

# Morphology and Thermal Properties of PPS/ABS Blend Systems

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**ABSTRACT:** In this study the PPS/ABS blend system was investigated in order to collectively identify the relationship among blend morphology, chemical compatibilization, and thermal property. The ABS resin was chemically modified by the incorporation of maleic anhydride through reactive extrusion for enhanced compatibilization, and ABS/PPS and the modified ABS/PPS blends were prepared by a twin-screw extruder. The effect of chemical modification of ABS on the morphological, mechanical, and thermal properties of the resulting blend was examined. A strong chemical interaction between PPS and MABS was observed by optical

microscopy, scanning electron microscopy, and FTIR. The PPS/MABS blend showed a single glass-transition temperature in dynamic mechanical analysis, demonstrating pseudo-homogeneous phase morphology induced by chemical compatibilization. The PPS/MABS blend also exhibited an enhanced thermal stability and heat distortion temperature compared with the PPS/ABS blend. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 661–665, 2003

**Key words:** PPS/ABS blend; MABS; compatibilization

## INTRODUCTION

Poly(phenylene sulfide) (PPS) is a very stiff crystalline polymer in which sulfur and 1,4-phenylene groups are perfectly alternating. PPS has a glass-transition temperature of 80°C–90°C and a melting temperature of about 280°C. It has excellent dimensional stability, high stiffness, high modulus, chemical resistance, and fatigue resistance, which collectively make it comparable to metals.<sup>1,2</sup> For this reason, PPS has been increasingly applied to areas requiring high temperature and chemical resistance as well as to electrical, electronic, and automobile parts.<sup>3,4</sup> However, it should also be mentioned that PPS is brittle with low elongational strain, exhibiting a slow crystallization rate and low impact strength. Furthermore, chemical modification of PPS is extremely difficult. For the practical application of PPS, it is necessary to reduce the brittleness while maintaining its advantageous thermal, mechanical, and chemical properties.

To enhance the physical properties of PPS, several techniques have been applied. A crosslinking structure has been introduced to enhance the properties in order to increase the stiffness under high temperature in the presence of oxygen.<sup>5</sup> Composite materials have

also been prepared using carbon and glass fibers as reinforcement,<sup>6</sup> and blend systems using liquid crystalline polymers were also introduced to enhance its mechanical properties.<sup>7,8</sup> Also, CO<sub>2</sub> has been used as a plasticizer to decrease the melting point of PPS during melt processing.<sup>9</sup>

ABS resin is a copolymer of styrene, acrylonitrile, and polybutadiene and is a multiphase polymeric resin with butadiene rubber distributed as relevant-sized particles in the SAN matrix. ABS resin has been widely utilized in various areas because of its excellent properties such as the processibility of styrene, the chemical resistance of acrylonitrile, and the flexibility and impact property of butadiene.<sup>10</sup> Therefore, ABS resin is often utilized in the electricity, electronics, office machine, automobile, miscellaneous products, and construction materials areas. However, it has been pointed out that ABS has poor heat and ozone resistance because of the unsaturation of the butadiene moieties. To solve this problem, acrylic rubber, EPDM, or chlorinated PE has been replacing butadiene rubber; it has also been reported that heat resistance may be supplemented by blending with such excellent heat-resistant resins as a polycarbonate consisting of an aromatic ring.<sup>11–13</sup>

It was our aim to enhance the physical properties of PPS and ABS by the preparation of a novel PPS/ABS blend. In the preparation of PPS/ABS blend systems, ABS resin was chemically modified to enhance its compatibility. The ABS resin was chemically modified by reacting ABS with maleic anhydride (MAH) using

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a reactive extrusion process to produce modified ABS (MABS). In this article we describe the effect of the chemical modification of ABS in the PPS/ABS blend on the morphology and thermal viscoelastic properties of blends.

## EXPERIMENTAL

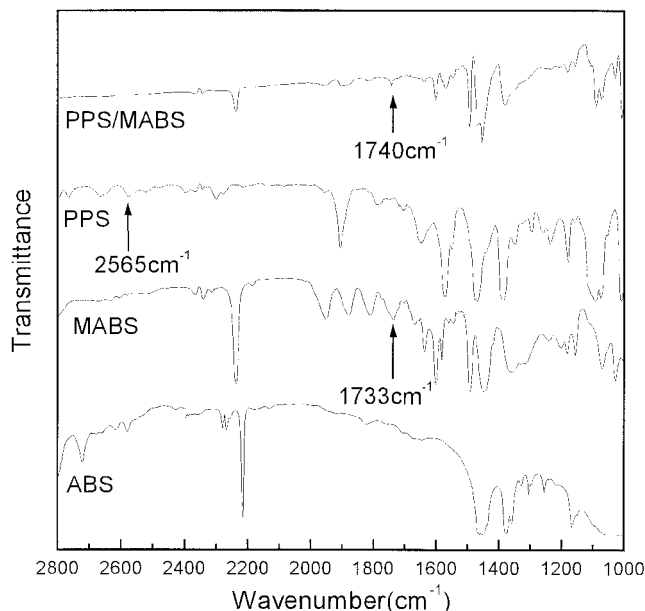
The PPS (Grade P-4) used in this study was provided by Toflen Co., Japan; acrylonitrile butadiene styrene (ABS) was obtained from LG Chemicals Inc. (HI121; melt flow index = 18.0 g/10 min,  $M_w = 100,000$ ). MAH and dicumyl peroxide were purchased from Aldrich and used without further purification.

The reactive extrusion process was used to modify the chemical structure of ABS by adding 0.5 phr of MAH into the ABS. A twin-screw extruder (HAAKE system 90) was used for the reactive extrusion at barrel temperatures of 230°C, 240°C, and 250°C and a die temperature of 240°C. The screw velocity was 20 rpm. Dicumyl peroxide and Irganox B1171 (0.15 phr each) were used as a radical initiator and a heat stabilizer, respectively.

The PPS/ABS and PPS/MABS blend systems were produced at ratios of 100:0, 70:30, 50:50, and 30:70 by weight. The blends were prepared by using a twin-screw extruder (HAAKE system 90) at barrel temperatures of 250°C, 270°C, and 300°C and through a 3-mm-diameter die at 280°C. The screw velocity was set between 20 and 30 rpm. The extrudate from the die was frozen in ice water to decrease phase separation and then cut into pellets. The blend was injection-molded for test specimens by ENGEL (ES 330/80). The die temperature was 100°C, the injection pressure was 62 bar, and the injection velocity was 94.6 mm/s.

A Mattson 1000 for Fourier transform infrared spectroscopy (FTIR) was used to analyze the chemical structure of the blend systems. A polarized optical microscope (Nikon) and a scanning electron microscope (SEM; JEOL Co.) were used to investigate the morphology. In the optical microscopy investigation, the heating rate of the hot stage was set as 2°C/min.

The glass-transition temperature and complex moduli were measured by DMA983 (TA Instruments). The size of a specimen was 10 × 35 × 1.9 mm, and the heating rate was 10°C/min. Thermal stability was monitored using the TGA-7 (Perkin Elmer) at a constant heating rate of 20°C/m. Heat distortion temperature (HDT) was measured using an HDT-VICAT tester (model MP/3) in the silicon oil bath (ATS Farr Co.). The testing method was according to the Korean Standard Testing Method (KSTM-3065) in which a specimen (3.17 × 12.7 × 3.2 mm) was under a constant stress of 1820 KPa (or a load of 638 g).



**Figure 1** IR spectra of ABS, MABS, PPS, and PPS/MABS: PPS:ABS = 7:3; PPS:MABS = 7:3; PPS:ABS = 5:5; PPS:MABS = 5:5; PPS:ABS = 3:7; and PPS:MABS = 3:7.

## RESULTS AND DISCUSSION

MABS was produced by grafting a small amount (0.5 phr) of MAH onto ABS by using reactive extrusion process. The unreacted MAH was extracted by water after the extrusion process. The grafting reaction was monitored by FTIR spectroscopy. As seen in Figure 1, the characteristic peak of the carbonyl group at 1733  $\text{cm}^{-1}$  appeared after the reaction, which confirms that MAH was successfully grafted onto ABS. The monitoring of the exact concentration of grafted MAH onto ABS using a typical acid/base titration method was extremely difficult because of limited solubility.

PPS and ABS (or MABS) were blended by using a twin-screw extruder at the barrel temperatures of 250°C, 270°C, and 300°C for complete melt mixing. The screw velocity was set between 20 and 30 rpm because the extrusion was interrupted by gas evolution in case the speed was increased to more than 30 rpm. The blend was collected through a die 3 mm in diameter at 280°C. The extrudate from the die was passed through cold water to decrease phase separation as well as to remove unreacted MAH moieties, and then it was cut into pellets. The blend was injection-molded for further tests.

The presence of grafted MAH in the PPS/ABS blend was observed by FTIR spectroscopy. Comparing the FTIR spectra of PPS/MABS and MABS, in Figure 1, shows the characteristic peak of the carbonyl group of MABS and PPS/MABS was detected at 1733  $\text{cm}^{-1}$  and 1740  $\text{cm}^{-1}$ , respectively. The peak shift was conceivably due to the reaction between the MAH moieties in

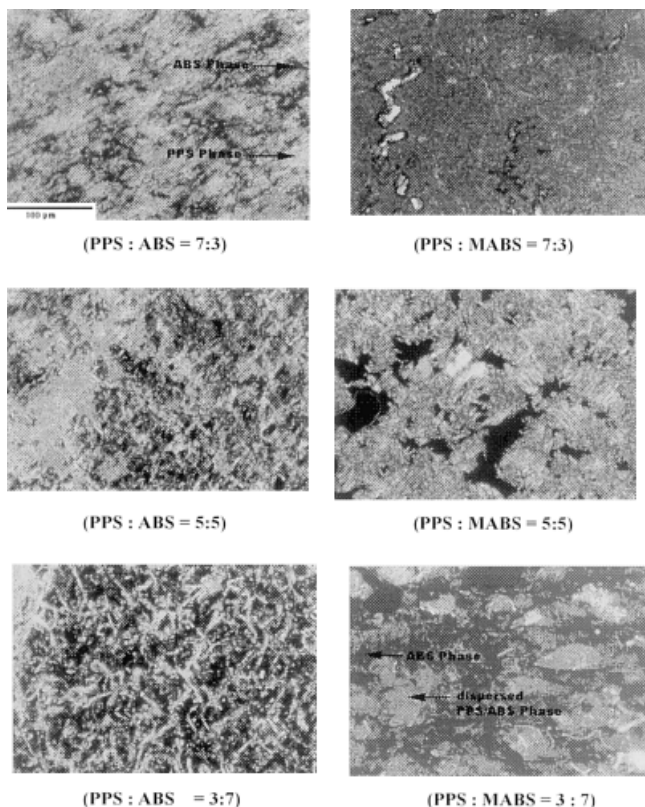


Figure 2 Polarized optical microscopy images of blends.

MABS and the sulfide group of PPS. The occurrence of a chemical reaction between MAH and sulfide can be further confirmed by monitoring IR spectra, in which the characteristic peak of the sulfide group at  $2565\text{ cm}^{-1}$  disappears after blend formation.

Figure 2 shows the polarized optical microscopy images of the PPS/ABS and PPS/MABS blends at various ratios. The bright area, referred to as the PPS phase, increased in proportion to the amount of PPS in both blend systems. The morphology of these two systems exhibits different features in the distribution and dispersion of each phase. In the 7:3 PPS/ABS blend, relatively large ABS and PPS phases are evenly distributed in the specimen. However, in the PPS/MABS blend, MABS and PPS are well dispersed to form a seemingly homogeneous mixture, with the MABS island appearing as a large dark area in case an excessive amount of MABS (PPS/ABS = 5:5 and 3:7) were to be incorporated into the blend. Overall, ABS and MABS in the blend exhibited good distribution and good dispersion characteristics, respectively. It can be clearly observed that the size of the MABS phase was reduced compared with the ABS for the blend system (PPS/ABS = 7:3) in which the proportion of the each component was well balanced. This finding can also be confirmed by increase in the size and the number of MABS island as the MABS amount

increased to more than 50%. However, in the ABS/PPS blend system, such an irregular ABS island was not detected, but the dark area (ABS phase) was evenly distributed and also increased as the ABS amount increased in the blend. This confirms that MAH compatibilizer reduced the surface tension of the MABS/PPS interphase via reaction and thus reduced the size of the MABS phase.

Figure 3 shows SEM photomicrographs of the fractured surface of the blend specimens. The number of ABS (or MABS) particles increased in proportion to the amount of ABS incorporated. It can be seen that the particle size of MABS is slightly smaller than that of ABS in the blend system of PPS/ABS(7:3). An interesting fact that can be seen in the SEM photomicrographs is that the MABS particles are sometimes fractured with the PPS matrix, which is indicated by the arrows in PPS/MABS blend. Such a fractured surface of ABS is not observed in ABS/PPS systems. To clarify this finding, the magnified image of the area where the MABS particles are fractured is shown in Figure 4, in which the interface of MABS and PPS can be clearly observed. Conclusively, the adhesive force between ABS/PPS blend systems is increased by adopting the reactive compatibilizer MAH, and thus the mechanical properties are expected to be improved.

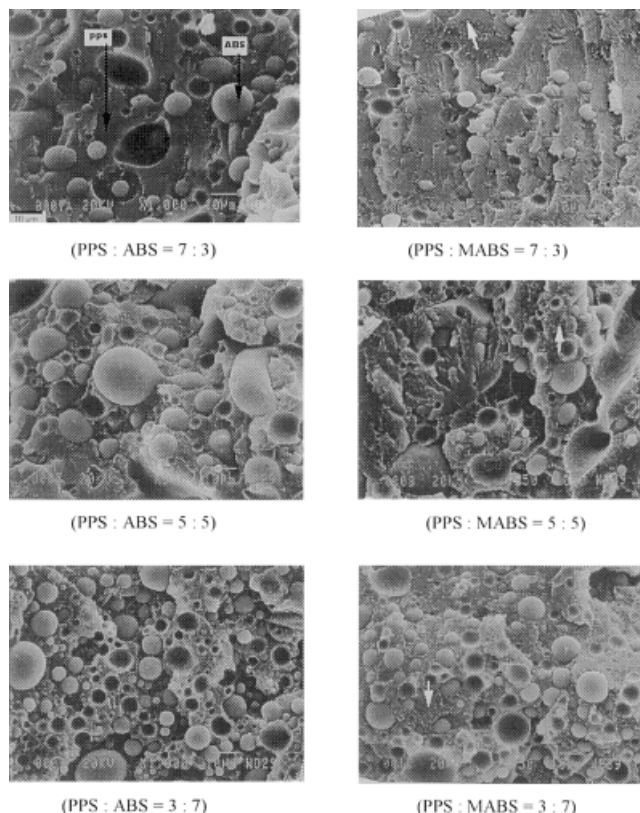
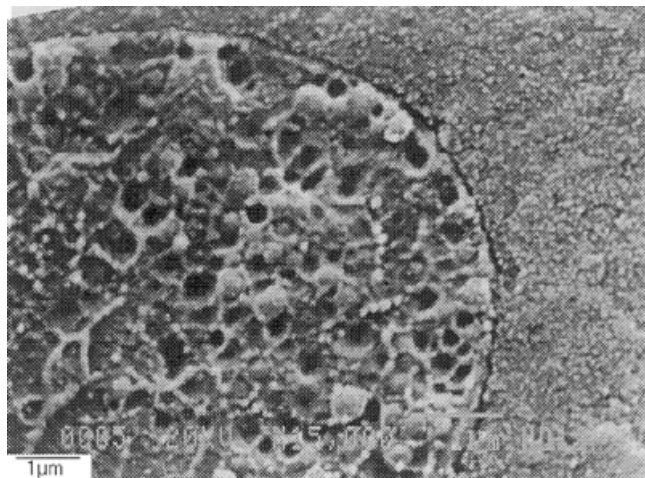


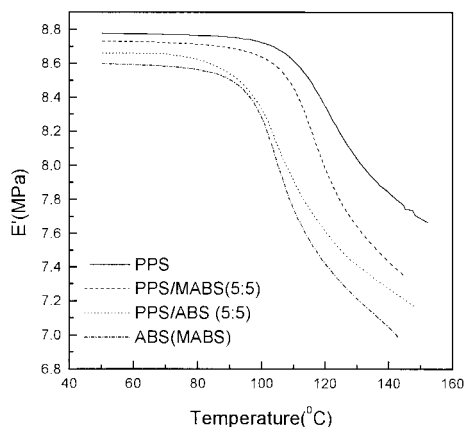
Figure 3 SEM image of fracture surface.



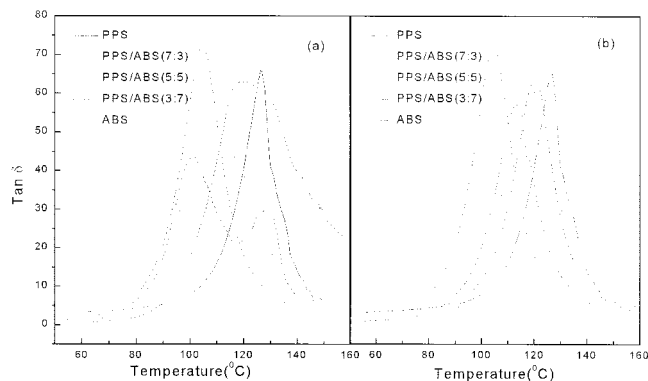


**Figure 4** Magnified SEM image of the PPS/MABS (7:3) blend.

Figures 5 and 6 compare  $\epsilon'$  and  $\tan \delta$  of PPS/ABS and PPS/MABS blend systems measured by DMA at a constant heating rate. As can be seen, the glass-transition temperature as well as the storage modulus increase as the amount of PPS increases. The ABS and MABS show nearly the same  $\epsilon'$  and  $\tan \delta$  results. In the PPS/ABS blends at 50 and 70 wt % of ABS, two peaks of  $\tan \delta$  are attained corresponding to each  $T_g$  of PPS and ABS, which represents typical phase-separation behavior of physical blend systems with poor compatibility. However, with 50 wt % of ABS, each peak moves to a closer temperature range; further, at 30 wt % of ABS the ABS peak disappears, and a broad peak of  $\tan \delta$  appears in the  $T_g$  range of PPS. Accordingly, compatibility seems to be dependent on the composition of the blend. The chemical affinity between the  $-S$  or  $-SH$  of PPS and the  $-C\equiv N$  of ABS is likely to change with the amount of each component. However, Figure 5(b) exhibits  $\tan \delta$  as a function



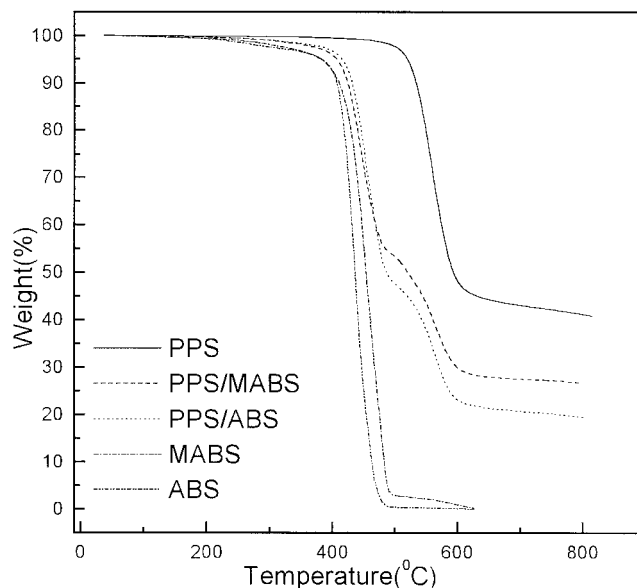
**Figure 5** Storage moduli of PPS, ABS (MABS), and blends.



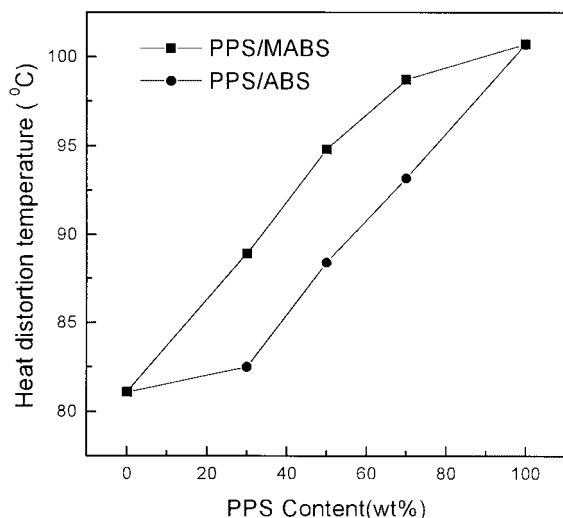
**Figure 6**  $\tan \delta$  values of (a) PPS/ABS and (b) PPS/MABS blends.

of PPS/MABS blend compositions, where only a single sharp peak is observed in all the compositions of the blend systems. The glass-transition temperature of the blend increases as the PPS amount increases. It demonstrates that the two polymers in the blend are well mixed to form a homogeneous mixture because of the facile reactions of  $-SH$  in PPS with MAH. So, from the monitoring of the  $\tan \delta$  peaks of PPS/MABS and PPS/MABS systems, it has been clearly demonstrated that a PPS/ABS and PPS/MABS blend forms a physical blend having independent phases and a chemically bonded pseudo-homogeneous phase, respectively.

Figure 7 shows the TGA thermograms of PPS, ABS, MABS, and PPS/MABS in a nitrogen atmosphere at a heating rate of  $20^\circ\text{C}/\text{min}$ . As can be seen in Figure 7,



**Figure 7** TGA thermograms of PPS, ABS, MABS, and blends.



**Figure 8** Heat distortion temperature depending on PPS contents.

pure PPS and ABS begin to lose weight at 520°C and 400°C, respectively, and the blend systems show two stages of weight loss depending on the blend ratio. The degradation behavior does not seem to be affected by the chemical treatment with MAH.

The heat distortion temperature (HDT) of the blends is usually affected by particle size, particle-size distribution, phase morphology, adhesive force, and residual stress. In Figure 8 the HDT of PPS/ABS and PPS/MABS systems are compared as a function of PPS amount. Overall, the PPS/MABS blend exhibits 6°C–7°C higher HDT than the PPS/ABS blend.

## CONCLUSIONS

1. PPS and ABS were successfully blended by using MAH as a reactive compatibilizer in the twin-screw melt extrusion process.
2. The adhesive force between PPS and ABS was increased by the facile reaction of MAH with a sulfide group, resulting in well-dispersive morphology in melt blending.
3. The PPS/MABS blend exhibited a single glass-transition temperature and higher HDT because of the chemical reactions between PPS and ABS through MAH.

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