

Effects of Maleated Syndiotactic Polystyrene on the Morphology, Mechanical Properties, and Crystallization Behavior of Syndiotactic Polystyrene/Polyamide 6 Blends

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ABSTRACT: The compatibilization of syndiotactic polystyrene (sPS)/polyamide 6 (PA-6) blends with maleic anhydride grafted syndiotactic polystyrene (sPS-g-MA) as a reactive compatibilizer was investigated. The sPS/PA-6 blends were *in situ* compatibilized by a reaction between the maleic anhydride (MA) of sPS-g-MA and the amine end group of PA-6. The occurrence of the chemical reaction was substantiated by the disappearance of a characteristic MA peak from the Fourier transform infrared spectrum. Morphology observations showed that the size of the dispersed PA-6 domains was significantly reduced and that the interfacial adhesion was much improved by the addition of sPS-g-MA. As a result of reactive compatibilization, the impact strengths of the sPS/PA-6 blends increased with an increase in the sPS-g-MA content. The crystallization behaviors of the

blends were affected by the compatibilization effect of sPS-g-MA. A single melting peak of sPS in the noncompatibilized blend was gradually split into two peaks as the amount of the compatibilizer increased. A single crystallization peak of PA-6 in the noncompatibilized blend became two peaks with the addition of 3 wt % sPS-g-MA. The new peak was a result of the fractionation crystallization. As the amount of sPS-g-MA increased, the intensity of the new peak increased, and the original peak nearly disappeared. Finally, the crystallization peak of PA-6 disappeared with 20 wt % sPS-g-MA in the blend. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2502–2506, 2003

Key words: syndiotactic; polystyrene; compatibilization; blending

INTRODUCTION

Syndiotactic polystyrene (sPS) is a new engineering thermoplastic. In addition to its good properties from atactic polystyrene (aPS), sPS has additional excellent properties, such as high modulus and excellent resistance to heat and chemicals, which are due to its crystalline nature.

Polymer blends are known to be a very economic route for extending the applications of materials. Therefore, polymer blends containing sPS are of great interest from a commercial viewpoint.

Recently, it has been reported that sPS is completely miscible with aPS over the entire composition.¹ The miscibility between sPS and other polymers such as poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(vinyl methyl ether), which have been reported to be miscible with aPS,^{2,3} has also been investigated.^{4–8}

Except for a few polymer pairs such as aPS and PPO, sPS is not miscible with most polymers because of unfavorable mixing enthalpy. A suitable compatibilizer for those sPS-based blends is necessary for

desirable mechanical properties to be obtained. Copolymers containing aPS, such as poly(styrene-*co*-maleic anhydride), styrene-butadiene-styrene block copolymer, and styrene/hydrogenated butadiene/styrene (SEBS) copolymers, can be used as compatibilizers for sPS-based blends. Unfortunately, aPS-based copolymers are not efficient enough to compatibilize sPS-based blends because they reduce the crystallization rate of sPS and, therefore, deteriorate the good properties of sPS coming from its crystalline nature. It has been reported that sPS in sPS/aPS blends reduces the crystallization rate^{1,9} and that sPS/SEBS blends do not provide good mechanical properties.¹⁰ Therefore, copolymers containing sPS chain segments are preferable. A copolymer used as a compatibilizer can either be synthesized in advance^{11,12} or be formed *in situ*^{11,13,14} during the processing. The latter, a so-called reactive compatibilizer, is especially preferred in industry.

The most common example of the *in situ* compatibilization of polymer blends is the application of maleated polymers with polyamides, in which the blends are compatibilized by copolymers formed by a chemical reaction between maleic anhydride (MA) and amine end groups of polyamide 6 (PA-6) during a melt-mixing process.^{15–18} In addition to amine groups,

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MA groups can react with other functional groups such as oxazoline, ester, and carboxylic acid. Therefore, the preparation of MA-functionalized sPS is very attractive and challenging.

The copolymerization of styrene with MA by syndiospecific polymerization is not practical because of the unfavorable reaction between MA and the catalyst or cocatalysts. Instead of MA, Tazaki and coworkers^{19,20} copolymerized styrene with maleimide by a metallocene catalyst, and they found that the copolymer so made was insufficient as a reactive compatibilizer for sPS/polyamide blends.

The synthesis of a maleic anhydride grafted syndiotactic polystyrene (sPS-g-MA) copolymer by radical polymerization is an alternative route to be considered. The radical grafting of MA onto syndiotactic poly(styrene-co-divinylbenzene) has been reported.²¹ However, there is no work on radical grafting onto an sPS backbone.

Recently, we successfully synthesized sPS-g-MA by a technique developed in our laboratory. By this technique, sPS-g-MA was synthesized without any degradation in its molecular weight or any deterioration in the crystallizability of sPS. The technical details for the synthesis of sPS were described in a previous article.²² In this article, we present experimental results for the compatibilization of sPS/PA-6 blends and demonstrate the effectiveness of sPS-g-MA made as a reactive compatibilizer.

EXPERIMENTAL

Materials

sPS was synthesized in our laboratory (weight-average molecular weight = 612,800; molecular weight distribution = 2.21; SI = 99.5%). The PA-6 used was a commercial product (Kolon KN171; number-average molecular weight = 30,000). Dicumyl peroxide, used as a radical initiator for the synthesis of sPS-g-MA, and MA were purchased from Aldrich Chemicals. sPS-g-MA with an MA content of 1.5 wt % was synthesized in our laboratory. The method for the preparation of sPS-g-MA is summarized in the next section.

Preparation of sPS-g-MA

The maleation of sPS was carried out for 8 h in a 2-L glass reactor equipped with a mechanical agitator. sPS powder (1 kg) was introduced into the glass reactor, which was then purged by nitrogen gas for a few hours. Toluene was poured into the reactor until the sPS powder was completely soaked with toluene. Toluene was used to swell the sPS so that the diffusion of the initiator and MA into the sPS solid particle was enhanced. A radical initiator, dicumyl peroxide, was then fed into the reactor, and the temperature was

TABLE I
Composition of the Blends (wt %) Used in This Study

Notation	sPS	sPS-g-MA	PA-6
sPS/PA (80/20)	80	0	20
sPS/sPS-g-MA/PA (77/3/20)	77	3	20
sPS/sPS-g-MA/PA (75/5/20)	75	5	20
sPS/sPS-g-MA/PA (70/10/20)	70	10	20
sPS/sPS-g-MA/PA (60/20/20)	60	20	20
sPS/sPS-g-MA (80/20)	80	20	0

maintained at 70°C. The mixture was stirred by the mechanical agitator at 80 rpm for 1 h. The reactor temperature was elevated to 100°C, and then MA was added into the reactor; the mixture was stirred for 8 h at a high speed (ca. 400 rpm). The product obtained in this way was washed twice with methanol and acetone, respectively. Filtration was applied at each washing step. Finally, methyl ethyl ketone was used to extract the unreacted MA for several hours. The final product was dried at 80°C for 5 h.

Preparation of the sPS/PA-6 blends

The compositions of the blends used are shown in Table I. All the blends were melt-blended in a Haake Rheocord 600 equipped with roller blades. Blending was carried out at 280°C and 50 rpm for a period of 6 min. The samples, after mixing, were immediately removed from the mixer, quenched in a water bath, and ground into small pieces.

Characterization of the polymer blends

The samples were molded into plaques 2 mm thick and then fractured in liquid nitrogen. The morphology of the fractured surface was examined with scanning electron microscopy (SEM; model 840A, JEOL) at 20 kV after the surface was coated with gold.

The Izod impact strength of the blends was measured on a Toyoseiki impact tester. The average impact strength was calculated with at least five specimens. The samples were heat-molded into sheets at 280°C and then cut into pieces (63 mm × 13 mm × 2 mm).

Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer FTIR spectrometer. Films were obtained by hot-plate pressing and then dried at 80°C under vacuum for 6 h before analysis.

The thermal properties of the blends were measured with differential scanning calorimetry (DSC; 2010 DSC V4.1B, DuPont) under a nitrogen atmosphere. First, the samples were completely melted at 300°C for 5 min to erase the thermal history and were quenched to 30°C as fast as technically possible. The samples were then heated to 300°C at a rate of 10°C/min (heating scan), equilibrated for 3 min, and cooled down to 30°C at a rate of -10°C/min (cooling scan).

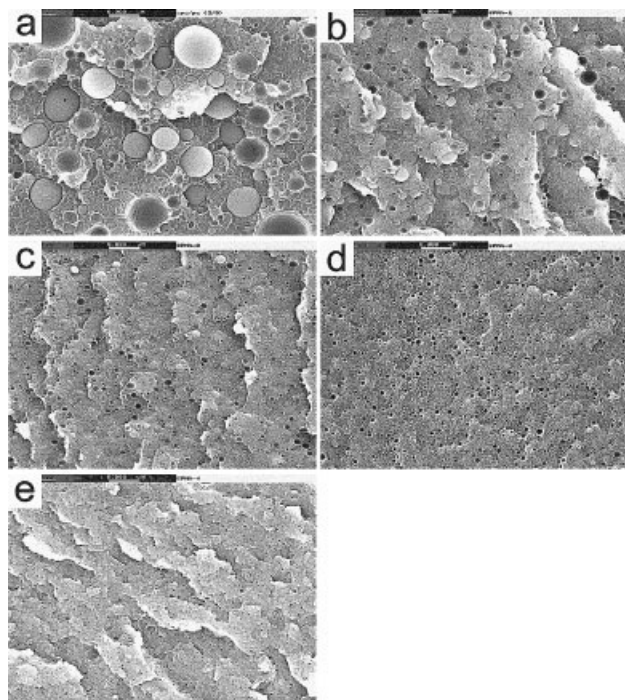


Figure 1 SEM micrographs of uncompatibilized and compatibilized sPS/PA-6 blends: (a) sPS/PA-6 (80/20), (b) sPS/sPS-g-MA/PA-6 (77/3/20), (c) sPS/sPS-g-MA/PA-6 (75/5/20), (d) sPS/sPS-g-MA/PA-6 (70/10/20), and (e) sPS/sPS-g-MA/PA-6 (60/20/20).

RESULTS AND DISCUSSION

The presence of MA functional groups in sPS-g-MA can be confirmed directly when it is used as a reactive compatibilizer in an sPS/PA-6 blend and followed by morphology observations. The sPS backbone in sPS-g-MA is expected to cocrystallize with the pure sPS matrix in the sPS/PA-6 blends as a strong anchor, whereas the MA group in sPS-g-MA, which is pendent from the sPS backbone, reacts with the amine end group of PA-6, forming proliferating side chains embedded in the PA-6 domain as another anchor, so that the sPS/PA-6 blends are compatibilized by the *in situ* formed sPS/PA-6 copolymer.

Figure 1 shows SEM micrographs of the sPS/PA-6 blends compatibilized with various amounts of sPS-g-MA as a reactive compatibilizer. The blend without sPS-g-MA (80/20 sPS/PA-6) shows a highly incompatible nature, as expected [Fig. 1(a)]. The large and nonuniformly distributed PA-6 domains can clearly be seen. The smooth and clear surface of the PA-6 domains indicates poor interfacial adhesion between two phases. With the addition of 3 wt % sPS-g-MA, the size of the PA-6 domain is significantly reduced [Fig. 1(b)], and the domain size decreases with the further addition of sPS-g-MA [Fig. 1(c–e)]. In the blend containing 20 wt % sPS-g-MA, the dispersed PA-6 domains can hardly be recognized. The remarkable reduction of the domain size in the compatibilized blends is attributed to the

strong compatibilization effect of the sPS-PA-6 copolymer formed *in situ* by a reaction between MA in sPS-g-MA and amine end groups in PA-6 during the mixing process.

The formation of the sPS/PA-6 copolymer may also be proven by FTIR spectra. Figure 2 shows the FTIR spectra of sPS/sPS-g-MA (80/20) and sPS/sPS-g-MA/PA-6 (60/20/20). The disappearance of the MA characteristic peak at 1778 cm^{-1} can be attributed to the reaction between MA and amine groups. The disappearance of the double peak at 1335 and 1351 cm^{-1} indicated by arrows can also be attributed to the reaction.

As discussed previously, the sPS/PA-6 copolymer as a compatibilizer in the sPS/PA-6 blends strengthens the adhesion between the two phases and reduces the size of the PA-6 domains. The improved interfacial properties result in better mechanical properties. Figure 3 shows Izod impact strengths versus the amount of sPS-g-MA in the blends. The Izod impact strength of the blend increases linearly with the amount of sPS-g-MA up to 5 wt % and then remains almost constant with the further addition of the reactive compatibilizer.

Because PA-6 has better toughness than sPS, the PA-6 domains can absorb more impact energy than sPS. Therefore, compatibilized sPS/PA-6 blends should have better impact strength than sPS. The sPS/PA-6 blend without a compatibilizer shows a very low impact strength, even lower than that of pure sPS because of the weak interface and the poor force transfer caused by the poor adhesion between two phases. The increase in the Izod impact strength with the addition of sPS-g-MA is attributed to the improved adhesion between the two phases and the increased number of domains. In the blend with 5 wt % sPS-g-MA, the optimum domain size seems to be obtained, and so the blend has the maximum impact strength. In the blends with 20 wt % sPS-g-MA, the PA-6 domains are too small, and the effectiveness for absorbing impact energy is diminished; this yields lower impact

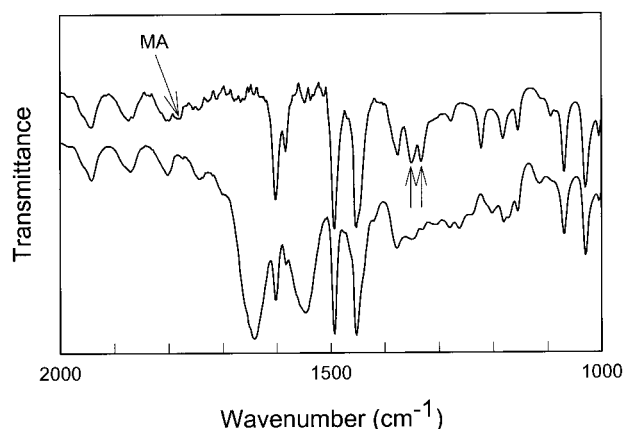


Figure 2 FTIR spectra for 80/20 sPS/sPS-g-MA (top) and 60/20/20 sPS/sPS-g-MA/PA (bottom).

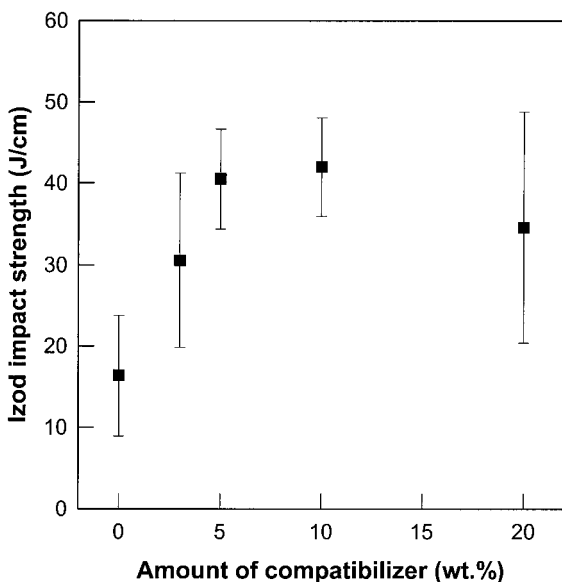


Figure 3 Impact strength of sPS/PA-6 blends versus the amount of the reactive compatibilizer.

strength even though the adhesion is most likely the strongest among all the blends.

Figure 4 shows heating thermograms of the sPS/PA-6 blends used in this study. The blend without a compatibilizer, sPA/PA-6 (80/20), shows two melting peaks (PA-6, 221°C; sPS, 273°C). The melting peak of sPS in the blends is gradually split into two peaks with the addition of the compatibilizer. We designate the strong peak as a normal melting peak and the weak shoulder as an unusual peak. The normal melting temperature of sPS does not change with the amount of the compatibilizer, whereas the intensity of the unusual peak increases and the unusual peak temperature decreases. To clarify the effect of sPS-g-MA on this double melting behavior, we investigated DSC for neat sPS-g-MA and an sPS/sPS-g-MA (3/1 wt %/wt %) mixture. Neat sPS-g-MA also shows double melting behavior, with one strong melting peak at 293 and the other weak melting peak at 269. However, the sPS/sPS-g-MA (3/1) mixture shows one melting peak with a very weak shoulder. These results imply that the double melting behavior of neat sPS-g-MA is diluted in the sPS/sPS-g-MA/PA-6 blends and the double melting behavior of the sPS/sPS-g-MA/PA-6 blends results from the compatibilization effect.

As revealed in many studies on maleated polymers and polyamide blends, such as maleated polyolefin and PA-6 blends,^{23,24} sPS/PA-6 copolymer is *in situ* formed by a chemical reaction between the MA and amine end groups of PA-6. This sPS/PA-6 copolymer compatibilizes sPS/PA-6 blends. In the blend without the copolymer (80/20 sPS/PA-6), the sPS melting peak is not affected by PA-6 because of its incompatible nature. With the addition of sPS-g-MA, the inter-

facial tension decreases and the interpenetration between the two phases is enhanced. The interpenetration between the two phases increases the portion of the interface. The hampering effect of PA-6 prevents the perfect crystallization of sPS (thick lamellae) at the interface, resulting in a melting temperature lower than the melting temperature in the bulk. With the increase in the amount of sPS-g-MA in the blends, the portion of the interface increases, and this leads to the increased intensity and decreased melting temperature of the peak appearing at the lower temperature.

The cooling thermograms of sPS/PA-6 blends compatibilized with various amounts of sPS-g-MA are shown in Figure 5. The blend without the compatibilizer shows two crystallization peaks (sPS, 254°C; PA-6, 192°C). The crystallization peaks of both components are affected by the addition of the compatibilizer. The mechanism for the change of the crystallization peak of sPS with various amounts of the compatibilizer is unclear, and it is not discussed here. What interests us is the change of the crystallization behavior of PA-6 by the compatibilizer. With the addition of 3 wt % compatibilizer, the crystallization peak of PA-6 is split into two peaks. In addition to the normal crystallization peak at 192°C (type I), a new crystallization peak at 186°C (type II) appears. With the increase in the amounts of the compatibilizer, the normal crystallization peak becomes weak and nearly disappears when the compatibilizer content reaches 10 wt %. Simultaneously, the lower crystallization peak (type II) decreases further and then almost disappears when the compatibilizer content reaches 20 wt %.

The crystallization behavior in polymer blends is much affected by the compatibility between phases. In

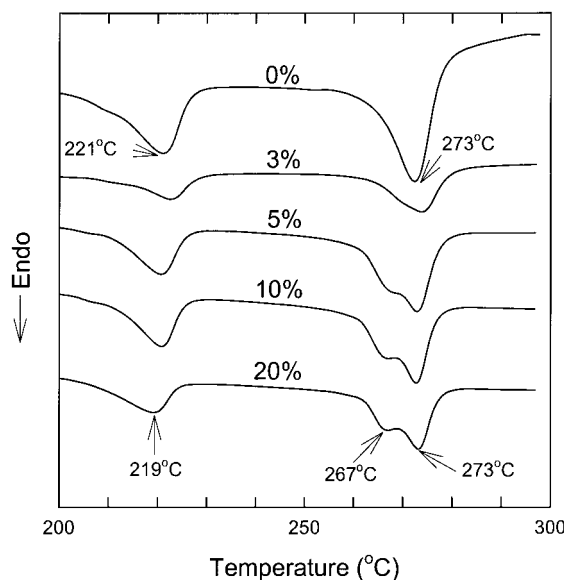


Figure 4 Heating thermogram of the sPS/PA-6 blends with various amounts of sPS-g-MA.

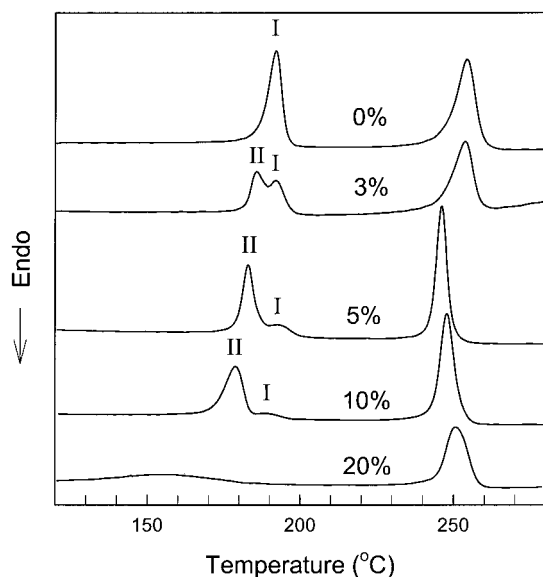


Figure 5 Cooling thermogram of the sPS/PA-6 blends with various amounts of sPS-g-MA.

the sPS/PA-6 blend without the compatibilizer, a highly incompatible nature between sPS and PA-6 makes them crystallize independently. With the addition of the compatibilizer, interpenetration between the two phases probably occurs. The crystallization behavior of both components is affected mutually by the coexistence with the counterpart component in both phases. Because PA-6 is enclosed by sPS and the amount of PA-6 in the blend is lower than that of sPS, the crystallization of PA-6 is more affected by the compatibilization than sPS.

According to crystallization-fractionation theory, fractionation crystallization occurs at a temperature lower than the normal crystallization temperature when the dispersed phase size is smaller than a critical value.²⁵⁻²⁷ With the addition of 3 wt % sPS-g-MA, the domain size becomes very small, and the size distribution becomes broader. The sizes of some domains are probably lower than the critical value, and this results in a fractionation-crystallization peak in addition to the normal crystallization peak. With the increase in sPS-g-MA from 3 to 10 wt %, the population of small domains, the size of which is smaller than the critical value, increases further. As a result, the normal crystallization peak becomes much weaker and eventually disappears (10 wt % sPS-g-MA). More interestingly, with the further increase of sPS-g-MA to 20 wt %, even the fractionation-crystallization peak nearly disappears. This means that the domain sizes of PA-6 is too small for the crystallization of PA-6 or that the PA-6 crystalline size is too small to be detected by DSC. Tang et al.²⁴ reported that there were no crystallization peaks of polyamide 12 (PA-12) in a DSC heat-

ing run of a PP-MA/PA-12 (3/1 w/w) blend when the domain size of PA-12 was less than 0.3 μm .

CONCLUSIONS

It has been proven that an immiscible sPS/PA-6 blend can successfully be compatibilized with sPS-g-MA as a reactive compatibilizer. The addition of sPS-g-MA to sPS/PA-6 blends reduces the size of the dispersed PA-6 domains and makes the PA-6 domains well dispersed. The impact strength increases with the addition of sPS-g-MA, and this is followed by a small decrease with the further addition of the compatibilizer. With FTIR, it has been observed that the reaction between MA and amine end groups occurs during a melt-mixing procedure in sPS/sPS-g-MA/PA-6 blends. The crystallization behaviors of both components in the blends are affected by the reactive compatibilizer, sPS-g-MA.

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