

Effects of Maleated Styrene–(Ethylene-*co*-Butene)–Styrene on the Morphology and Mechanical and Thermal Properties of Polystyrene/Polyamide 1212 Blends

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ABSTRACT: Polystyrene (PS)/polyamide 1212 (PA 1212) blends were compatibilized with a maleated triblock copolymer of styrene–(ethylene-*co*-butene)–styrene (SEBS-*g*-MA). Scanning electron microscopy revealed that the addition of SEBS-*g*-MA was beneficial to the dispersion of PA 1212 in the PS matrix because of the reaction between them. The variation of the fraction of SEBS-*g*-MA in the blends allowed the manipulation of the phase structure, which first formed a sheetlike structure and then formed a cocontinuous phase containing PA 1212/SEBS-*g*-MA core–shell morphologies. As a result, the mechanical properties, especially the Charpy notched impact resistance, were significantly improved with

the addition of SEBS-*g*-MA. Differential scanning calorimetry (DSC) data indicated that the strong interaction between SEBS-*g*-MA and PA 1212 in the blends retarded the crystallization of PA 1212. The heat distortion temperature of the compatibilized blends was improved in comparison with that of the unmodified blend, probably because of the apparent increase in the glass-transition temperature with an increasing concentration of SEBS-*g*-MA. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1354–1360, 2005

Key words: compatibilization; polyamides; polystyrene; toughness

INTRODUCTION

Many polymer pairs are thermodynamically incompatible and produce blends with very poor mechanical properties because of their poor interfacial adhesion.^{1–3} The compatibility can be improved by the addition of a block or graft copolymer as a compatibilizer. Such a compatibilizers affect the morphology and properties of blends by adsorption at the interface between the incompatible polymers.^{3–6}

The most important attributes of some polyamides with longer alkane segments (\geq deodecane), such as polyamide 1212 (PA 1212), are superb toughness, high tensile strength, abrasion resistance, dimensional stability, and excellent wet strength retention.

Atactic polystyrene (aPS) has high heat resistance and a high modulus of elasticity, a low dielectric constant, and excellent resistance to chemicals. In addition to these desirable properties, aPS has the drawback of inherent brittleness. Thus, aPS might be favorably applied predominantly in blends with other polymers or composites.^{7,8}

However, polystyrene (PS) is immiscible with PA 1212 and would lead to poor mechanical properties through simple blending. A maleated triblock copolymer of styrene–(ethylene-*co*-butene)–styrene (SEBS-*g*-MA), used as a kind of elastomer, contains blocks miscible with PS and blocks immiscible with PS. The elastomeric phase of SEBS-*g*-MA is grafted with maleic anhydride, which can react with amide groups at the ends of polyamides to form copolymers during melt processing, providing the required interfacial adhesion and controlling the morphology of the blends. Therefore, SEBS-*g*-MA can be used as an effective compatibilizer for PS and PA 1212.

In this work, SEBS-*g*-MA was used as a compatibilizer for aPS/PA 1212 blends. The effects of SEBS-*g*-MA on the mechanical properties of the aPS/PA 1212 blends were investigated. The influence of the compatibilizer on the morphology and thermal properties of the blends was also studied.

EXPERIMENTAL

Materials

PA 1212 was obtained from Shangdong Dongchen Chemical Co. (Shangdong, China) with a melt-flow index of 40 g/10 min (220°C, 5 kg). PS with a melt-

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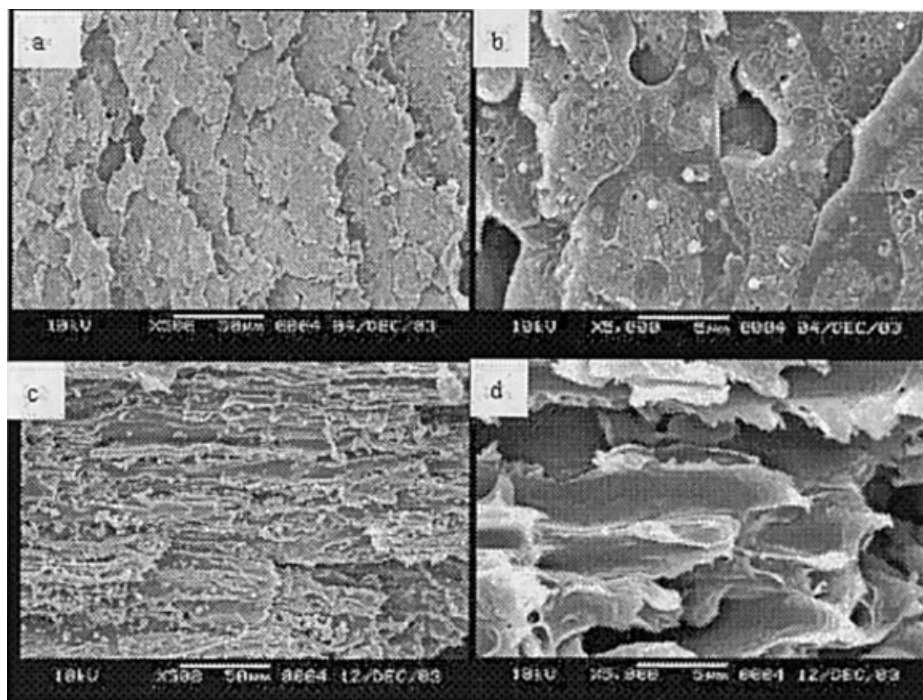


Figure 1 SEM microphotographs of freeze-fractured surfaces of PS/PA 1212 (70/30): (a,b) unetched and (c,d) etched.

flow index (220°C, 5 kg) of 24 g/10 min was obtained from Qimei Chemical Material Co., Ltd. (Guangdong, China). SEBS-*g*-MA was supplied by Shanghai Lingen Chemical Co. (Shanghai, China). The grafting ratio of maleic anhydride was about 1 wt %.

Preparation of the blends

All materials were dried at 80°C for at least 12 h in an oven before blending. The blends were prepared on a $\phi 35$ twin-screw extruder (TE-35, Jiangsu Keya Chemical Engineer Co., Ltd., Nanjing City, China) in the proper proportions. The series of barrel temperatures and the screw speed of the extruder were set at 190–201–201–210–210°C and 120 rpm, respectively. The extruded materials were then dried and injection-molded into standard testing specimens according to ASTM standards in an injection-molding machine (J80M2V, Zhendan Plastic Machinery Co., Wuxi City, China).

Morphological observations

The compatibilization and morphology of the blends were estimated with scanning electron microscopy (SEM; JSM-5600LV, JEOL, Tokyo, Japan). The surfaces of the freeze-fractured samples in liquid nitrogen and those of impact-fractured specimens at room temperature were observed after they were gold-coated in a vacuum chamber.

Mechanical testing

The tensile and flexural tests were performed on an Instron 1122 universal tensile tester (SANS, Shenzhen City, China) according to ASTM D 638 and ASTM D 790, respectively. The notched Izod impact strength was measured with an impact tester (XJU-22, Chengde Tester Manufactory, Chengde City, China) according to ASTM D 256. For all these tests, at least five specimens were used for each measurement.

DSC analysis

All the DSC measurements were performed on a PerkinElmer Pyris-1 differential scanning calorimeter (DSC; Perkin-Elmer Pyris-1, Boston, MA) from room temperature to 250°C at a heating rate of 10°C/min under a nitrogen atmosphere, and the melting temperature (T_m) was determined in the second scan. The heat distortion temperature (T_d) was measured according to ASTM D 648.

RESULTS AND DISCUSSION

Morphology investigation

Morphology control is one of the key factors for achieving the final properties of polymer blends. As shown in Figure 1, sheets of the dispersed polyamide phase were observed in the uncompatibilized PS/PA 1212 (70/30 w/w) blend. These sheets were present in the form of

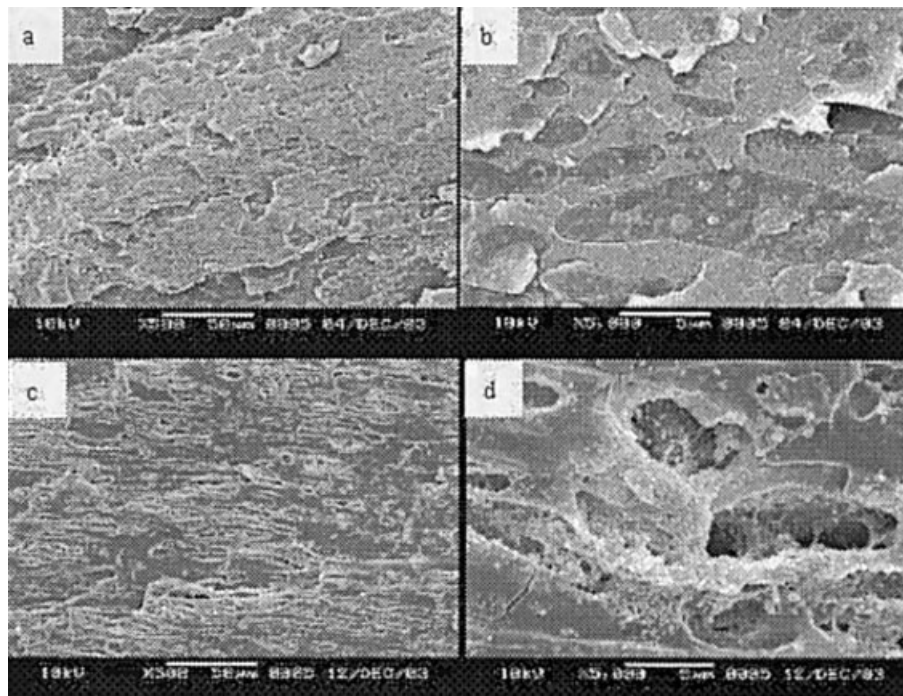


Figure 2 SEM microphotographs of freeze-fractured surfaces of PS/PA 1212/SEBS-g-MA (70/30/5): (a,b) unetched and (c,d) etched.

large phase domains, with a width (as measured across the flow direction) of about 3–10 μm , surrounded by the continuous PS matrix. The ratio of the melting indices of PS and PA 1212 was 3/5, and this meant that the viscosity of PA 1212 was smaller than that of PS. Therefore, the sheet-structure appearance of PA 1212 in the PS/PA 1212 blends agreed with the general criteria for phase inversion; that is, the lower viscosity component formed a continuous phase.⁹ The smooth surface of PS after being etched indicated that the interfacial adhesion between PS and PA 1212 was poor.

The freeze-fractured surfaces of the blend with 5 wt % SEBS-g-MA (Fig. 2) revealed that many ribbons or ligaments several micrometers wide appeared. The ribbons had more complex domain structures. After the etching, the ribbons turned into many gaps with a netlike structure inside. The interface became rougher with the addition of 5 wt % SEBS-g-MA, in comparison with that of the uncompatibilized PS/PA 1212 blend.

As shown in Figure 3, with 10 wt % SEBS-g-MA added, a cocontinuous phase appeared. Many spherical holes with diameters of approximately 2–3 μm were found in the freeze-fractured surfaces of the blend. These holes were surrounded by white layers and may have constituted a kind of quasi-core-shell structure, which could improve the impact resistance of PS.

When more than 15 wt % SEBS-g-MA was added (see Fig. 4), many core-shell spherical particles with diameters of approximately 5–10 μm appeared, and some of them congregated together to form a network

like an aerogel. The spherical holes in the core-shell structure had a diameter of approximately 1 μm , less than that in the blend with 10 wt % SEBS-g-MA; this demonstrated that PA 1212 was more finely dispersed in the matrix of PS.

With the addition of 20 wt % SEBS-g-MA [Fig. 4(c,d)], a denser SEBS-g-MA/PA 1212 netlike structure was formed. Some slightly larger spherical holes with a diameter of approximately 10 μm were found and might have resulted from more difficult processing because of the greater amount of SEBS-g-MA added. In fact, the extruder was blocked up several times during the melt mixing of the PS/PA 1212/SEBS-g-MA (70/30/20) blend.

Generally, with the addition of SEBS-g-MA, the PA 1212 phase became less elongated, and the interfacial adhesion between PS and PA 1212 was much improved. These results agreed with previous studies.^{10,11} Copolymers of PA 1212 and SEBS could be formed through the reaction of maleic anhydride in SEBS-g-MA with amide groups at the end of PA 1212 during the melt blending. As compatibilizers, the copolymers reduced the interfacial tension, and this led to the fine dispersion of PA 1212 in the PS matrix.

Mechanical properties of the PS/PA 1212 blends

The large difference in the morphology observed for the PS/PA 1212 blends containing SEBS-g-MA was also reflected in their mechanical behavior.

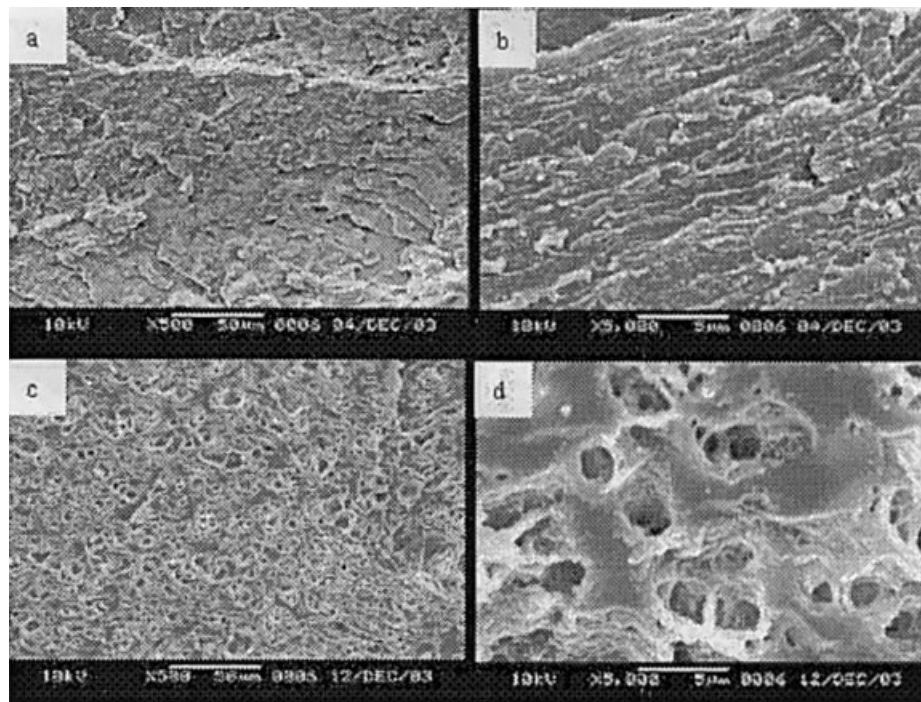


Figure 3 SEM microphotographs of freeze-fractured surfaces of PS/PA 1212/SEBS-g-MA (70/30/10): (a,b) unetched and (c,d) etched.

The addition of SEBS-g-MA to PS/PA 1212 blends led to a reduction of brittleness (see Fig. 5). With 10% SEBS-g-MA added, there was an apparent increase in the impact strength. This may have been caused by the

appearance of a cocontinuous phase structure (Fig. 3); the sample deformed and fractured in a more or less rubberlike fashion. With more SEBS-g-MA added, PA 1212 was dispersed more finely in the rubber phase,

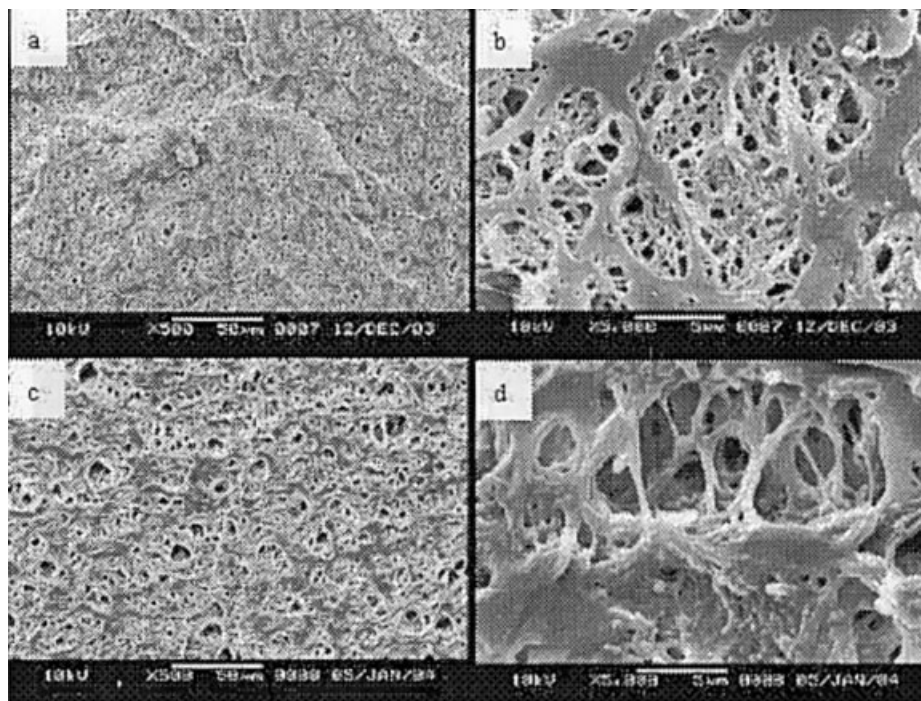


Figure 4 SEM microphotographs of etched freeze-fractured surfaces of PS/PA 1212/SEBS-g-MA: (a,b) 70/30/15 and (c,d) 70/30/20.

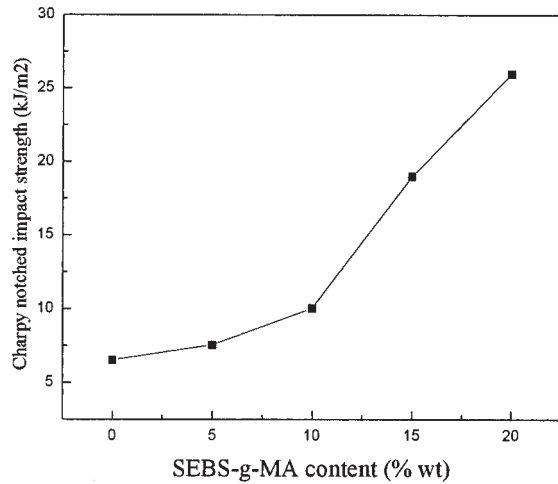


Figure 5 Charpy notched impact strength versus the SEBS-g-MA content for the blends.

and some rubbery particles agglomerated together to a larger volume of the rubber network. This network structure made the crack-opening displacement on the order of several hundred micrometers (Fig. 6). These displacements may have been the result of large local strains in a small volume of the rubber network near the crack tip, as in craze formation, or an accumulation of smaller strains over a much larger one.¹²

Figure 7 shows the tensile and flexural properties of PS/PA 1212 (70/30) blends modified by various amounts of SEBS-g-MA. The binary PS/PA 1212 blend exhibited slightly low tensile strength and flexural strength because of the poor adhesion between the PS phase and PA 1212 phase. The addition of 5 wt % SEBS-g-MA resulted in an improvement in the tensile strength and flexural strength. This may have arisen from the more effective entanglements by SEBS-g-MA in the interfacial region and the increase in the crystallinity of PA 1212 with 5 wt % SEBS-g-MA (see Table I). The tensile

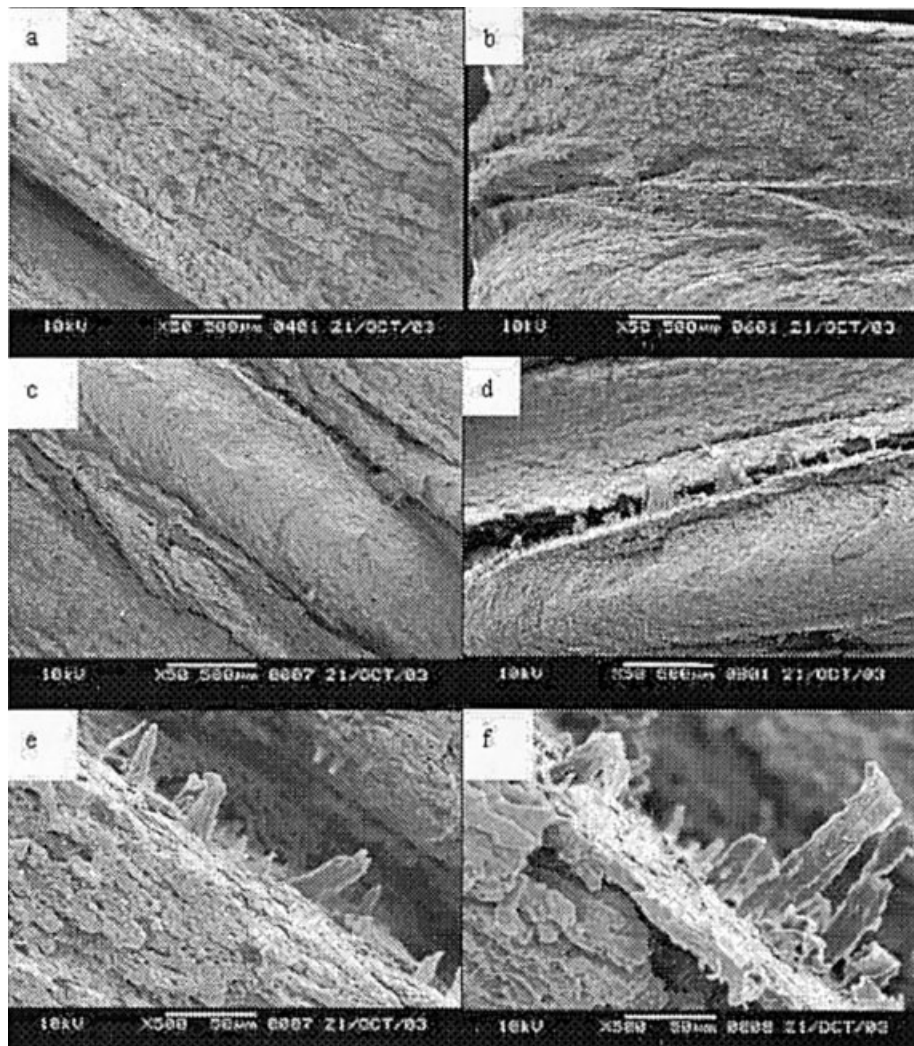


Figure 6 SEM microphotographs of impact-fractured surfaces at room temperature of PS/PA 1212/SEBS-g-MA: (a) 70/30/0, (b) 70/30/10, (c,e) 70/30/15, and (d,f) 70/30/20.

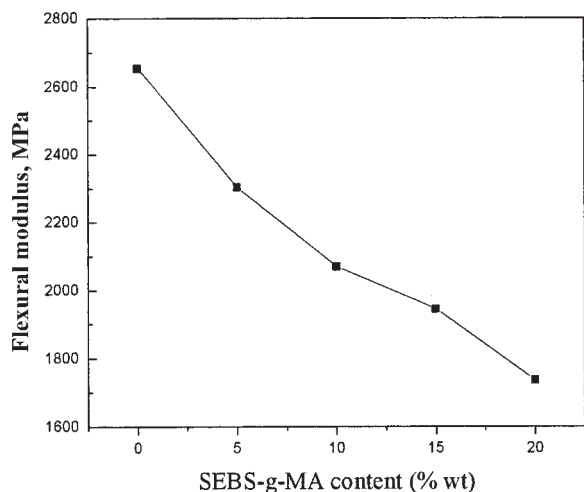


Figure 9 Flexural modulus versus the SEBS-g-MA content for the blends.

effect on T_m of PA 1212, ΔH_m in the compatibilized blends with 5 wt % compatibilizer was much higher than that in the uncompatibilized blends (Table I). This may be ascribed to the effect of the nucleation of the PS hard segment close to the PA 1212/PS interface. With a further increase in the concentration of SEBS-g-MA to 10 wt %, ΔH_m began to decrease sharply from 92.89 to 82.28 J/g. With more SEBS-g-MA added, ΔH_m continued to decrease. A nucleation influence of PA 1212 was observed only at SEBS-g-MA concentrations lower than 5 wt %. The trend of crystalline change with the addition of SEBS-g-MA was in agreement with that of the aforementioned mechanical and morphological variations.

The crystallization temperature (T_c) of the blends also changed with the amount of SEBS-g-MA used in preparing the blends. As shown in Table I, with 5% SEBS-g-MA added, T_c was almost unchanged. However, with the addition of 5–20 wt % SEBS-g-MA, T_c slowly decreased. This was accompanied by a broadening of the degree of supercooling (ΔT). The observed behavior was probably an effect of SEBS-g-MA on the PA 1212 domain volume. Because each of the small PA 1212 domains had to be nucleated independently, and the strong bond interaction of SEBS-g-MA and PA 1212 retarded the crystallization of PA 1212, crystallization only occurred at a higher ΔT value than normal. This effect is called fractionated or cold crystallization in the literature.⁴

The glass-transition temperature (T_g) also varied with the amount of SEBS-g-MA. As shown in Table I, T_g increased from 90.92 to 100.5°C with an increase in the SEBS-g-MA concentration in the range of 0–20 wt %. This may have been caused by the entanglement of SEBS-g-MA or the incorporation of more PS into the crystals of PA 1212 because of the compatibilization of SEBS-g-MA, which restricted the motion of the PS segment.

Table I also shows the effect of the content of SEBS-g-MA on T_d . At 5 wt % SEBS-g-MA, T_d was maximal because of the improved interfacial adhesion and relatively high crystallinity. With more SEBS-g-MA added, T_d began to decrease again because SEBS-g-MA was an elastomer with a quite lower heat distortion resistance, and the crystallinity decreased with the further addition of SEBS-g-MA. However, in comparison with that of the unmodified blend, T_d of the compatibilized blends was greatly improved, probably because of the apparent increase in T_g with an increasing concentration of SEBS-g-MA.

CONCLUSIONS

Blends based on 70 wt % PS and 30 wt % PA 1212 were modified with SEBS-g-MA as a compatibilizer. The uncompatibilized blend was unstable toward coalescence during melt processing and consequently exhibited a very coarse morphology with a smooth interface and poor mechanical properties. The use of 5% reactive SEBS-g-MA resulted in sheets of PA 1212 consisting of PA 1212 particles encapsulated with SEBS-g-MA. Varying the fraction of SEBS-g-MA in the blends allowed the manipulation of the phase structure, first to form sheet structures and then to form a cocontinuous phase with a core-shell structure. The core-shell particles, their partial agglomeration, and the reduction of the crystallinity of PA 1212 may have resulted in an apparent increase in the Charpy notched impact strength in comparison with that of the uncompatibilized PS/PA 1212 blend. The crystallization of PA 1212 was retarded when more than 5 wt % SEBS-g-MA was added. With an increase in the concentration of SEBS-g-MA, T_g of PS increased, and consequently T_d of the compatibilized blends was also improved.

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