

## NOTES

### *Rheological Properties and Microstructure of Multiphase Polymeric Systems*

#### INTRODUCTION

In many polymer-processing operations, one often uses blends of two or more homopolymers, copolymers containing the dispersed phase, polymers containing additives of low molecular weight, and polymers with fillers. In all such cases, one hopes to improve the mechanical/physical properties of the finished product, another material being present as either a reinforcing agent or a modifying agent.

Whereas plasticizers and lubricants remain in the form of liquids, reinforcing agents are in the form of solids. Moreover, additives often become incompatible with the base polymer and hence give rise to a two-phase system. When a reinforcing component is used, a three-phase system can easily be formed when the reinforcing component (solid particles as a filler) is present in a mixture of two incompatible liquids.

The rapidly growing interest in the development of engineering thermoplastics by the polymer industry has stimulated researchers to determine the rheological properties of multiphase polymeric systems. Multiphase systems cover virtually all polymeric materials being used in industry, including reinforced plastics and foamed thermoplastics. From the point of view of the availability of base materials, namely, polymer, solid reinforcing agent, and blowing (i.e., foaming) agent, an enormously large number of combinations are possible for producing new materials. However, from the point of view of practical usefulness, difficulty is often encountered in producing a new material with improved mechanical properties. This is mainly due to the fact that molecular bonding is lacking between two materials having different molecular structure, and between polymer and solid particles. In other words, reinforcement of plastics can be realized only when there is a strong bonding between the polymer and the solid particles. More often than not, one therefore uses a coupling agent (or agents) to enhance the bonding.

In this paper, we shall present recent experimental results of the rheological measurements of multiphase systems. The materials investigated were blends of polystyrene with calcium carbonate-filled polypropylene and blends of high-impact polystyrene with calcium carbonate-filled polypropylene. The former blend system gives rise to *three* phases, and the latter, to *four*. The rather complicated rheological behavior of the blend systems investigated was interpreted with the aid of photomicrographs of extrudate samples.

#### EXPERIMENTAL

The apparatus used is the slit rheometer, and its main feature and operating procedures have been described in previous papers by Han.<sup>1,2</sup> In the present study, a commercially available mixing device, called the Kenics Static Mixer (Kenics Corp., Thermogenizer), was used in addition to a 1-in. Killion screw extruder. The details of the design of the Static Mixer used are given in the literature.<sup>3</sup> The Static Mixer was attached at the extruder outlet so that additional mixing could be achieved. In other words, the polymer melt flowed from an extruder into the Static Mixer and then into a calming section about 18 in. long and 2 in. in diameter. From here, the melt flowed into the slit die.

The system is electrically heated by Calrod heaters and band heaters, and the entire system is heavily insulated with asbestos sheet. The temperature is monitored at various points with iron-Constantan thermocouples and controlled by a thermistor-operated regulator.

Pressure (more precisely stated, wall normal stress) measurements were taken along the axis of

TABLE I  
Summary of Materials Investigated

Sample code	Material
<b>Three-Phase System</b>	
PS	general-purpose polystyrene
PP-CaCO <sub>3</sub>	CaCO <sub>3</sub> -filled polypropylene (10 wt-% CaCO <sub>3</sub> )
PS/PP-CaCO <sub>3</sub> = 25/75	blend of 25 wt-% polystyrene with 75 wt-% CaCO <sub>3</sub> -filled polypropylene
PS/PP-CaCO <sub>3</sub> = 50/50	blend of 50 wt-% polystyrene with 50 wt-% CaCO <sub>3</sub> -filled polypropylene
PS/PP-CaCO <sub>3</sub> = 75/25	blend of 75 wt-% polystyrene with 25 wt-% CaCO <sub>3</sub> -filled polypropylene
<b>Four-Phase System</b>	
HIPS	high-impact polystyrene (24.5 wt-% rubber)
PP-CaCO <sub>3</sub>	CaCO <sub>3</sub> -filled polypropylene (20 wt-% CaCO <sub>3</sub> )
HIPS/PP-CaCO <sub>3</sub> = 25/75	blend of 25 wt-% high-impact polystyrene with 75 wt-% CaCO <sub>3</sub> -filled polypropylene
HIPS/PP-CaCO <sub>3</sub> = 50/50	blend of 50 wt-% high-impact polystyrene with 50 wt-% CaCO <sub>3</sub> -filled polypropylene
HIPS/PP-CaCO <sub>3</sub> = 75/25	blend of 75 wt-% high-impact polystyrene with 25 wt-% CaCO <sub>3</sub> -filled polypropylene

the slit die, using the instrumentation described in Han's earlier papers.<sup>1,2</sup> Details of the experimental procedure and the bounds of measurement error are as described therein.

Materials used in the present study are summarized in Table I. Note that high-impact polystyrene (HIPS) (Union Carbide, TGDB 2100) contains rubbery particles dispersed in the polystyrene matrix, thus giving rise to a two-phase system in the molten state. The CaCO<sub>3</sub>-filled polypropylene was prepared by the aid of a twin-screw compounding machine (Werner & Pfleiderer Corp., ZSK53/L), and the filled system contained 10% by weight of CaCO<sub>3</sub> particles (Camel-Wite, H. T. Campbell & Sons), thus giving rise to a two-phase system in the molten state. The difference between the two

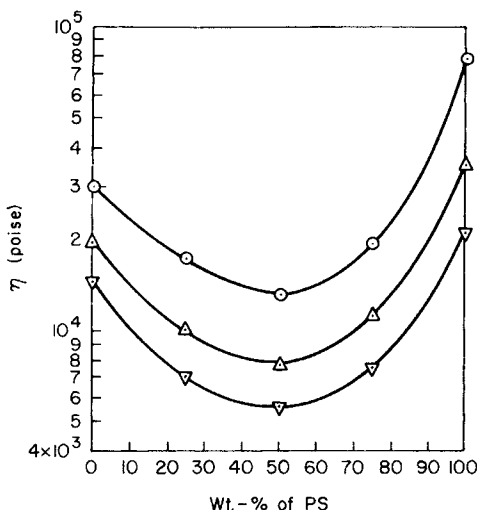


Fig. 1. Plots of viscosity  $\eta$  vs. blending ratio for the blends of CaCO<sub>3</sub>-filled polypropylene and polystyrene (PS) at various wall shear stresses  $\tau_w$  (dynes/cm<sup>2</sup>): (○)  $2 \times 10^5$ ; (△)  $3 \times 10^5$ ; (▽)  $4 \times 10^5$ .

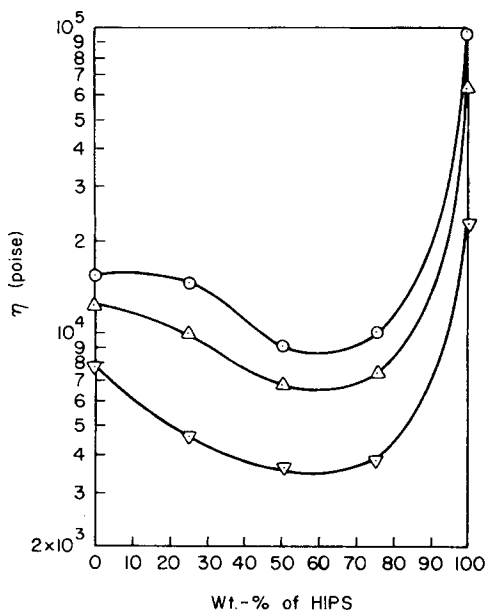


Fig. 2. Plots of viscosity  $\eta$  vs. blending ratio for the blends of  $\text{CaCO}_3$ -filled polypropylene and high-impact polystyrene (HIPS) at various wall shear stresses  $\tau_w$  (dynes/cm<sup>2</sup>): (○)  $4 \times 10^5$ ; (▲)  $6 \times 10^5$ ; (▼)  $8 \times 10^5$ .

two-phase systems described above should be noted. The former (i.e., HIPS) contains deformable rubbery particles, whereas the latter contains nondeformable solid particles. Later in this paper, we shall present photomicrographs of extrudate samples, describing the state of dispersion of all the components present in a given blend.

## RESULTS AND DISCUSSION

### Rheological Properties

Plots of viscosity  $\eta$  versus blending ratio are given in Figure 1 for the  $\text{CaCO}_3$ -PP/PS system, and in Figure 2, for the  $\text{CaCO}_3$ -PP/HIPS system. Note that the viscosities plotted in Figures 1 and 2 were determined using the expression

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

in which  $\tau_w$  is the wall shear stress defined as follows:

$$\tau_w = (-\partial p / \partial z) \frac{h}{2} \quad (2)$$

and  $\dot{\gamma}$  is the wall shear rate defined by

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

where  $(-\partial p / \partial z)$  is the pressure gradient that may be determined from the wall normal stress measurements,  $h$  is the slit thickness (i.e., the short side of the slit cross section), and  $\dot{\gamma}_{\text{app}}$  is the apparent shear rate defined by

$$\dot{\gamma}_{\text{app}} = 6Q / wh^2 \quad (4)$$

in which  $Q$  is the volumetric flow rate and  $w$  is the slit width (i.e., the long side of the slit cross section).

It is seen in Figures 1 and 2 that the blend viscosity tends to go through a minimum in the two blend

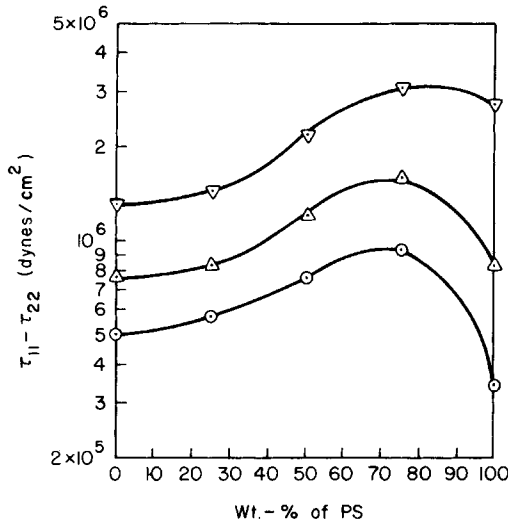


Fig. 3. Plots of first normal stress difference  $\tau_{11} - \tau_{22}$  vs. blending ratio for the blends of  $\text{CaCO}_3$ -filled polypropylene and polystyrene (PS) at various wall shear stresses  $\tau_w$  (dynes/cm<sup>2</sup>): (○)  $2 \times 10^5$ ; (▲)  $3 \times 10^5$ ; (▼)  $5 \times 10^5$ .

systems investigated. This observation is very similar to that reported in earlier publications by Han and co-workers.<sup>4-8</sup>

Plots of first normal stress difference  $\tau_{11} - \tau_{22}$  versus blending ratio are given in Figure 3 for the  $\text{CaCO}_3$ -PP/PS system, and in Figure 4 for the  $\text{CaCO}_3$ -PP/HIPS system. Note that the  $\tau_{11} - \tau_{12}$  plotted in Figures 3 and 4 were determined using the expression<sup>9</sup>

$$\tau_{11} - \tau_{22} = P_{\text{exit}} + \tau_w \frac{dP_{\text{exit}}}{d\tau_w} \tag{5}$$

in which  $P_{\text{exit}}$  denotes the exit pressure.

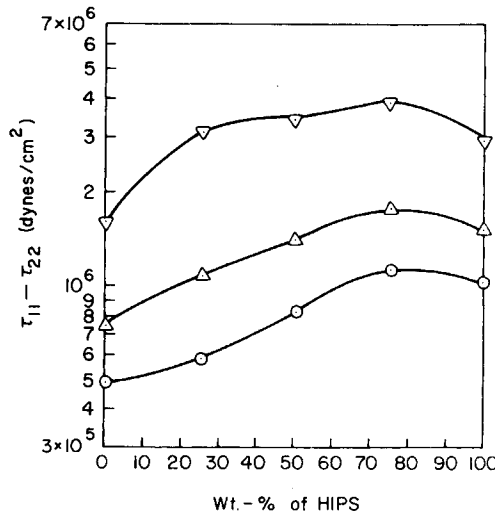


Fig. 4. Plots of first normal stress difference  $\tau_{11} - \tau_{22}$  vs. blending ratio for the blends of  $\text{CaCO}_3$ -filled polypropylene and high-impact polystyrene (HIPS) at various wall shear stresses  $\tau_w$  (dynes/cm<sup>2</sup>): (○)  $2 \times 10^5$ ; (▲)  $3 \times 10^5$ ; (▼)  $6 \times 10^5$ .

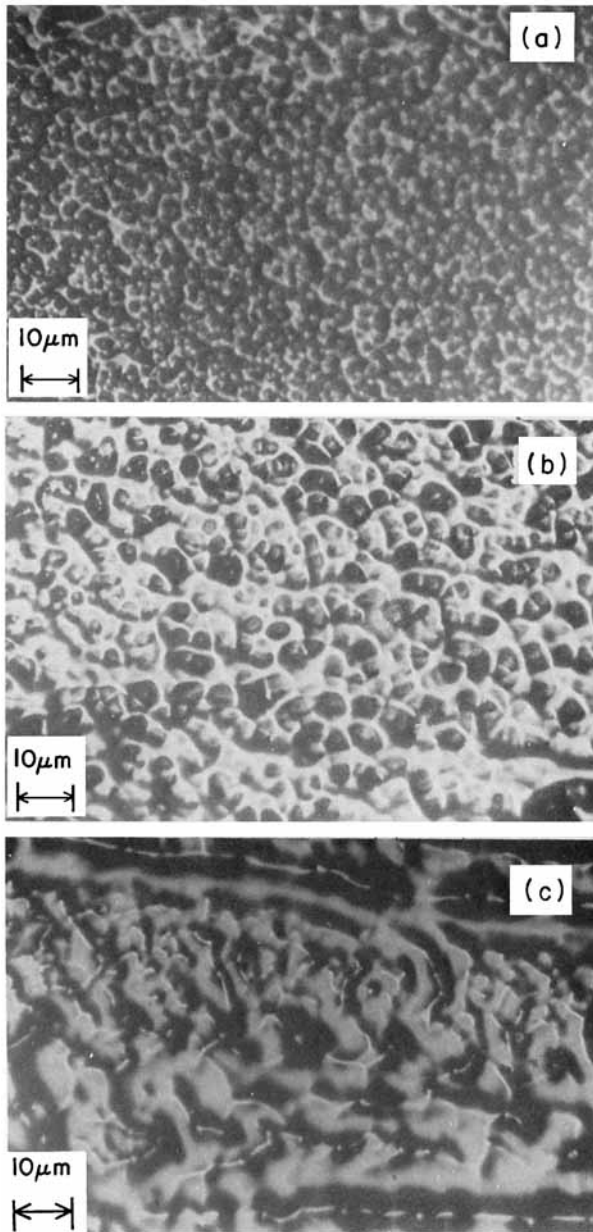


Fig. 5. Photomicrographs of extrudate cross section of blends of  $\text{CaCO}_3$ -filled polypropylene (PP) with polystyrene (PS): (a) blend of  $\text{CaCO}_3$ -PP/PS = 75/25 extruded at  $T = 200^\circ\text{C}$  and  $\tau_w = 2.97 \times 10^5$  dynes/cm<sup>2</sup>; (b) blend of  $\text{CaCO}_3$ -PP/PS = 50/50 extruded at  $T = 200^\circ\text{C}$  and  $\tau_w = 1.80 \times 10^5$  dynes/cm<sup>2</sup>; (c) blend of  $\text{CaCO}_3$ -PP/PS = 25/75 extruded at  $T = 200^\circ\text{C}$  and  $\tau_w = 3.27 \times 10^5$  dynes/cm<sup>2</sup>.

It is seen in Figures 3 and 4 that the blend  $\tau_{11} - \tau_{22}$  tends to go through a maximum in the two blend systems investigated. Again, this observation is very similar to that reported in earlier publications by Han and co-workers.<sup>4-8</sup>

There are some attempts reported in the literature<sup>10-13</sup> dealing with the determination of the flow properties of two-phase polymer systems using the Instron-type capillary rheometer. Such attempts,

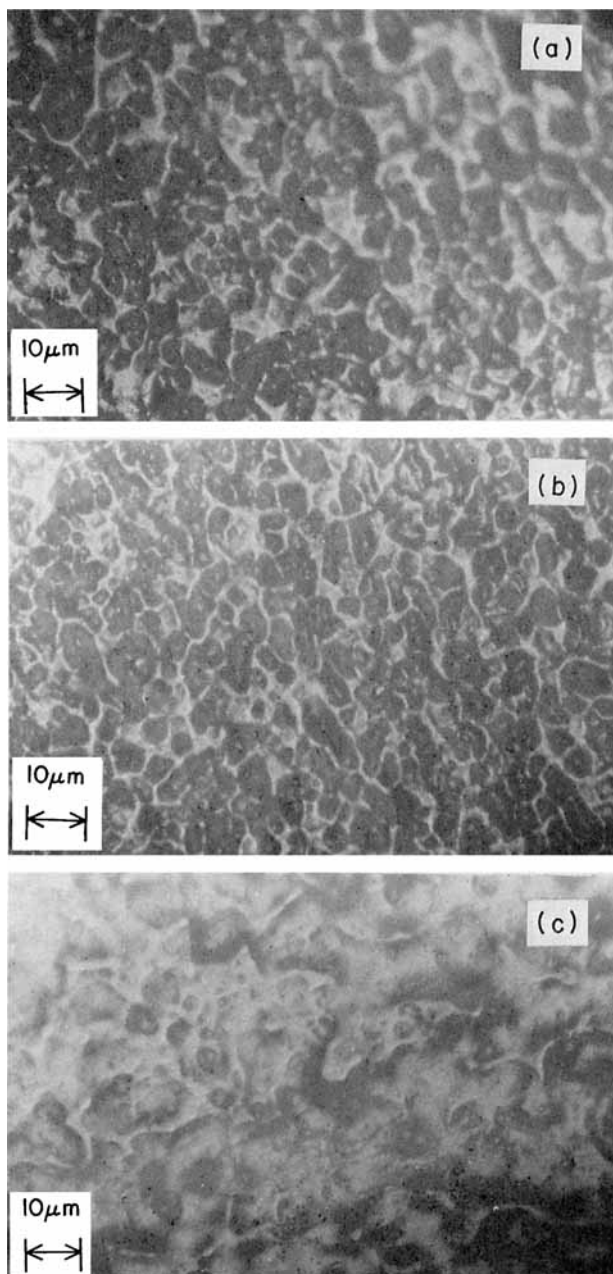


Fig. 6. Photomicrographs of extrudate cross section of blends of  $\text{CaCO}_3$ -filled polypropylene (PP) with high-impact polystyrene (HIPS): (a) blend of  $\text{CaCO}_3$ -PP/HIPS = 75/25 at  $T = 200^\circ\text{C}$  and  $\tau_w = 4.50 \times 10^5$  dynes/cm<sup>2</sup>; (b) blend of  $\text{CaCO}_3$ -PP/HIPS = 50/50 at  $T = 200^\circ\text{C}$  and  $\tau_w = 3.71 \times 10^6$  dynes/cm<sup>2</sup>; (c) blend of  $\text{CaCO}_3$ -PP/HIPS = 25/75 at  $T = 200^\circ\text{C}$  and  $\tau_w = 3.48 \times 10^5$  dynes/cm<sup>2</sup>.

however, are subject to serious criticism because, for two-phase systems in which one phase is present as droplets that deform in a different manner at different flow regimes (i.e., the die entrance and downstream in the capillary), the total pressure drop measured across the capillary is of questionable rheological significance. At this juncture, it is of interest to note that, in their recent study, Han

et al.<sup>14</sup> have demonstrated experimentally that viscoelastic droplets, initially spherical when upstream in the reservoir, elongated very much at the die entrance and recoiled somewhat in the fully developed region downstream of the die. They have also reported that at shear rates higher than a certain critical value, a deformed droplet broke into smaller droplets. This clearly indicates that the shape of the droplets suspended in the medium would greatly influence the local shear stress of the fluid system under test. Of course, the situation becomes much simpler when the suspended medium consists of solid particles that are *nondeformable* at all flow regimes of interest.

Note that in the use of the Instron-type capillary rheometer, one measures pressures upstream in the barrel of a capillary die and makes the entrance and exit correction in order to determine the wall shear stress and hence viscosity of the fluid under test, hopefully in the fully developed region. Even when one used high- $L/D$  capillaries in order to minimize entrance effects, as long as the suspended droplets change their shape in the entrance region, it is difficult to justify the use of pressure measurement, taken in the barrel of a capillary die, for determining the rheological properties of two-phase polymer systems.

On the other hand, the rheological properties presented above in Figures 1 through 4 are obtained from the measurements of wall normal stresses along the capillary, where the flow is fully developed, and *little* change occurs in the shape of droplets suspended in the medium, that is, where presumably an equilibrium state is reached with respect to the deformation of the dispersed droplets.

### State of Dispersion

In the present study, extrudate samples were collected from each experimental run and their microstructures were examined by taking photographs. Details of the experimental procedure for preparing samples and photographing are given in previous papers,<sup>4,5</sup>

Some representative photomicrographs of the extrudate samples are given in Figure 5 for the PS/CaCO<sub>3</sub>-PP system. In Figure 5, the *dark* area represents the polystyrene phase, and the *white* area represents the CaCO<sub>3</sub>-PP phase. It is seen in Figures 5a and 5b that the polystyrene forms the *discrete* phase (dark areas), and the CaCO<sub>3</sub>-PP forms the *continuous* phase (white areas). However, in Figure 5c, the state of dispersion of the blend looks quite different from that of the other two blends. It appears in this blend that the polystyrene forms the *continuous* phase (dark areas) and the CaCO<sub>3</sub>-PP forms the *discrete* phase (white areas). In other words, a phase inversion appears to have occurred.

Some representative photomicrographs of the extrudate samples are given in Figure 6 for the HIPS/CaCO<sub>3</sub>-PP system. Note in Figure 6 that the *dark* area represents the HIPS phase, and the *white* area represents the CaCO<sub>3</sub>-PP phase.

It should be mentioned that the state of dispersion depends on the blending ratio and on the processing conditions (e.g., melt temperature and shear stress). Processing conditions, in turn, influence the rheological properties of the individual components present. Needless to say, the mechanical device that may be used to mix two or more components plays an important role in controlling the size and distribution of the component dispersed in the continuous phase. In their earlier paper,<sup>7</sup> the authors have reported some quantitative observations of the effect of the mixing device on the rheological properties of some polymer blend systems.

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YOUNG WOO KIM  
CHANG DAE HAN

Department of Chemical Engineering  
Polytechnic Institute of New York  
Brooklyn, New York 11201

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