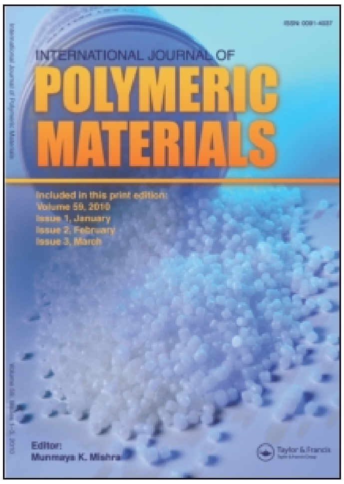

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Morphology and Rheological Properties of Poly(phenylene ether) and Polyamide-6 with a Compatibilizer

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The effect of styrene acrylic acid random copolymer on the phase behavior and rheological properties of poly(phenylene ether) and polyamide blends are examined as a function of acrylic acid content in styrene-acrylic acid copolymer.

KEY WORDS PPE/PA6 blends, acrylic acid-styrene copolymer, rheology.

INTRODUCTION

Multiphase polymer systems are becoming an increasingly important area of polymer science and the improvement of physical properties of blends depends to a large extent on the degree of dispersion.[1,2] The analysis of flow behavior is important and helpful for correlating the structure, morphology and rheological properties of blends.[3]

As a high performance polymer alloy, blends of poly(phenylene ether) (PPE) and polyamides (PA) have been of considerable interest. PPE has a unique combination of physical and electrical properties over a wide temperature range from a brittle point of about −170°C to a heat distortion temperature of about 190°C, but its processability is limited and the impact and chemical resistances are less than desired. On the other hand, polyamides have a good processability as well as chemical resistance. The combination of PPE and PA could give mutually complementary properties; however, their immiscibility requires a proper compatibilizer.[4] Although various compatibilizers have been developed to control the phase structure of these blends, details were concealed as patents.

In the present study, the effect of styrene-acrylic acid random copolymer (SAA) on the phase behavior and rheological properties of PPE/PA blends was examined as a function of the acrylic acid content in SAA copolymer.

EXPERIMENTAL

Materials. The poly(phenylene ether) (PPE) (T_g = 217.7°C, M_w = 45,000) and polyamide 6 (PA6) (T_m = 220.5°C, M_w = 60,000) are commercial additive-free

TABLE I

Properties of Copolymer

Sample code	Copolymer composition(mol% AA)[a]	T_g(°C)[b]
SAA 11	10.9	103.2
SAA 21	21.2	135.5
SAA 36	35.5	145.0
SAA 46	45.8	154.0

[a] determined by titration method

[b] determined by DSC

products, and were obtained from Nippon Polyether Co. and Tong Yang Nylon Co., respectively. They were used as received without further purification. The poly(styrene-*co*-acrylic acid) (SAA) was synthesized by bulk polymerization at 60°C using benzoyl peroxide as an initiator. The acrylic acid content of the copolymer was determined by titration in THF with a standardized methanolic NaOH solution using phenolphthalein as an indicator. Table I lists the properties of the synthesized copolymers. The number in each sample code denotes the approximate acrylic acid content in the copolymers.

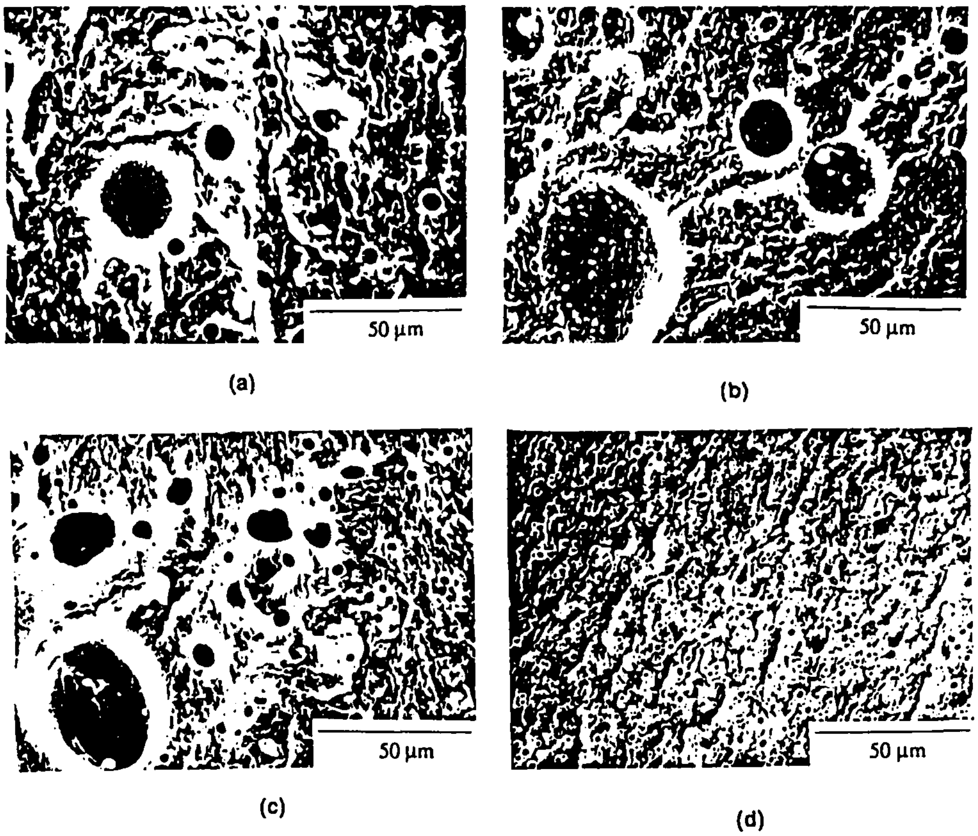
Preparation of Blends. Blends were prepared in the melt state at 280°C with a Rheomix 600 (Haake Buchler Instrument Inc., System 90 Torque Rheometer). The volume of the mixing head was 60 cc and mixing was continued for 10 min at 100 rpm.

Morphological Observation. Morphologies of the blends were observed with a scanning electron microscope (SEM) (Jeol JSM-35). Compression-molded samples were cryogenically fractured (in liquid nitrogen) and the fracture surface was treated with chloroform at room temperature for 30 min to remove the minor PPE domain.

Rheological Measurement. The rheological properties of the blends were measured at 250°C in a Rheometrics Dynamic Spectrometer with parallel plate mode. The parallel plate geometry has a 2 mm gap size and 12.5 mm radius. The samples were used after trimming into a disc and strain was maintained at 5% for all of the samples.

RESULTS AND DISCUSSION

Morphology. Figures 1 and 2 show the morphology changes of PPE/PA6 blends when the SAA copolymer is added. The SEM micrographs of the PPE/PA6 binary blends (Figures 1(a) and 2(a)) show the typical morphology of an immiscible mixture, i.e., very large, coarse and irregular domains were formed. When 3 wt% of SAA 36 was added to the blends, the morphology changes dramatically (Figures 1(d) and 2(d)); however, the addition of SAA 11 and SAA 21 give no significant change (Figures 1(b), 1(c), 2(b) and 2(c)). This observation suggests that the acrylic

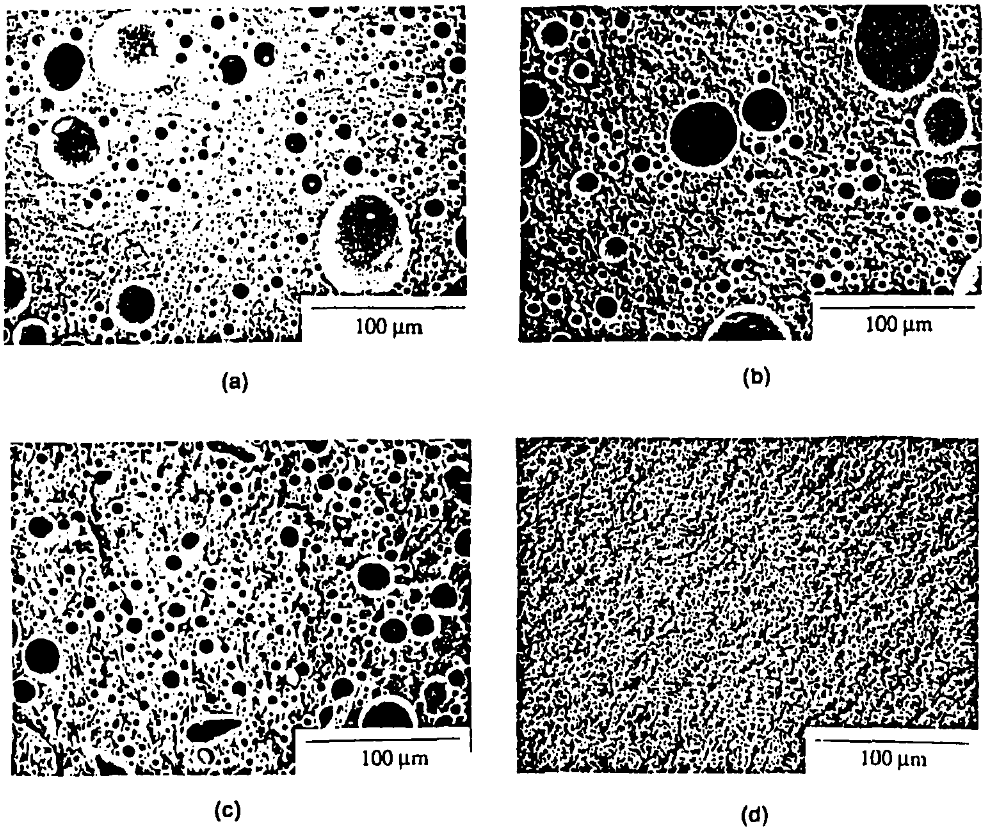


(a) (b) (c) (d)

FIGURE 1 Scanning electron micrographs of 10/90 PPE/PA blends: (a) without SAA, (b) 3 wt% SAA 11 added, (c) 3 wt% SAA 21 added, (d) 3 wt% SAA 36 added.

acid content in SAA copolymer should exceed a specific composition (around 36 mol%) in order for SAA copolymer to give a proper compatibilizing effect on the blend systems.

Rheological Properties. Complex viscosities of blends were plotted against frequency in Figures 3 and 4. The blends of PPE/PA6 (30/70) show Newtonian viscosity behavior over the entire range of frequency examined (Figure 3). When a small amount of SAA 11 or SAA 21 is added, the magnitude of the viscosity increases while the blend systems still show Newtonian behavior. However, when SAA 36 or SAA 46 is added, the Newtonian behavior is replaced by non-Newtonian power-law behavior at low frequency, so-called yield behavior. Harrel and Nakajima[5] reported that this behavior could be caused by long branching which might occur during processing (melt mixing). Therefore, in the present system, the low frequency non-Newtonian power-law behavior seems to result from long branching by chemical reaction between amine groups of PA6 and carboxyl groups of SAA during melt mixing. Recalling that the domain size is significantly reduced when SAA 36 is added to PPE/PA6 blends, it is conjectured that the formation of graft copolymer from PA6 and SAA 36 plays a role as a compatibilizer for such a blend system.



(a) (b) (c) (d)

FIGURE 2 Scanning electron micrographs of 30/70 PPE/PA blends: (a) without SAA, (b) 3 wt% SAA 11 added, (c) 3 wt% SAA 21 added, (d) 3 wt% SAA 36 added.

Figure 5 gives plots of storage modulus (G') or loss modulus (G'') versus frequency. As was observed in the viscosity data, significant differences exist among the samples. For the blend of PPE/PA6 (30/70), G'' dominates over the entire range of frequency examined. When SAA 21 is added to the blend, both G' and G'' shift to higher values, and G' shifts more than G''. This tendency becomes more prominent as the acrylic acid content in SAA copolymer increases. Thus, crossover is observed for the blend containing SAA 36 within the frequency range observed. The blend containing SAA 36 possesses two regions of response: the high frequency region dominated by the G' response, characteristic of elastic behavior, and the low frequency region dominated by the G'' response, characteristic of viscous behavior. Moreover, the crossover point shifts to low frequency as the acrylic acid content in SAA copolymer increases. In other words, the blend shows the characteristics of elastic behavior at the relatively lower frequency. This effect seems related to the branch formation by chemical reaction mentioned above. Similar results are observed for different blend ratios (Figure 6).

A modified Cole-Cole plot[5–7] is a useful method of rheological characterization. Many investigators have showed the usefulness of this plot for the rheological analyses of various polymer systems.[7–9] Figure 7 gives the modified Cole-Cole plots

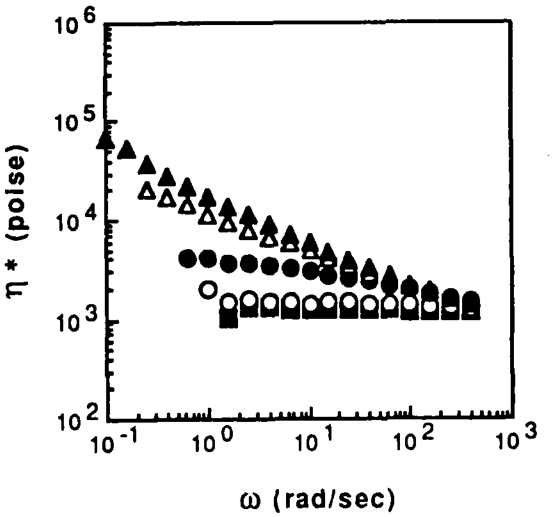


FIGURE 3 Complex viscosity vs. frequency for 30/70 PPE/PA6 blends: (■) without SAA, (○) 3 wt% SAA 11 added, (●) 3 wt% SAA 21 added, (△) 3 wt% SAA 36 added, (▲) 3 wt% SAA 46 added.

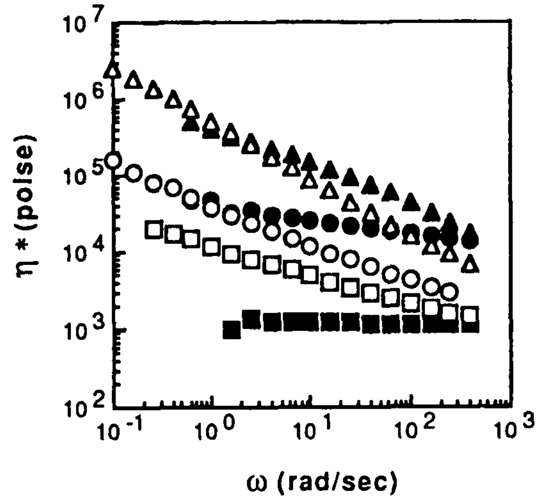


FIGURE 4 Complex viscosity vs. frequency for PPE/PA6 blends: (■) 30/70 PPE/PA6, (●) 50/50 PPE/PA6, (▲) 70/30 PPE/PA6, (□) 30/70 PPE/PA6 with 3 wt% SAA 36, (○) 50/50 PPE/PA6 with 3 wt% SAA 36 added, (△) 70/30 PPE/PA6 with 3 wt% SAA 36.

for the blends of PPE/PA6 (30/70). In the plot, the data above and to the left of the equi-modulus line indicate that the rheological properties of the sample are dominated by the viscous response (loss modulus) component, and to the right and below indicate that the rheological properties are dominated by the elastic response (storage modulus) component. The diagonal line itself is the crossover point of G' and G''. According to the data of Onogi and Masuda,[10] the branch polymer has a G' value higher than that of the linear polymer at an equal value of G''. Results

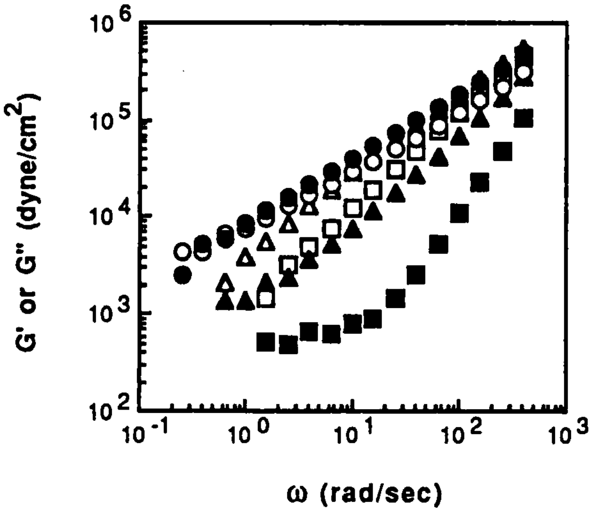


FIGURE 5 G' or G" vs. frequency for 30/70 PPE/PA6 blends. Square, without SAA; triangle, 3 wt% SAA 21 added; circle, 3 wt% SAA 36 added. Closed and open symbols represent G' and G", respectively.

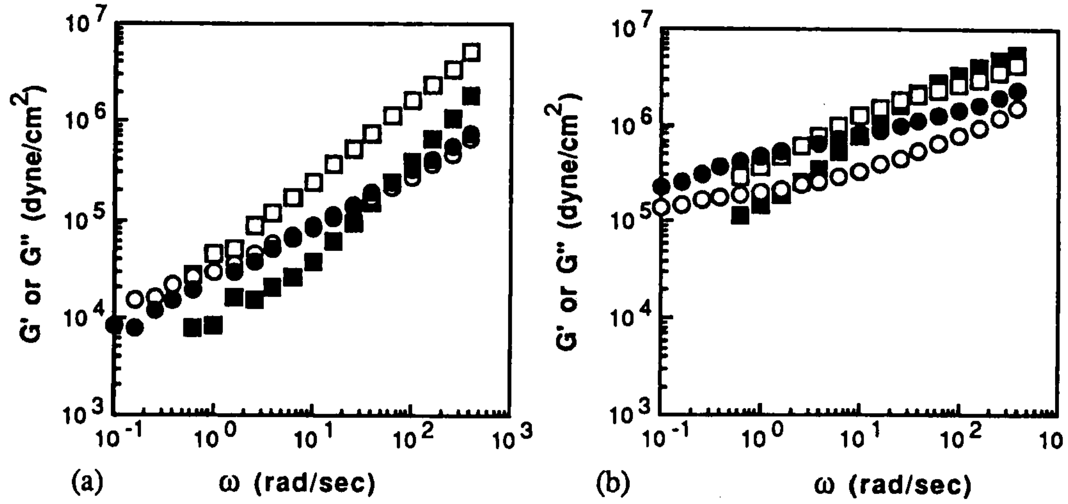


FIGURE 6 G' or G" vs. frequency for 30/70 PPE/PA6 blends. (a) 50/50 PPE/PA6, (b) 70/30 PPE/PA6. Closed and open symbols represent G' and G", respectively. Square: without SAA, circle: 3 wt% SAA 36 added.

of Shida and Shroff[11] show that the broadening of molecular weight distribution (MWD) can also shift the modified Cole-Cole plot to lower G" values and increase its slope. In Figure 7, the curve shifts from the upper left (viscous behavior region) to the lower right (elastic behavior region) and the slope increases with the acrylic acid content in SAA copolymer. From this result, it is believed that the SAA above a specific copolymer composition (36 mol% AA) reacts with the PA6 matrix, and thus some branching and MWD broadening take place. The branching may have a compatibilizing effect on such an immiscible blend. Figure 8 shows the changes

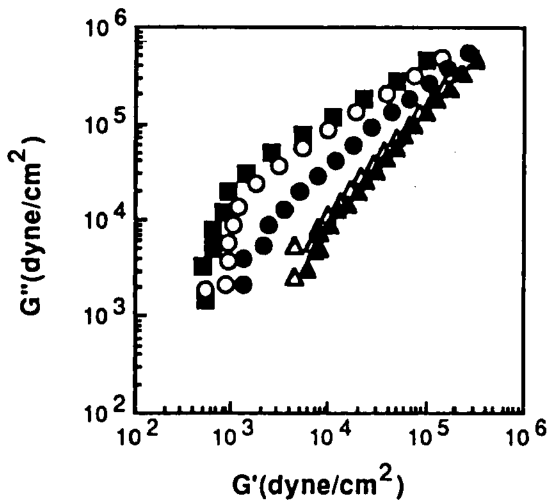


FIGURE 7 Modified Cole-Cole plots for 30/70 PPE/PA6 blends: (■) without SAA, (○) 3 wt% SAA 11 added, (●) 3 wt% SAA 21 added, (△) 3 wt% SAA 36 added, (▲) 3 wt% SAA 46 added.

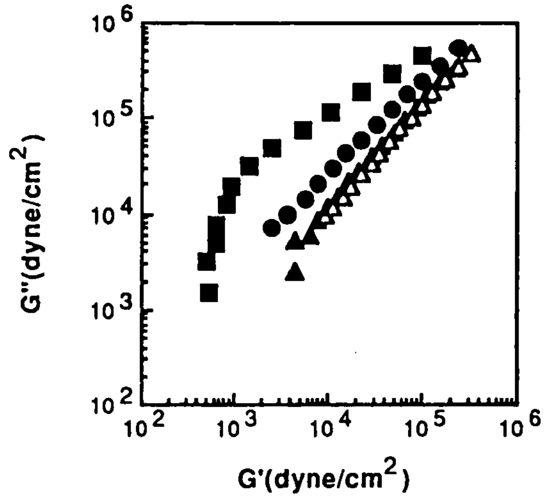


FIGURE 8 Modified Cole-Cole plots for 30/70 PPE/PA6 blends: (■) without SAA, (●) 1.5 wt% SAA 36 added, (▲) 3 wt% SAA 36 added, (△) 5 wt% SAA 36 added.

in modified Cole-Cole plot with the amount of compatibilizing agent. It is shown that about 3 wt% of copolymer is sufficient to act as a compatibilizing agent.

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