Effects of Maleated Styrene–*co*-butene)–Styrene on Compatibilization and Properties of Nylon-12,12/Nylon-6 Blends

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ABSTRACT: Effects of a maleated triblock copolymer of styrene–(ethylene-*co*-butene)–styrene (SEBS-*g*-MA) on compatibilization and mechanical properties of nylon-12,12/nylon-6 blends were investigated. The results showed that addition of SEBS-*g*-MA could improve the compatibility between nylon-12,12 and nylon-6. Nylon-12,12 could disperse very well in nylon-6 matrix, although the dispersion of nylon-6 was poor when nylon-6 was the dispersed phase. At a fixed nylon-12,12/nylon-6 ratio of 30/70, supertoughness was achieved with addition of 15% SEBS-*g*-MA in weight. Scanning electron microscopy of the impact-fractured surface indicated that cavitation and matrix shear yielding were the predominant mechanisms of impact energy dissipation. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1446–1453, 2004

Key words: compatibilization; maleated styrene–(ethylene-*co*-butene)–styrene (SEBS); nylon; toughness; impact energy

INTRODUCTION

Nylons (polyamides) occupy an important position in the field of engineering plastics. These kinds of polymers are widely used in the automotive industry, machinery, electronic equipment, and military applications because of their high strength, toughness, low creep, good temperature resistance, and other properties.[1,2] Many new nylons such as nylon-10,10 and nylon-12,12 were developed in recent decades. These long alkane-segment nylons possess excellent impact resistance at low temperature, good wet strength retention, abrasion resistance, and dimension stability.[1] The introduction of the long alkane-segment nylon into low nylons such as nylon-6 and nylon-6,6 would enhance the low-temperature properties, wet resistance, and dimension stability.

Nylon blends have been extensively investigated,[1,2] although the study on blending of nylons themselves is limited.[2–5] The work of Verma[3] showed that nylon-6 was either miscible or nearly miscible with nylon-6,6. Only one melt transition was observed in blends prepared with small amounts of one nylon in the other nylon and the minor component remained amorphous. However, in blends containing comparable amounts of the two nylons, each component crystallized independently. The study by Ong et al.[4] also demonstrated that nylon-6 and nylon-6,6 are compatible, but nylon-6 was incompatible with nylon-11, nylon-12, and nylon-12,12.

Most polymers in the crystalline state are immiscible at the molecular level, as governed by the laws of thermodynamics. To improve the compatibility of blends, a block or graft copolymer as a third component can be introduced. For nylon blends such as polypropylene (PP)/nylon-6,[6] high-density polyethylene/nylon-6,[7] PP/nylon-12,[8] poly(propylene oxide)/nylon-6,6,[9] PP/nylon-6,6,[10] acrylonitrile–butadiene–styrene/polyamine-6,[11] and maleated polyolefins or elastomers were usually used to enhance the compatibility of composites. The maleic anhydride groups reacted with amide groups at the end of nylons to form copolymers, which can decrease the interfacial tension between the dispersed phase and matrix to promote interfacial adhesion. Maleated polyolefins or elastomers might also improve the compatibility of nylon pairs because the amide groups at the end of nylon molecules can react with maleic anhydride groups, to form grafting copolymers, to decrease the interfacial tension.

In this work, the compatibilization between nylon-6 and nylon-12,12, using a maleated triblock copolymer of styrene–(ethylene-*co*-butene)–styrene (SEBS-*g*-MA) as the compatibilizer, was investigated. The mechanical properties and toughening mechanism were also studied.

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EXPERIMENTAL

Materials

Nylon-12,12 was obtained from Shangdong Dongchen Chemical Company (Shangdong Province, China) with a melt index of 30 g/10 min (230°C, 2.16 kg). Nylon-6 was a commercial product of Guangdong Xinhui Meida Nylon Co. (Guangdong Province, China), under the trade name of M22800, with a melt index of 23 g/10 min (230°C, 2.16 kg). Maleated SEBS was supplied by Shanghai Lingen Chemical Co. (Shanghai, China). The grafting ratio of maleic anhydride was about 1% by weight.

Blend preparation

All materials were dried at 80°C for at least 12 h in an oven before blending. Blends were prepared on a Φ35 twin-screw extruder (TE-35, Jiangsu Keya Chemical Engineering Co., China) with a proper proportion. The barrel temperatures and the screw speed of the extruder were set at 225–230–240°C and 240 rpm, respectively. The extruded materials were then dried and injection molded into standard testing specimens according to ASTM in an injection-molding machine (J80M2V, Zhendan Plastic Machinery Co., China).

Morphology observation

The compatibilization and morphology of blends were estimated using a scanning electron microscope (SEM; JSM-5600LV, JEOL, Tokyo, Japan). The surfaces of 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 a universal tensile tester (Instron 1122, Canton, MA) according to ASTM-D638 and ASTM-D790, respectively. The notched Izod impact strength was measured with an impact tester (XJU-22, Chengde Tester Manufactory, China) according to ASTM-D256. For all these tests, at least five specimens were used for each measurement.

RESULTS AND DISCUSSION

Compatibilization of nylon-12,12/nylon-6 blends

SEM is a direct method for studying the morphology of blends. In this study, the freeze-fractured surface of the blend in liquid nitrogen was observed by SEM to evaluate the compatibility of composites. Figure 1 shows the SEM microphotographs of freeze-fractured surfaces of blends at a fixed ratio of nylon-12,12/nylon of 30/70 with different contents of SEBS-g-MA. It can be seen from Figure 1(a) that the phase separation was significant without SEBS-g-MA as the compatibilizer and the distribution of particle size was wide, which means nylon-12,12 is incompatible with nylon-6. By use of dynamic mechanical analysis (DMA), Ong et al.[4] also confirmed that nylon-6 and nylon-6,6 were compatible, but nylon-6 and nylon-12 were incompatible. However, with the addition of 2% SEBS-g-MA in weight, the particle size decreased sharply, and the particle size distribution also decreased. When the content of SEBS-g-MA is up to 10%, scarcely any particles are visible under the present magnification. This suggests that the maleic anhydride groups grafting onto SEBS react with amide end groups of nylons to form nylon-12,12-co-SEBS-co-nylon-6 copolymers. These copolymers act as compatibilizers to decrease the interfacial tension between the two components to favor the dispersion of nylon-12,12 in the nylon-6 matrix.

With the addition of 15 wt % SEBS-g-MA, large quantities of small particles appeared. Under higher magnification [Fig. 1(g)], these particles show complex shapes and a broad size distribution. We believe that these particles are not nylon-12,12 but SEBS. Studies by Paul et al.[12–17] showed that for monofunctional nylons (i.e., nylon-6, nylon-11, and, nylon-12), each chain can chemically attach only once to a maleated elastomer phase. This type graft is efficient for lowering interfacial tension and steric stabilization against particle coalescence and lead to small particles. For difunctional nylons such as nylon-6,6 and nylon-12,12, however, some molecules can react twice to the same particle (loops) or bridge two particles. These grafting forms may encourage occlusion and complex shapes. They also found that addition of 10% nylon-6,6, poly(m-xylene adipamide) (MXD6), or nylon-12,12 to nylon-6 led to rubber particle enlargement and toughening.[14]

We investigated whether nylon-6 also can be well dispersed in the nylon-12,12 matrix with SEBS-g-MA. Figure 2 shows the SEM microphotographs of ternary blends with fixed SEBS-g-MA content of 10%. In this figure, the ratio of nylon-12,12/nylon-6 is changed to 50/50 and 70/30. Whether at low or high magnification, the phase separation is significant. Dispersed-phase particles of nylon-6 are large and the size distribution is also broad. It can also be seen that the dispersed-phase particles are nearly all broken in liquid nitrogen. This implies that nylon-6 cannot be dispersed homogeneously in the nylon-12,12 matrix, even with 10 wt % SEBS-g-MA.

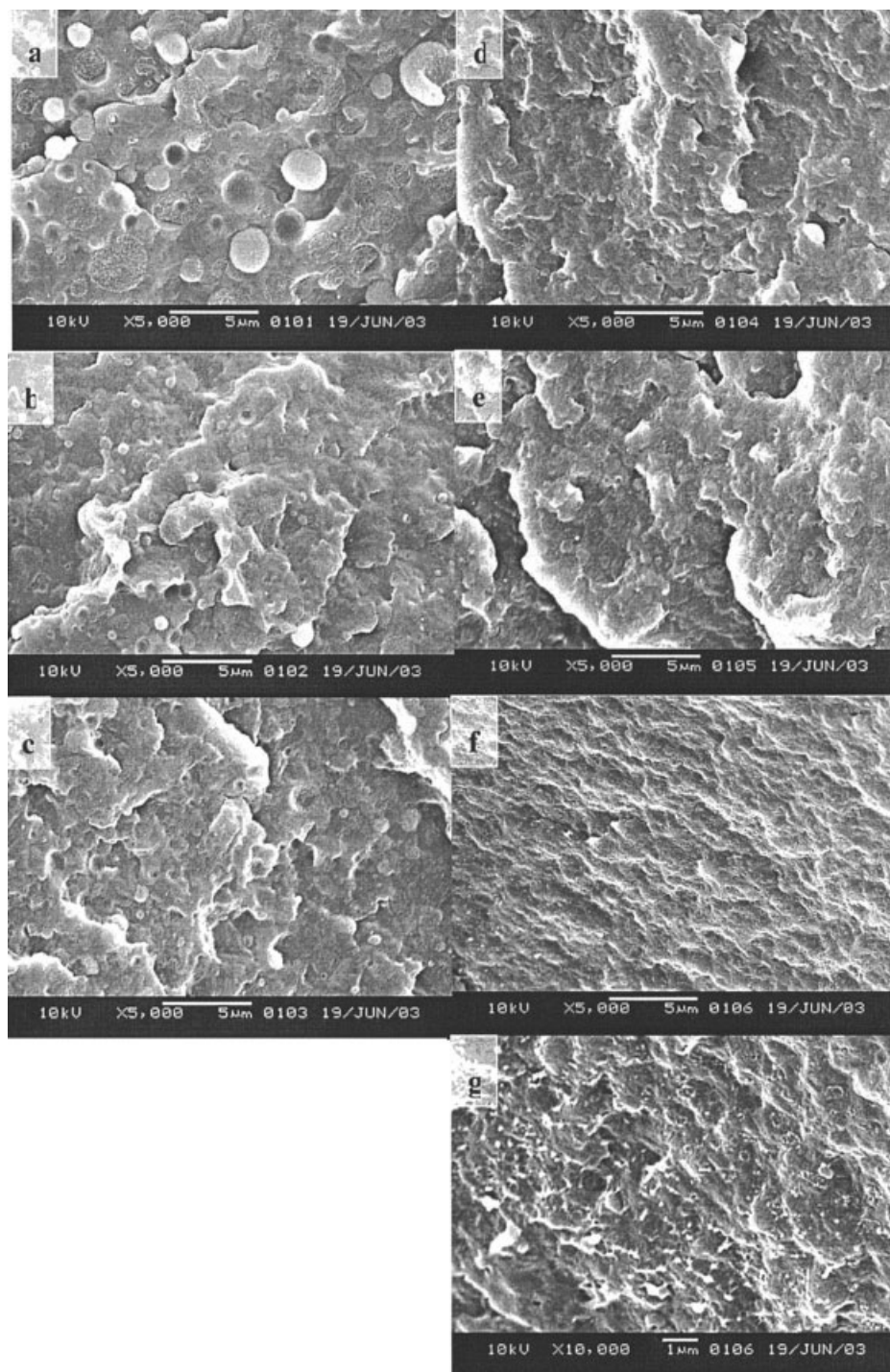The difference of dispersions of nylon-12,12 and nylon-6 may be attributed to the following two reasons:

Figure 1 SEM microphotographs of freeze-fractured surfaces of blends of nylon-12,12/nylon-6 (=30/70) with SEBS-*g*-MA: (a) 0%; (b) 2%; (c) 4%; (d) 6%; (e) 10%; (f) 15%; (g) 15%.

1. The large difference in viscosity between the two components of nylons plays an important role in determination of the dispersed domain.[11,36] With a higher viscosity of the dispersed phase (nylon-6), a fine breakup would be more difficult. Thus nylon-12,12 can be easily dispersed in nylon-6 because of the low viscosity, although nylon-6 can be dispersed in the nylon-12,12 matrix only with difficulty because of its higher viscosity.

2. Nylon-12,12 with potential amide groups on both ends of one molecule has a much greater possibility of reacting with maleic anhydride grafting on SEBS compared with nylon-6, which has only one amide group of one molecule.[18] Thus, when nylon-12,12 is the minor phase, suf-
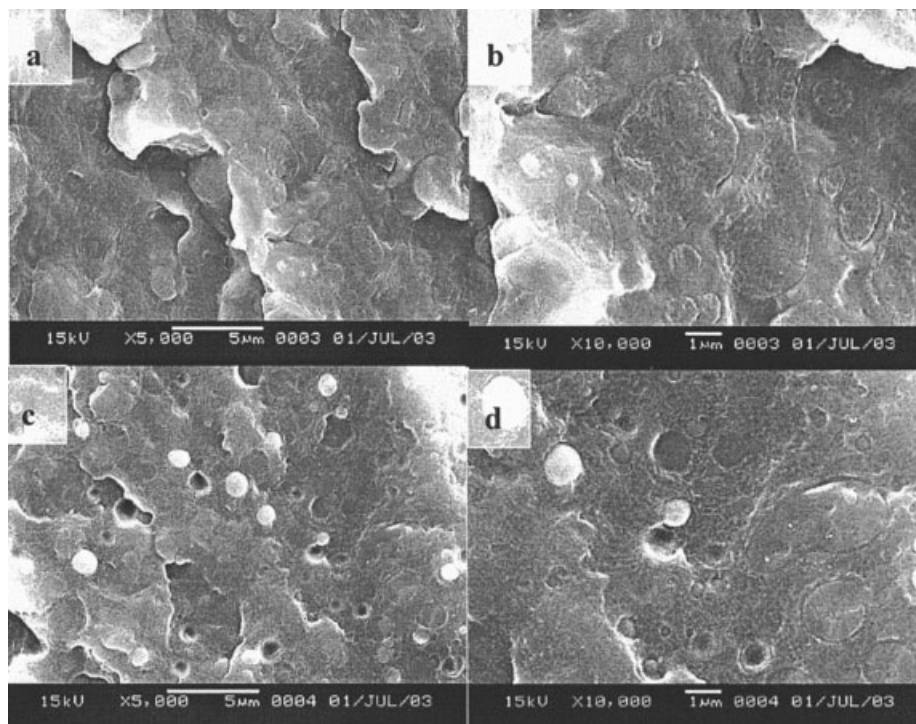
Figure 2 SEM microphotographs of freeze-fractured surfaces of ternary blends with 10% SEBS-*g*-MA under low and high magnification: (a) and (b) nylon-12,12/nylon-6 = 50/50; (c) and (d) nylon-12,12/nylon-6 = 70/30.

ficient numbers of nylon-12,12 molecules are available to react with SEBS-*g*-MA to form nylon-12,12-*co*-SEBS-nylon-6 copolymers to effectively reduce the interfacial tension. However, when nylon-6 is the dispersed phase, fewer nylon-6 molecules graft onto SEBS to form enough tricopolymers to enhance the interface adhesion.

Mechanical properties of nylon-12,12/nylon-6 blends

The room-temperature mechanical properties of starting nylons are listed in Table I. As can be seen, the tensile and flexural properties of nylon-12,12 are lower than those of nylon-6, but the notched Izod impact strength and elongation are much higher for nylon-12,12. This means that nylon with long alkane segments possess excellent impact resistance because of

the more flexible chains, in contrast with nylon containing short alkane segments.

Figures 3 and 4 show the tensile and flexural properties of ternary blends at a fixed nylon-12,12/nylon-6 ratio of 30/70. It can be seen that the tensile strength, flexural strength, and flexural modulus decrease gradually with the addition of SEBS-*g*-MA. This is the general characteristic of a rubber with low-modulus toughening plastics.[19,20] The elongation of ternary blends by the content of SEBS-*g*-MA is demonstrated in Figure 5. The elongation of blend without SEBS-*g*-MA is only 7.7%, substantially lower than that of nylon-12,12 and nylon-6 (see Table I). The low elongation is attributed to the severe phase separation resulting from the incompatibility between nylon-12,12 and nylon-6. With the addition 2 wt % SEBS-*g*-MA, the compatibility of these blends is greatly improved, and the elongation also increases sharply. The

TABLE I
Mechanical Properties of Nylons

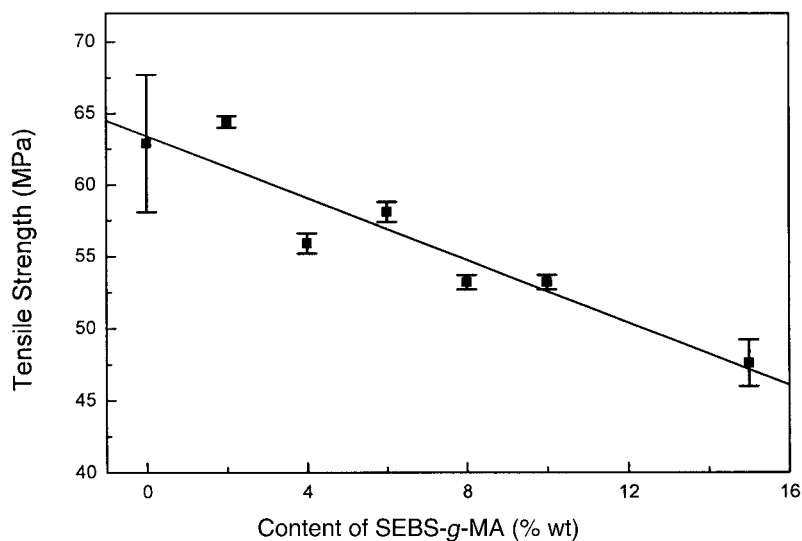| Nylon	Flexual strength (MPa)	Flexual modulus (MPa)	Tensile strength (MPa)	Elongation (%)	Notched impact strength (J/m)
Nylon-12,12	45.5	1330	45.8	352	220
Nylon-6	82.6	2900	73.0	105	74

Figure 3 Tensile strength versus SEBS-*g*-MA content for blends.

elongation reaches a maximum value at 4 wt % of SEBS-*g*-MA and then declines gradually as the content of SEBS-*g*-MA increases. After that, the elongation changed only slightly, even with 15 wt % of SEBS-*g*-MA.

Figure 6 shows the effect of SEBS-*g*-MA content on the room-temperature notched Izod impact strength with a fixed nylon-12,12/nylon-6 ratio of 30/70. In the absence of SEBS-*g*-MA compatibilizer, the impact strength is lower than that of each component (see Table I). This is attributed to the poor compatibility between nylon-12,12 and nylon-6, as seen in Figure 1. The impact strength increases slightly with the SEBS-*g*-MA content up to 10 wt %, but the blend is still brittle. However, as the content of SEBS-*g*-MA is increased from 10 to 15%, a sharp brittle–ductile transi-

tion occurs and supertoughness is achieved. For comparison, the notched Izod impact strengths of pure nylon-12,12 and nylon-6 with 15% SEBS-*g*-MA are listed in Table II. The impact strength of nylon-6 with 15% SEBS-*g*-MA is only 179 J/m, which means the blend is still brittle. For nylon-12,12 with 15% SEBS-*g*-MA, however, the impact strength reaches 849 J/m and supertoughness is achieved. These phenomena have been extensively studied by Paul et al.[12–17] Their studies show that binary blends of SEBS-*g*-MA with nylon-6 yield only small rubber particles (~ 0.05 μm in diameter) that are obviously too small for toughening. To toughen nylon-6, the combination of SEBS-*g*-MA and SEBS is needed to increase particle size into an optimum range for toughening. They also found that addition of 10% nylon-6,6, poly(*m*-xylene adipam-
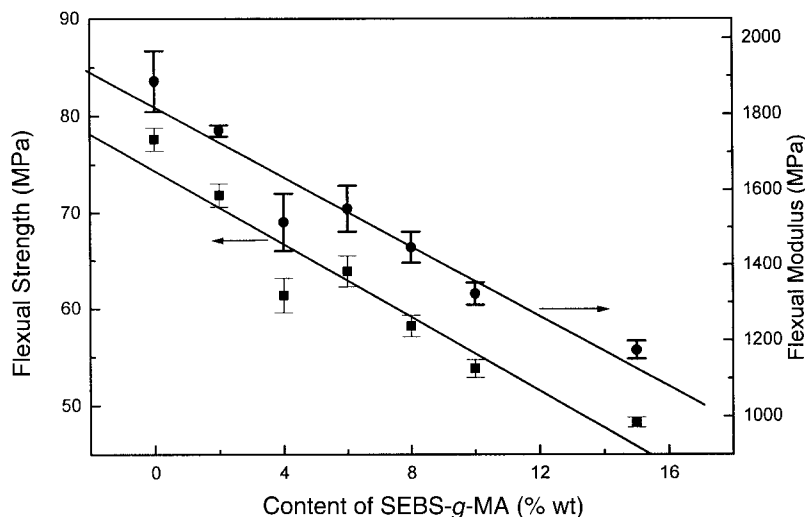

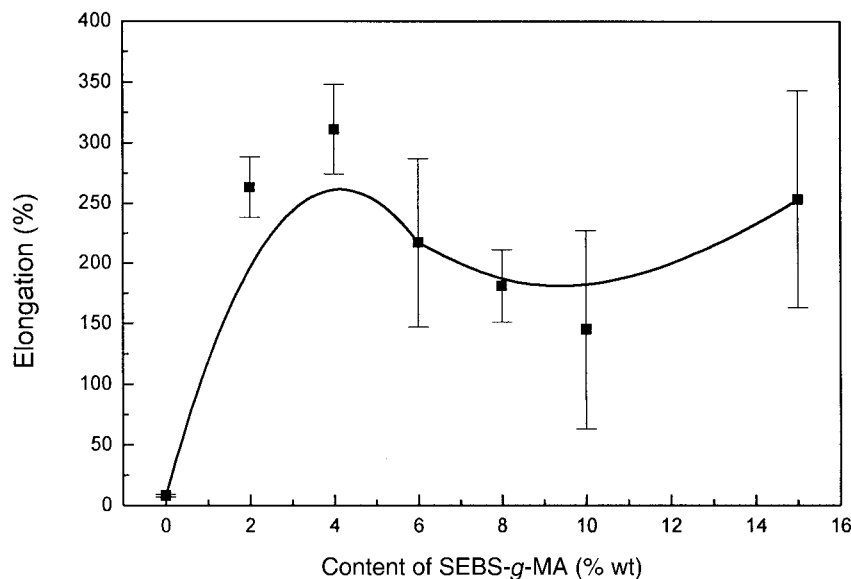**Figure 4** Flexural strength and flexural modulus versus SEBS-*g*-MA content for blends.

Figure 5 Elongation versus SEBS-g-MA content for blends.

ide) (MXD6), or nylon-12,12 to nylon-6 led to rubber particle enlargement and toughening.[14]

The research of Wu[21–23] revealed that the brittle–tough transition was controlled by critical surface-to-surface interparticle distance (τ_c). When the average surface-to-surface interparticle distance was lower than τ_c, then the brittle–ductile transition occurred. Actually, the particle size also plays an important role, given that very small rubber particles might not cavitate.[24,25] For nylon-6/SEBS-g-MA system, the rubber particle size is too small (only about 0.05 μm) to cavitate effectively, so the blend is still brittle. However, with addition of nylon-12,12, the size of SEBS particles

is enlarged enough to cavitate. At the condition of $\tau < \tau_c$, the toughness of the matrix can be achieved.

Fracture study

The impact-fractured surfaces of blends were previously studied to understand the mechanism of toughening.[26–32] Figure 7 shows the SEM microphotographs of the impact-fractured surfaces of ternary composites with a fixed nylon-12,12/nylon-6 ratio of 30/70. Obviously, for blends without SEBS-g-MA, the fracture surface shows a brittle failure. The poor compatibility between nylon-12,12 and nylon-6 can also be seen in
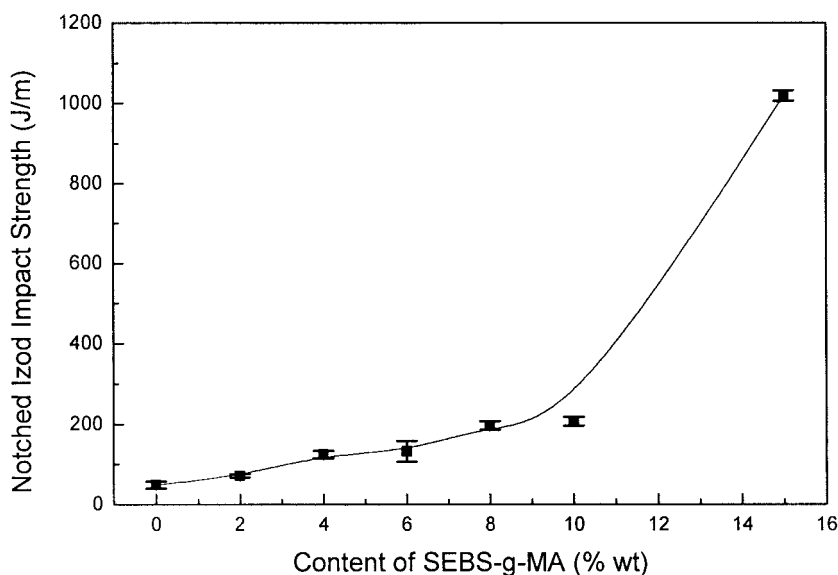

Figure 6 Notched impact strength versus SEBS-g-MA content for blends.

TABLE II
Notched Izod Impact Strength of Blends with 15 wt % SEBS-*g*-MA

	Nylon-12,12/nylon-6 (=30/70)	Nylon-6	Nylon-12,12
Notched Izod impact strength (J/m)	1019	179	849

Figure 7(a). With the addition of <10 wt % SEBS-*g*-MA, no cavitation and matrix shear yielding are observed, which means that failure of the blend is still in the brittle mode. In the case of brittle fracture, the dispersed particles may still be seen in and on the surface, although the particle size decreases and scarcely any particles are visible because the content of SEBS-*g*-MA is 6%. These results are consistent with those from observations of freeze-fractured surfaces and indicate that the compatibility between nylon-12,12 and nylon-6 is improved with SEBS-*g*-MA.

The surface of the ternary composite with 10 wt % SEBS-*g*-MA shows a slight voiding around the dispersed particles, but no matrix shear yielding takes place. The blends are still brittle. Corresponding to the high impact strength value, the topography of the surface of blends with 15% SEBS-*g*-MA [Fig. 7(e)] is much different. Profuse cavitation and extensive matrix shear yielding are observed. It is generally believed that the shear yielding mechanism constitutes cavitation of elastomer particles followed by shear yielding throughout the matrix.[33–35]
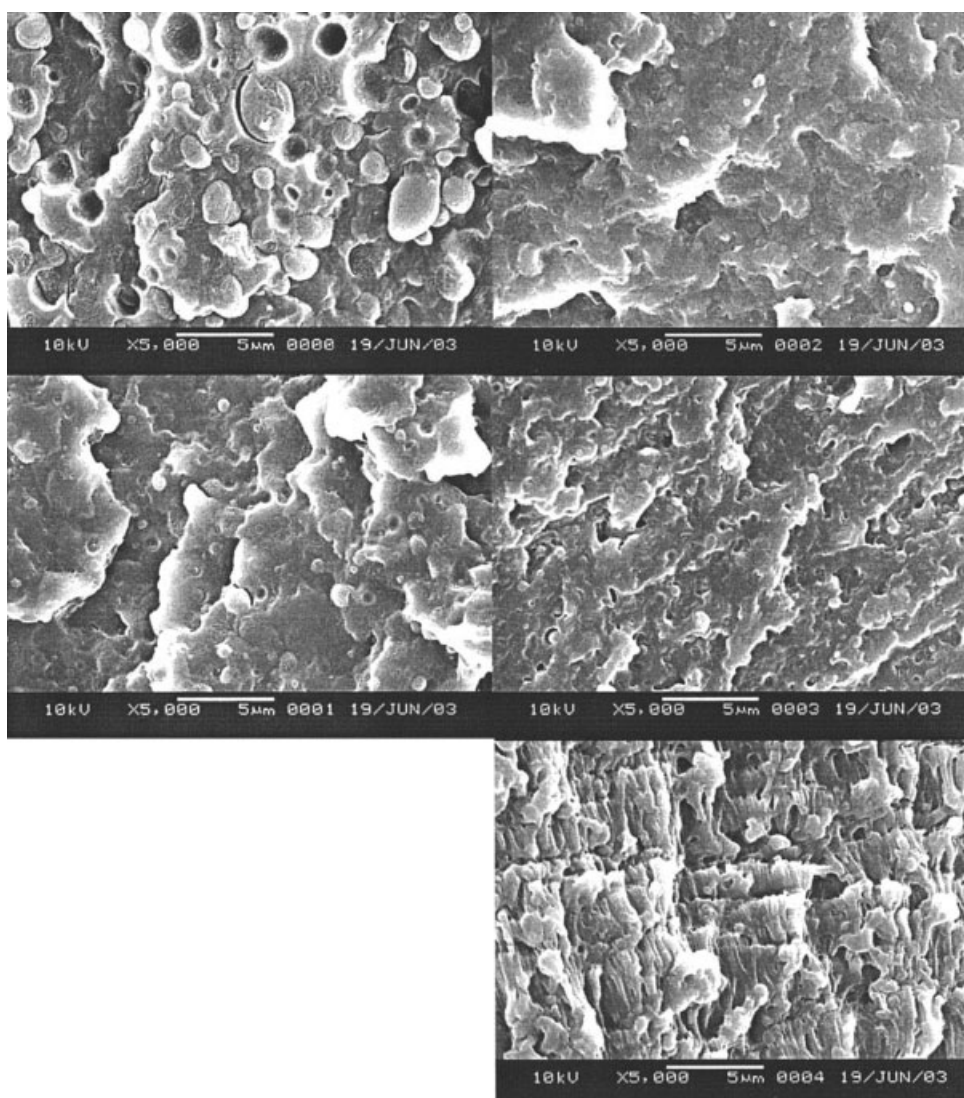

Figure 7 SEM microphotographs of impact-fractured surfaces of blends at a fixed nylon,12,12/nylon-6 ratio of 30/70 with content of SEBS-*g*-MA: (a) 0%; (b) 2%; (c) 6%; (d) 10%; (e) 15%.
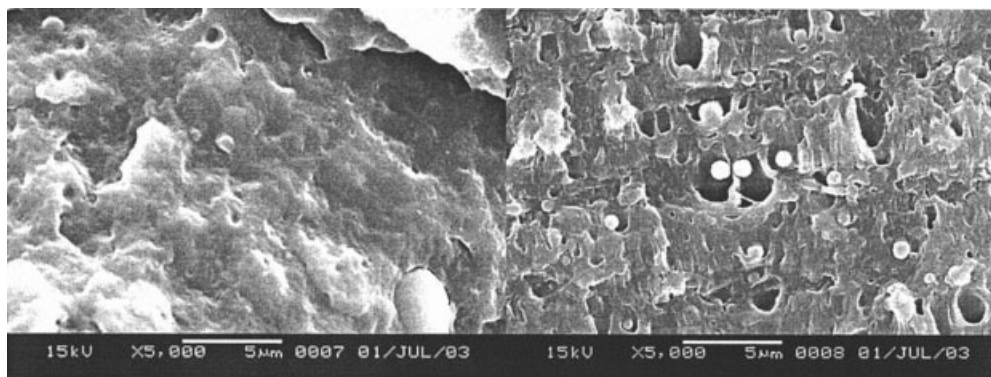
Figure 8 SEM microphotographs of impact-fractured surfaces of nylons with 15 wt % SEBS-*g*-MA: (a) nylon-6; (b) nylon-12,12.

Figure 8 shows the SEM microphotographs of the impact-fractured surfaces of nylon-6/SEBS-*g*-MA and nylon-12,12/SEBS-*g*-MA blends with 15% SEBS-*g*-MA. The surface of the nylon-6/SEBS-*g*-MA blend is smooth and no cavitation is visible because of its low impact strength. This indicates that the rubber particles are too small to cavitate effectively.[24,25] For the nylon-12,12/SEBS-*g*-MA blend with high impact strength, the cavitation around rubber particles and matrix shear yielding are the main energy-absorbing mechanisms, as shown in Figure 8(b).

CONCLUSIONS

Nylon-12,12 can be easily dispersed in nylon-6 matrix using SEBS-*g*-MA as a compatibilizer. However, the dispersion of nylon-6 in nylon-12,12 matrix is poor. These phenomena can be attributed to the difference in viscosity between the two nylon components and the ability of nylons to form copolymers with SEBS-*g*-MA. At a fixed nylon-12,12/nylon-6 ratio of 30/70, supertoughness is achieved with only 15 wt % SEBS-*g*-MA. However, the notched impact strength of nylon-6 was increased only about twofold with 15 wt % SEBS-*g*-MA, which is attributed to the too small rubber particles formed in the monofunctional nylon.

The impact fracture studies show that cavitation and matrix shear yielding are the main mechanisms of the impact energy dissipation upon impact testing. The surface of nylon-6 with 15 wt % SEBS-*g*-MA is smooth and no cavitation is visible because of its low impact strength.

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