellets prepared in this manner were extruded again

TABLE I
Sample Codes and Blending Ratios of Two-Phase System Investigated

Sample code	Blending ratio, wt-%
PS	100% polystyrene
HDPE	100% high-density polyethylene
HDPE/PS = 25/75	25% polyethylene and 75% polystyrene
HDPE/PS = 50/50	50% polyethylene and 50% polystyrene
HDPE/PS = 75/25	75% polyethylene and 25% polystyrene

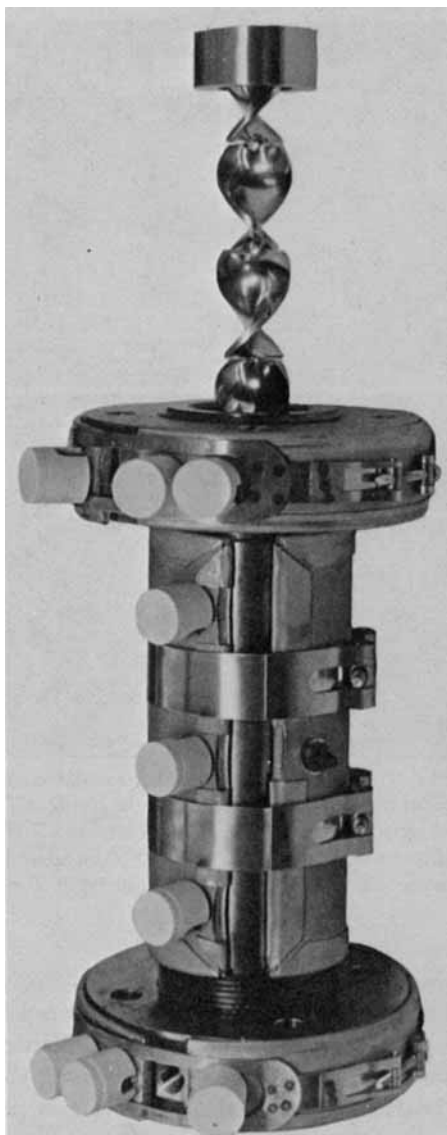


Fig. 2. Photograph of Kenics mixer (Thermogenizer).

by means of the single-screw extruder, but without a static mixer, through a capillary die for wall normal stress measurement.

In order to determine the rheological properties of the polymer blends in the molten state, measurements were taken of wall normal stresses along the axis of a capillary die having a length-to-diameter (L/D) ratio of 20 and a flat die entry (180° included angle). It should be pointed out that the present study has a reservoir-to-capillary diameter (D_R/D) ratio of 16. Note that the elastic properties of materials extruded through a capillary die depend on the D_R/D ratio, for a fixed L/D ratio and a given die entrance geometry. Details of the experimental procedure employed have been described in previous papers by Han.^{3,4}

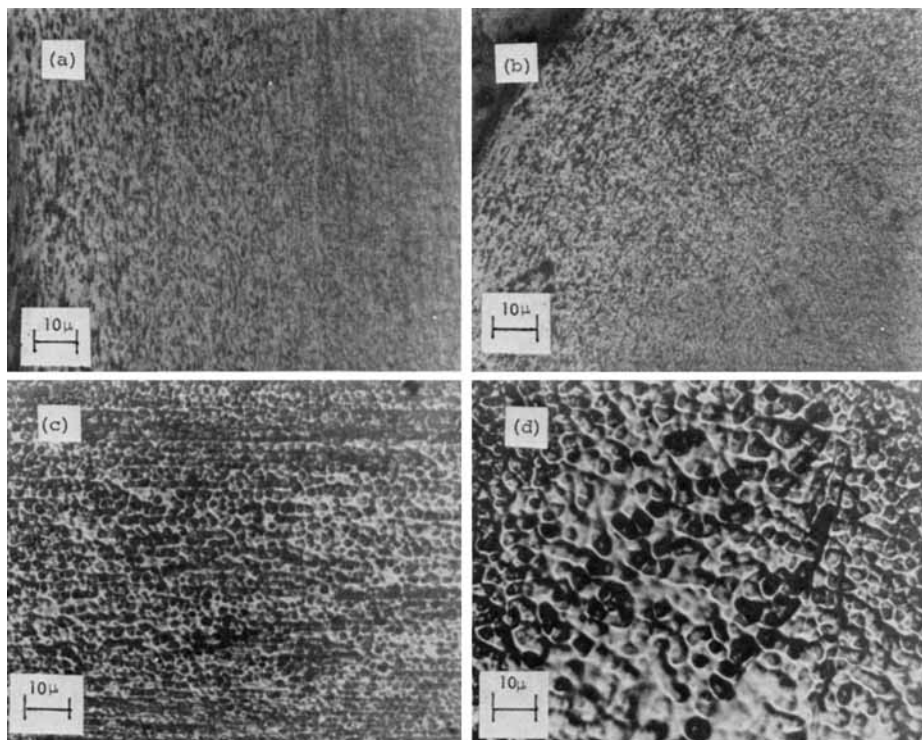


Fig. 3. Microphotographs of extrudate samples obtained with a single-screw extruder plus static mixer: (a) longitudinal section of the PS/PP = 75/25 blend at $T = 200^{\circ}\text{C}$ and $\tau_w = 0.465 \times 10^6$ dynes/cm²; (b) cross section of the PS/PP = 75/25 blend at $T = 200^{\circ}\text{C}$ and $\tau_w = 0.465 \times 10^6$ dynes/cm²; (c) longitudinal section of the PS/PP = 50/50 blend at $T = 200^{\circ}\text{C}$ and $\tau_w = 0.457 \times 10^6$ dynes/cm²; (d) cross section of the PS/PP = 50/50 blend at $T = 200^{\circ}\text{C}$ and $\tau_w = 0.457 \times 10^6$ dynes/cm².

During the experimental runs, extrudate samples were collected at different extrusion conditions. They were cut and mounted in epoxy (room temperature cure) and, subsequently, ground and polished. The polystyrene phase was then dissolved with toluene. In this way, the polystyrene phase remains to provide positive identification of the two phases. Photographs were then taken in reflection by use of an optical microscope (Reichert, Olsen Scientific Instruments) in order to obtain the *in situ* distribution of the components.

RESULTS AND DISCUSSION

Modes of Dispersion

Figure 3 shows photographs of the microstructure for extrudate samples obtained by use of the single-screw extruder with the static mixer. It should be noted in these pictures that the black portion represents polystyrene and the white portion represents polypropylene. It is seen that the polystyrene forms the discrete phase, dispersed in the polypropylene forming the continuous phase.

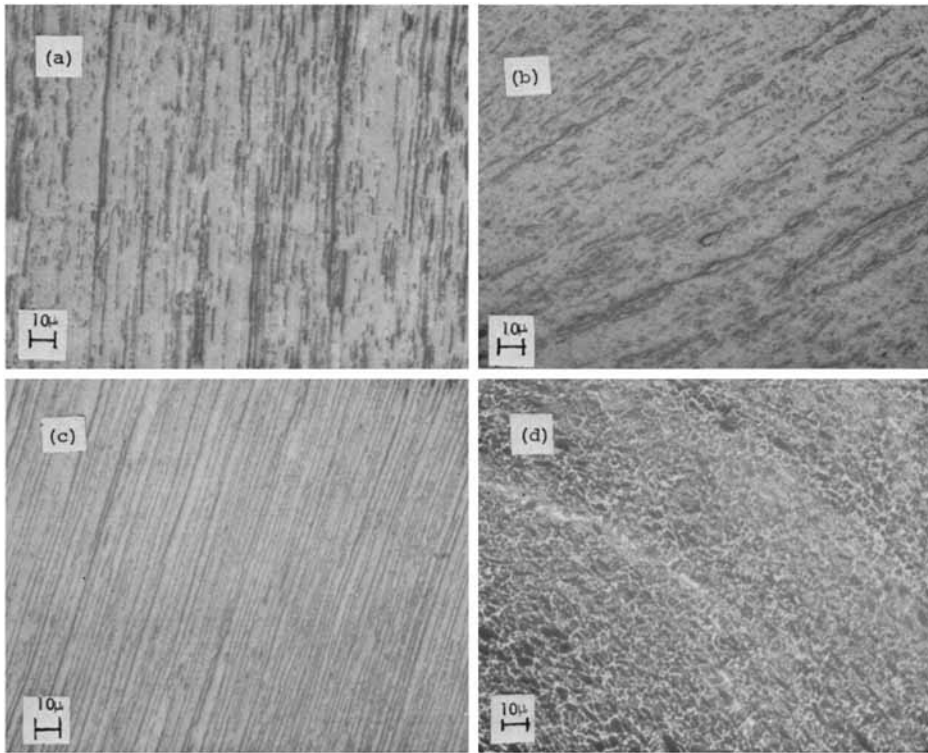


Fig. 4. Microphotographs of extrudate samples obtained by means of a single-screw extruder, alone: (a) longitudinal section of the PS/PP = 20/80 blend at $T = 200^{\circ}\text{C}$; (b) cross section of the PS/PP = 20/80 blend at $T = 200^{\circ}\text{C}$; (c) longitudinal section of the PS/PP = 50/50 blend at $T = 200^{\circ}\text{C}$; (d) cross section of the PS/PP = 50/50 blend at $T = 200^{\circ}\text{C}$.

Figure 4 shows microphotographs of samples, obtained by use of the single-screw extruder alone. When Figure 3 is compared with Figure 4, it is quite clear that the modes of dispersion are quite different. When only a single-screw extruder was used, the polystyrene phase formed long fibrils (see Figs. 4a and 4c), whereas when the static mixer was used together with the single-screw extruder, the polystyrene phase formed particles of well-defined shape (see Figs. 3a and 3c). It may, therefore, be concluded that the use of the static mixer significantly affects the state of dispersion in the flow of two incompatible polymers. The improvement in mixing may be attributable to the breakup of long fibrils of the dispersed phase (i.e., polystyrene) into smaller particles as the molten polymer passes through the stationary mixing elements.

Figure 5 shows microphotographs of samples obtained by use of a twin-screw extruder. It can be seen in these pictures that the state of dispersion obtained with the twin-screw compounding machine is somewhat different from that obtained with the single-screw extruder plus static mixer (see Fig. 3).

It does not appear, however, that the twin-screw compounding machine necessarily gives a better dispersion than the single-screw with the static mixer, for the particular blends investigated. This conclusion has been

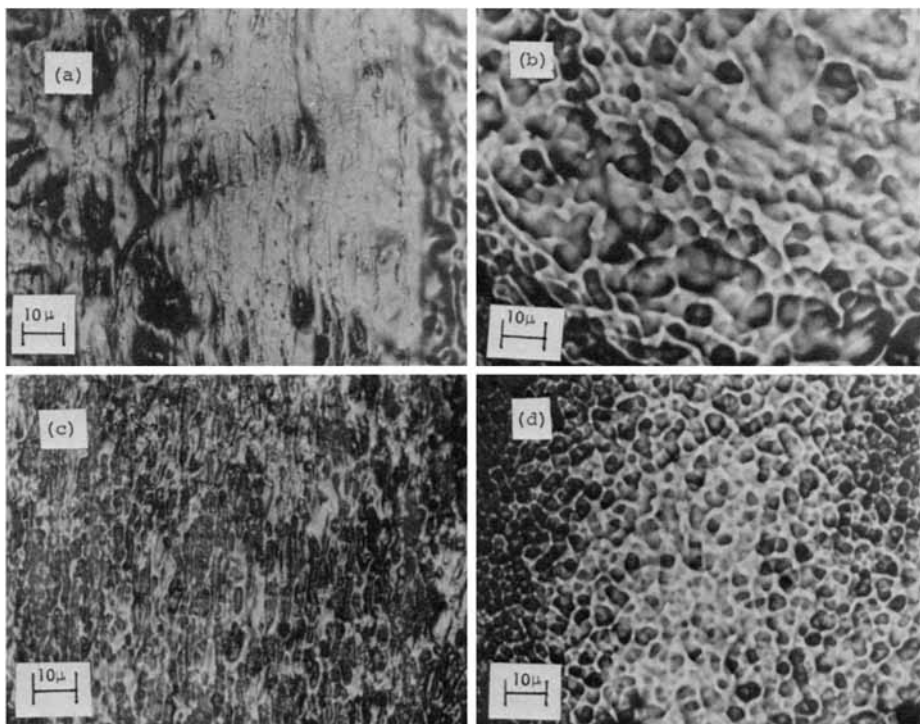


Fig. 5. Microphotographs of extrudate samples obtained by means of a twin-screw compounding machine: (a) longitudinal section of the PS/PP = 25/75 blend at $T = 200^{\circ}\text{C}$ and $\tau_w = 0.517 \times 10^6$ dynes/cm²; (b) cross section of the PS/PP = 25/75 blend at $T = 200^{\circ}\text{C}$ and $\tau_w = 0.17 \times 10^6$ dynes/cm²; (c) longitudinal direction of the PS/PP = 50/50 blend at $T = 200^{\circ}\text{C}$ and $\tau_w = 0.417 \times 10^6$ dynes/cm²; (d) cross section of the PS/PP = 50/50 blend at $T = 200^{\circ}\text{C}$ and $\tau_w = 0.417 \times 10^6$ dynes/cm².

reached based on hundreds of pictures taken for a number of extrudate samples, at many different extrusion conditions. However, as will be discussed below, even moderately different modes of dispersion can give rise to pronounced differences in the "apparent" rheological properties of blends in the molten state. This is because the rheological properties of the bulk of a two-phase system will depend, among many other things, on the size, size distribution, and the shape of the discrete phase droplets dispersed in the continuous phase.

Very recently, other investigators^{6,7} also studied the state of dispersion of two incompatible polymers, as affected by extrusion conditions.

Rheological Properties of Two-Phase Polymer Blends

Measurement of wall normal stresses along the axis of a capillary die permits one to determine the melt viscosity and melt elasticity.^{3,4,8,9} Figure 6 shows plots of viscosity versus shear rate for two homopolymers and three blends. Note that the viscosity is determined from the expression

$$\eta = \tau_w / \dot{\gamma}_t. \quad (1)$$

In eq. (1), τ_w is the true shear stress defined by

$$\tau_w = \left(\frac{-\partial p}{\partial x} \right) \frac{D}{4} \quad (2)$$

where $(-\partial p/\partial x)$ is the pressure gradient, D is the capillary diameter, and $\dot{\gamma}_t$ is the true wall shear rate defined by

$$\dot{\gamma}_t = \frac{\dot{\gamma}_{app}}{4} \left[3 + \frac{d \ln \dot{\gamma}}{d \ln \tau_w} \right] \quad (3)$$

in which $\dot{\gamma}_{app}$ is the apparent shear rate defined by

$$\dot{\gamma}_{app} = \frac{32Q}{\pi D^3} \quad (4)$$

where Q is the volumetric flow rate.

It is seen in Figure 6 that each material follows a power law over the range of shear rates tested, and that the viscosities of blends are lower than those of homopolymers. To elucidate this point, crossplots of Figure 6 are given in Figure 7, with shear rate as a parameter. It is seen that viscosity goes through a minimum. A similar observation has been noted in previous papers by Han.⁸⁻¹¹

According to Han,^{3,4,12} measurement of wall normal stresses in the fully developed region indicates nonzero "exit pressure," permitting one to determine normal stress differences. Figure 8 shows plots of first normal stress difference, $\tau_{11} - \tau_{22}$, versus true wall shear rate, in which $\tau_{11} - \tau_{22}$ was determined from the expression¹²

$$\tau_{11} - \tau_{22} = P_{exit} + \tau_w \frac{dP_{exit}}{d\tau_w} \quad (5)$$

P_{exit} denoting the exit pressure. Figure 9 shows crossplots of Figure 8, with shear rate as a parameter. It is seen in Figure 9 that no systematic correlation appears to exist when $\tau_{11} - \tau_{22}$ is plotted against blending ratio with shear rate as a parameter.

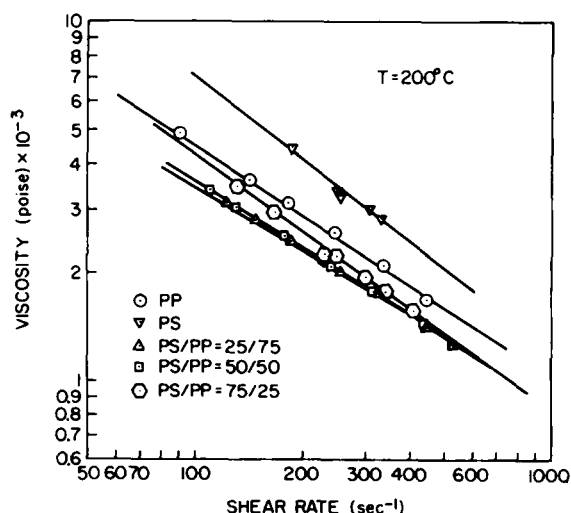


Fig. 6. Viscosity vs. shear rate for PS/PP blends prepared by means of a single-screw extruder plus static mixer.

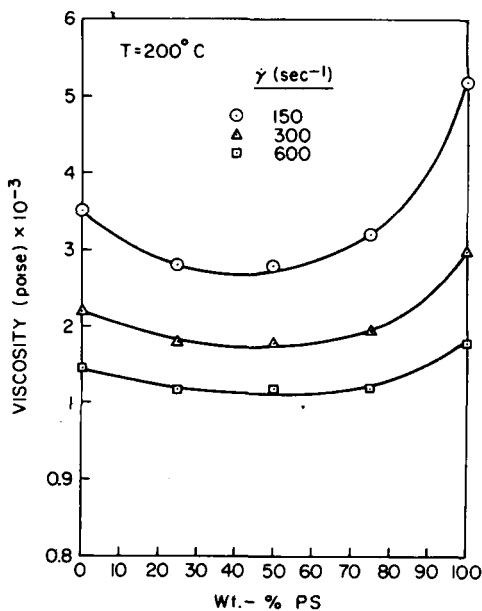


Fig. 7. Viscosity vs. blending ratio with shear rate as a parameter.

Now, the fact that Figure 9 does not show any systematic correlation may be understood when one realizes that shear rate may not be the correct parameter to use in correlating the rheological data of two-phase polymer systems.⁹ In other words, in two-phase flow, shear rate may *not* be continuous at the phase interface, but shear stress may be. Consider the situation where the dispersed phase (polystyrene droplets in this case) can deform while flowing through a capillary. The extent of deformation of the dispersed phase would be different for different blends. Therefore, shear rate at the phase interface would vary from one location to another in the capillary. However,

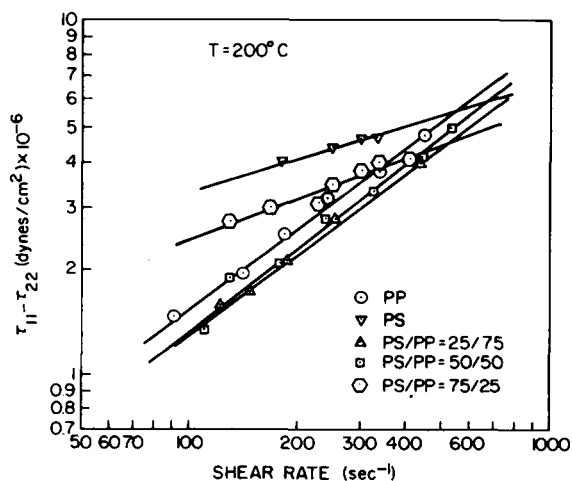


Fig. 8. Plot of $\tau_{11} - \tau_{22}$ vs. shear rate for PS/PP blends prepared by means of a single-screw extruder plus static mixer.

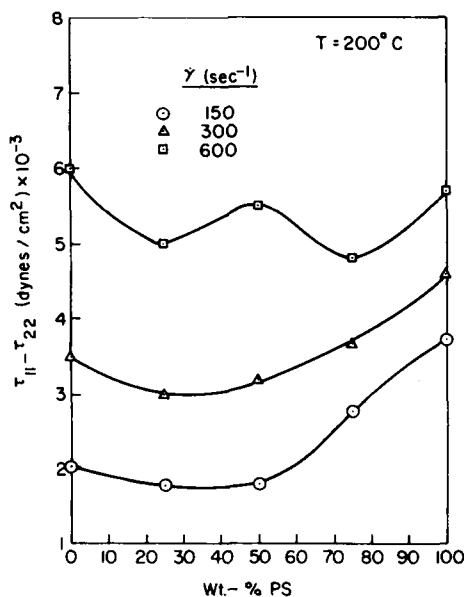


Fig. 9. Plot of $\tau_{11} - \tau_{22}$ vs. blending ratio with shear rate as a parameter.

shear stress would be continuous at the phase interface, so long as there is no slippage at the phase interface, regardless of the extent of deformation of the dispersed phase.

This, then, suggests that, instead of shear rate, shear stress be used for correlating the rheological behavior of two-phase systems.

Figure 10 gives plots of viscosity versus shear stress, and Figure 11 gives crossplots of Figure 10, with *shear stress* as a parameter. It is seen in Figure 11 that viscosity goes through a minimum, although the shape of the curves in Figure 11 is somewhat different from that in Figure 7. In other words, the

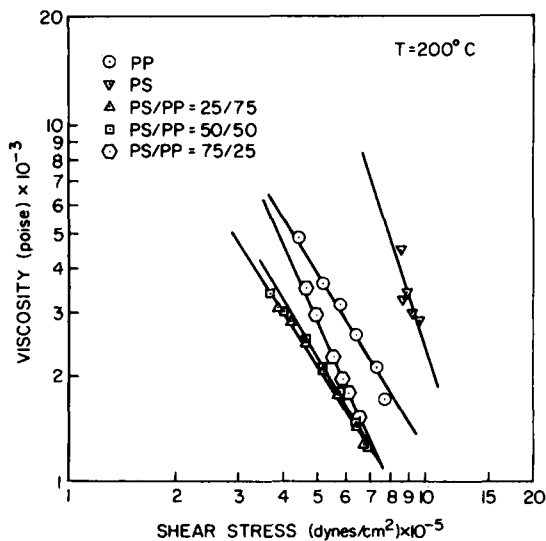


Fig. 10. Viscosity vs. shear stress for PS/PP blends prepared by means of a single-screw extruder plus static mixer.

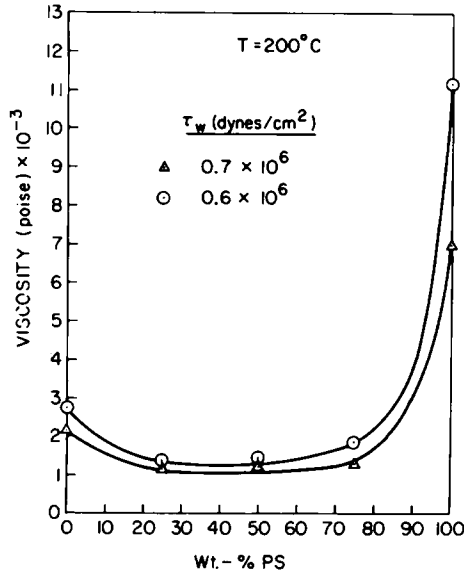


Fig. 11. Viscosity vs. blending ratio with shear stress as a parameter.

characteristic of the viscous behavior of two-phase systems may be seen unchanged, whether shear rate or shear stress is used as a parameter in correlating data.

Figure 12 gives plots of first normal stress difference, $\tau_{11} - \tau_{22}$, versus

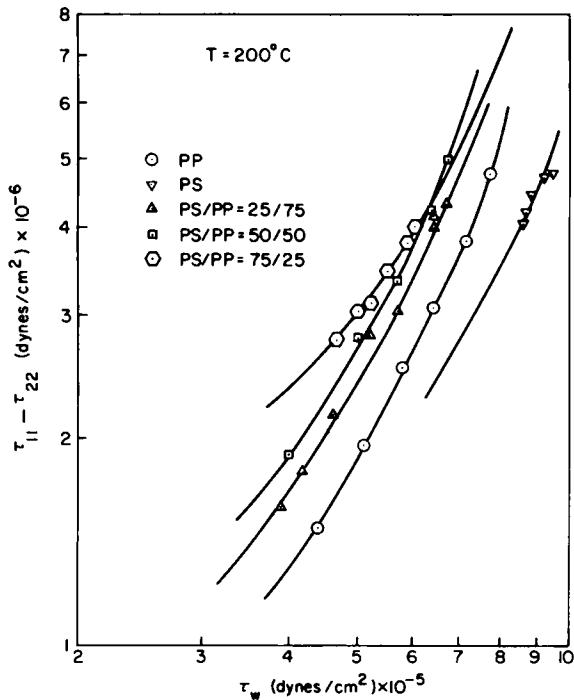


Fig. 12. Plot of $\tau_{11} - \tau_{22}$ vs. shear stress for PS/PP blends prepared by means of a single-screw extruder plus static mixer.

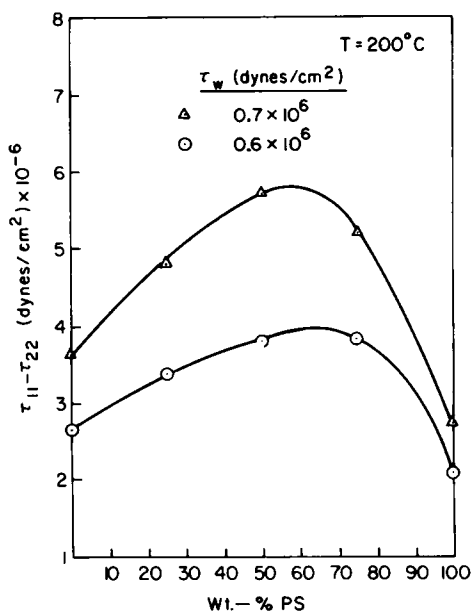


Fig. 13. Plot of $\tau_{11} - \tau_{22}$ vs. blending ratio with shear stress as a parameter.

shear stress τ_w , and Figure 13 gives crossplots of Figure 12, with shear stress as a parameter. It is of great interest to note in Figure 13 that there exists a clear correlation in the plot of $\tau_{11} - \tau_{22}$ versus blending ratio, when *shear stress* is used as a parameter. In other words, comparison of Figure 13 and Figure 9 confirms that, instead of shear rate, shear stress should be used in correlating the elastic behavior of two-phase systems. It should be noted that the above observation is consistent with the earlier studies by Han.⁸⁻¹¹

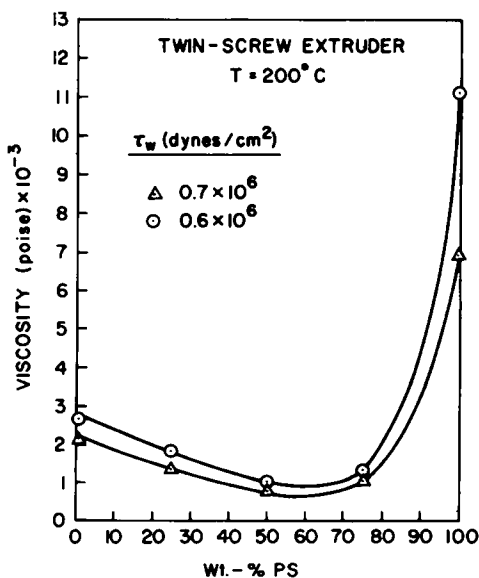


Fig. 14. Viscosity vs. blending ratio for PS/PP blends prepared by means of a twin-screw extruder.

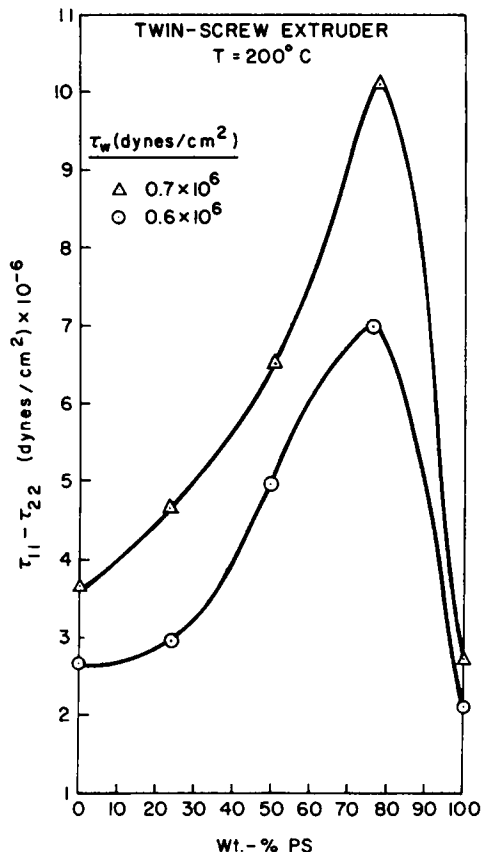


Fig. 15. Plot of $\tau_{11} - \tau_{22}$ vs. blending ratio for PS/PP blends prepared by means of a twin-screw extruder.

It should be mentioned that similar observations have also been reported by other investigators.¹³⁻¹⁵

Measurements of wall normal stresses were also taken with polymer blends prepared in a twin-screw compounding machine. Figure 14 gives plots of viscosity versus blending ratio, and Figure 15 gives plots of first normal stress differences versus blending ratio for three such blends. Note, in Figures 14 and 15, that *shear stress* is used as a parameter.

It is seen in Figures 14 and 15 that melt viscosity goes through a minimum and melt elasticity goes through a maximum at a certain blend ratio, in a manner very similar to the observation made in Figures 11 and 13. It should be noted, however, that the exact shape of the curves is dependent upon the type of mixing devices used for preparing the blends. This is not surprising when one considers the fact that the rheological behavior of the two-phase polymer blends under investigation would depend on the size and size distribution of the droplets dispersed in the continuous phase (in the present study polystyrene and polypropylene, respectively) and that the droplet size and size distribution, in turn, would depend on how mixing actually takes place. (See Figs. 3 through 5.) The shape of the discrete phase also plays an important role in controlling the "apparent" rheological properties discussed above.

Since there are so many droplets dispersed in the bulk of the melt under deformation, interaction among the droplets must also be considered in explaining the rather unusual behavior of the rheological properties of two-phase polymer systems. This seems to be an interesting research area, and of practical importance, as undoubtedly it is of great scientific value from the standpoint of the multiphase flow of viscoelastic fluids.

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