

## Morphology, rheological and mechanical properties of poly(phenylene ether) and polyamide-6 blends with a compatibilizer

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### SUMMARY

The compatibilizing effect of styrene-acrylic acid random copolymers (SAA) on the morphology, rheological and mechanical properties of poly(phenylene ether) (PPE) and polyamide-6 (PA6) blends was investigated. By addition of a small amount (ca. 3wt%) of SAA copolymer, the blends show non-Newtonian power-law behavior at low frequency and the contribution of the storage modulus ( $G'$ ) to the total response increases. The blends containing SAA copolymer having acrylic acid content higher than 36mol% show more regular and finer dispersion and exhibit about 10% increased mechanical properties. It is believed from Molau test and MFI data that these results seem to attribute to the branch formation and MWD broadening by chemical reaction between terminal amine groups of PA6 and carboxyl groups of SAA.

### INTRODUCTION

Multiphase polymer systems are becoming as an increasingly important area of polymer science and technology.<sup>1,2</sup> In such heterogeneous multicomponent polymer mixtures, each of the component retains its own properties and then sums up in a final product that may also display some new features due to the particular phase morphology. Actually, the improvement of physico-mechanical properties of such blends depends to a large extent on the degree of dispersion. For correlating the structure, morphology and rheological properties of blends, the analysis of flow behavior is important and helpful.<sup>3</sup>

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 all temperature range from a brittle point of about  $-170^{\circ}\text{C}$  to an heat distortion temperature of about  $190^{\circ}\text{C}$ , 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, this blend is immiscible thus a proper compatibilizer is required to yield desirable physico-mechanical properties.<sup>4</sup> Although various compatibilizers have been developed to control the phase structure of these blends, details were concealed as patents.<sup>5,6</sup>

In the present study, the effect of styrene-acrylic acid random copolymer (SAA) on the phase behavior, rheological and mechanical 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) ( $T_g = 217.7^{\circ}\text{C}$ ,  $M_w = 45,000$ ) and polyamide-6 (PA6) ( $T_m = 220.5^{\circ}\text{C}$ ,  $M_w = 60,000$ ) were commercial additive-free products 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  $60^{\circ}\text{C}$  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 1 lists the properties of the synthesized copolymers. The number behind sample code denotes the approximate acrylic acid content in copolymers.

Table 1. Properties of Copolymer

Sample code	Copolymer composition(mol% AA) <sup>a</sup>	T <sub>g</sub> (°C) <sup>b</sup>
SAA 11	10.9	103.2
SAA 21	21.2	135.5
SAA 36	35.5	145.0
SAA 46	45.8	154.0

<sup>a</sup> determined by titration method

<sup>b</sup> determined by DSC

**Preparation of Blends** All polymers were completely dried under vacuum before blending. Blends were prepared in the melt state at 280 °C with a Rheomix 600 (Haake Buchler Instrument Inc., System 90 Torque Rheometer) for 10 min at 100 rpm.

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

**Rheological Measurement** The rheological properties of the blends were measured at 250°C in a Rheometrics Dynamic Spectrometer with parallel plate mode under a nitrogen atmosphere. Parallel plate geometry has 2 mm in gap size and 12.5 mm in radius. Strain was maintained at 5% for all of the samples.

**Mechanical Test** Premixed polymers were compounded at 280°C in a corotating type twin extruder (Berstorff). The extrudate was pelletized and dried at 75°C for 4 hours and then injected (Battenfeld Unilog 4000) into dumbbell and prism type molds. Tensile, flexural and compressive tests were performed after drying all samples under constant condition(75°C, overnight).

## RESULTS AND DISCUSSION

**Morphology** Figures 1 and 2 show the morphology changes of 30/70 PPE/PA6 blends when SAA copolymers are added. The SEM micrograph of the PPE/PA6 binary blend (Figure 1a) shows 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 (Figure 1d) while the addition of SAA 11 and SAA 21 give no significant change in phase morphology (Figures 1b and 1c). This observation suggests that the acrylic acid content in SAA copolymer should exceed a specific composition (ca. 36 mol %) in order for SAA copolymer to give a proper compatibilizing effect on the blend systems. The magnified SEM micrograph of the raw fracture surface without chloroform treatment is shown in Figure 2. Though it looks weak, the evidence of interaction between dispersed phase (PPE) and matrix (PA6) can be seen at the interface. It is believed that this interaction contributes to the improvement of the mechanical properties which will be discussed later.

**Rheological Properties** Complex viscosities of blends were plotted against frequency in Figures 3 and 4. The blend of PPE/PA6 (30/70) shows the Newtonian viscosity behavior at 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<sup>7</sup> reported that the yield 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 attribute to 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 SAA36 is added to PPE/PA6 blends, it is considered that the formation of graft copolymer from PA6 and SAA36 plays a role as a compatibilizer for such a blend system.

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 (Figure 5a). When SAA21 is added to the blend, both  $G'$  and  $G''$  shift to the higher value, and  $G'$  shifts more greatly than  $G''$ . This tendency becomes more prominent as the acrylic acid content in SAA copolymer increases. Thus, crossover is observed for the blend containing SAA36 within the frequency range observed. The blend containing SAA36 possesses two regions of response: the high frequency region dominated by the  $G'$  response, characteristics of elastic behavior and the low frequency region dominated by the  $G''$  response, characteristics of the 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 to attribute to the branch formation by chemical reaction mentioned the above.<sup>7</sup> A Similar result is observed for a 50/50 blend (Figure 5b).

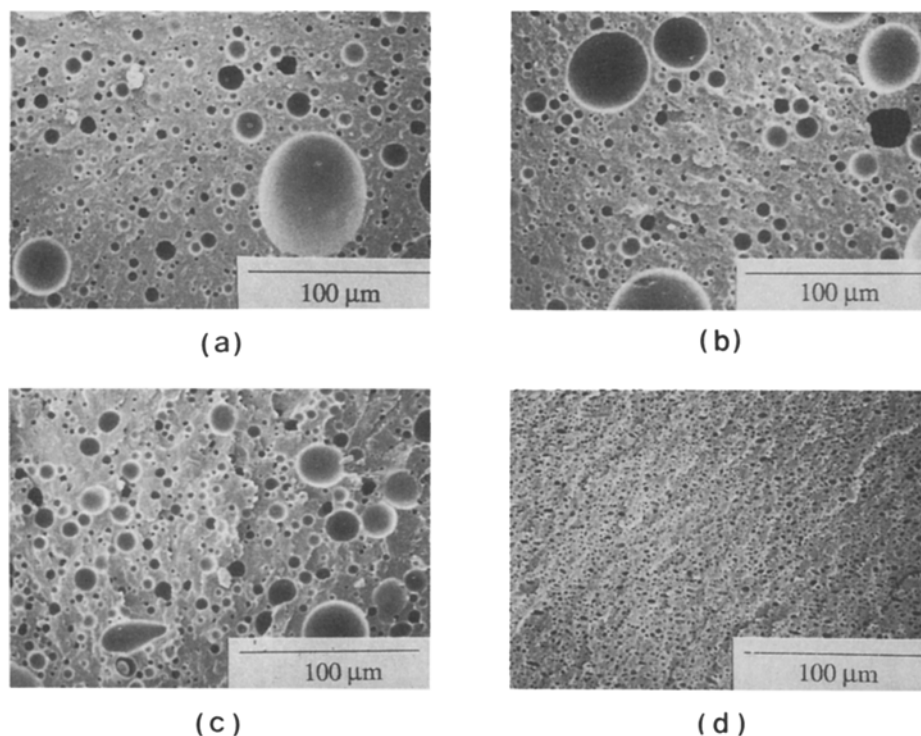


Fig.1. Scanning electron micrographs of 30/70 PPE/PA6 blends: (a) without SAA, (b) 3wt% SAA11 added, (c) 3wt% SAA21 added, (d) 3wt% SAA36 added.

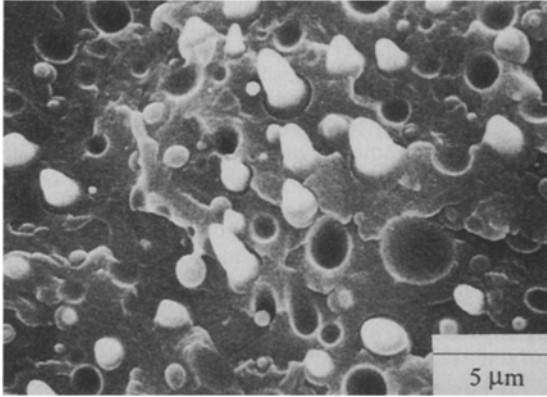


Fig.2. Scanning electron micrograph of 30/70 PPE/PA6 blend with 3wt% SAA36. Minor phase dissolution is not performed.

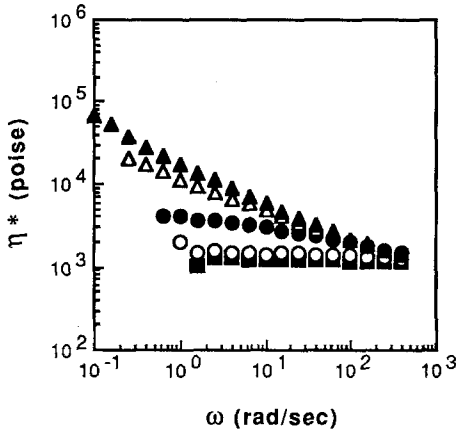


Fig. 3. Complex viscosity vs. frequency for 30/70 PPE/PA6 blends: (■) without SAA, (○) 3 wt% SAA11 added, (●) 3 wt% SAA21 added, (△) 3 wt% SAA36 added, (▲) 3 wt% SAA46 added.

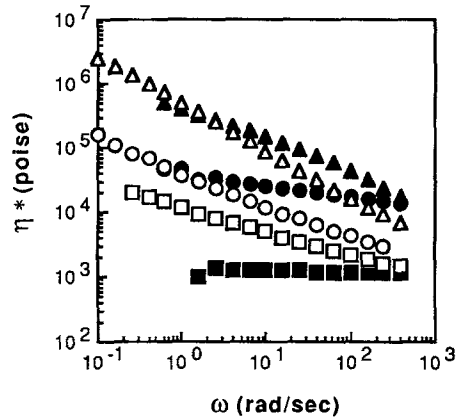


Fig. 4. Complex viscosity vs. frequency for PPE/PA6 blends: (■) 30/70 PPE/PA6, (●) 50/50 PPE/PA6, (▲) 70/30 PPE/PA6, (□) 30/70 PPE/PA6 with 3 wt% SAA36, (○) 50/50 PPE/PA6 with 3 wt% SAA36, (△) 70/30 PPE/PA6 with 3 wt% SAA36

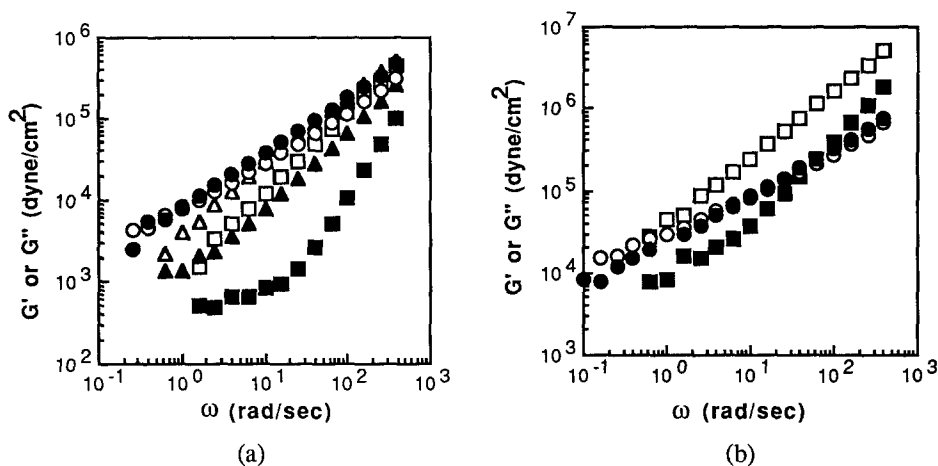


Fig. 5.  $G'$  or  $G''$  vs. frequency for PPE/PA6 blends. (a) 30/70 PPE/PA6, (b) 50/50 PPE/PA6. Tetragon, without SAA; triangle, 3 wt% SAA21 added; circle, 3 wt% SAA36 added. Closed and open symbols represent  $G'$  and  $G''$ , respectively.

The modified Cole-Cole plot<sup>7-9</sup> is a useful method of rheological characterization. Many investigators showed the usefulness of this plot for the rheological analyses of various polymer systems.<sup>9-11</sup> Figure 6 shows the modified Cole-Cole plots for the blends of 30/70 PPE/PA6. In the plot, the data of the left and above the equi-modulus line indicate that the rheological properties of the sample are dominated by the viscous response (loss modulus) component, and the right and below indicate that the rheological properties are dominated by the elastic response (storage modulus) component. Intersection of this line is the crossover point of the  $G'$  and  $G''$ . According to the data of Onogi and Masuda,<sup>12</sup> the branch polymer has a  $G'$  value higher than that of the linear polymer at an equal value of  $G''$ . Results of Shida and Shroff<sup>13</sup> explain that the broadening of molecular weight distribution (MWD) can also shift the modified Cole-Cole plot to lower  $G''$  values and that the broadening increases its slope. In Figure 6, the curve shifts from the left and above (viscous behavior region) to the right and below (elastic behavior region) and the slope increases as the acrylic acid content in SAA copolymer increases. From this result, it is assumed 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 give a compatibilizing effect on such an immiscible blend. Figure 7 shows the changes in the 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.

**Mechanical Properties** Figure 8 shows the strength and modulus data of tensile, flexural and compressive tests for 30/70 PPE/PA6 blends. when 3wt% SAA36 is added, both strength and modulus are improved about 10% for all tests. From these results, it is believed that SAA-PA6 graft copolymer is formed *in situ* during mechanical mixing thus finer dispersion and improved interfacial adhesion are achieved. Both particle size reduction and interfacial adhesion effect seem to contribute to the improvement of strength and modulus.

Figure 9 shows the melt flow index (MFI) data of the blends. The presence of SAA results in great reduction of melt flow index. This indicates that structural changes such as the formation of graft copolymer take place. Other evidence supporting the formation of graft

copolymer is Molau's solubility test.<sup>14</sup> In our case the blend is placed in formic acid, which is a solvent for PA6 and a nonsolvent for PPE. If there is no graft copolymer present, the dispersed phase (PPE) will separate and float on the solution. When the blend containing SAA was placed in formic acid, the blend shows swelling phenomenon without separating or floating of minor phase, indicating the presence of SAA-PA6 graft copolymer.

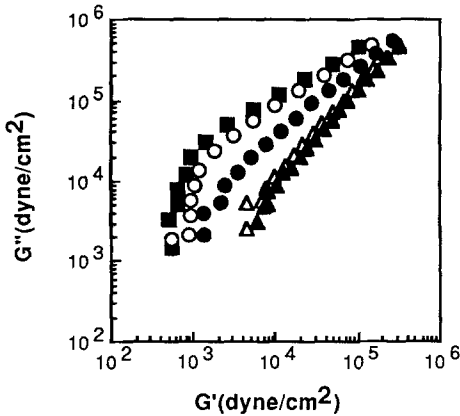


Fig. 6. Modified Cole-Cole plots for 30/70 PPE/PA6 blends: (■) without SAA, (○) 3 wt% SAA11 added, (●) 3 wt% SAA21 added, (△) 3 wt% SAA36 added, (▲) 3 wt% SAA46 added.

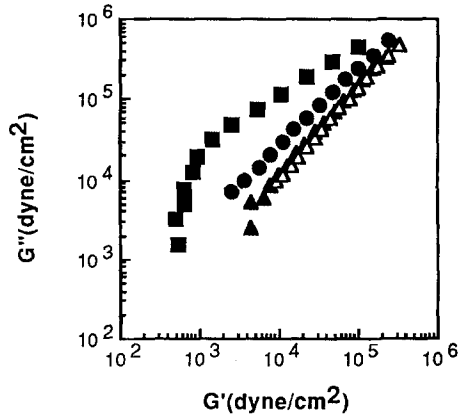


Fig. 7. Modified Cole-Cole plots for 30/70 PPE/PA6 blends: (■) without SAA, (●) 1.5 wt% SAA36 added, (▲) 3 wt% SAA36 added, (△) 5 wt% SAA36 added.

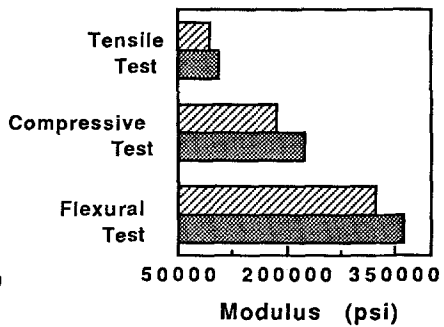
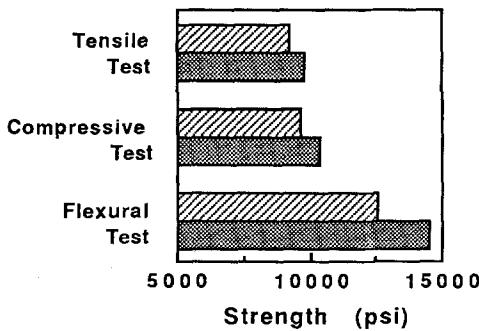


Fig.8. Strength and modulus data of 30/70 PPE/PA6 blends:   
 ▨, without SAA; ■, 3wt% SAA36 added.

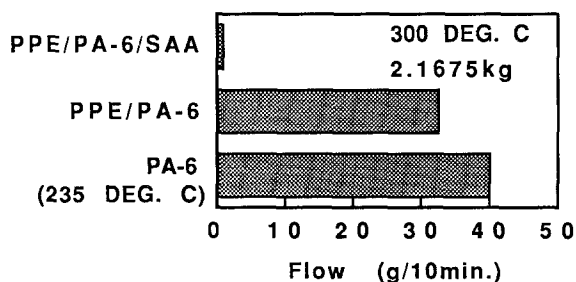


Fig.9. Melt flow index data of 30/70 PPE/PA6 blends.

## CONCLUSIONS

The styrene-acrylic acid random copolymer having acrylic acid content higher than 36 mol% plays an interfacial agent for PPE and PA-6 blends; thus more regular and finer dispersion is observed upon addition of a small amount of SAA copolymer. In the presence of a copolymer, the blends show non-Newtonian power-law behavior at low frequency and shift from the viscous behavior region to the elastic behavior region in the modified Cole-Cole plot. This seems to attribute to the branch formation and MWD broadening by chemical reaction between amine groups of PA-6 and carboxyl groups of SAA. In addition, Molau test and MFI data show that a graft copolymer has been formed by the chemical reaction. By modifying a small amount (ca. 3wt%) of copolymer, the blends exhibit about 10% increased mechanical properties

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