

Effects of Reactive Functional Groups in the Compatibilizer on Mechanical Properties of Compatibilized Blends

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SYNOPSIS

The compatibility of blends of polyamide-6/[styrene-(ethylene-butylene)-styrene] triblock copolymer (SEBS) was enhanced with a compatibilizer, maleated SEBS, whose compositions were varied from 0 to 4 wt % of the blends. The maleated SEBS (MA-g-SEBS) was synthesized by reacting (grafting) maleic anhydride (MA) with SEBS in the laboratory at various maleic anhydride concentrations ranging from 8 to 13 wt % of the maleated compatibilizer. The effects of graft levels of the reactive MA functional group in the compatibilizer on the effectiveness in compatibilizing the blends were investigated. The morphology and the impact strengths of the compatibilized blends were determined. It was found that, depending on the maleated extents, the compatibilizer influenced significantly the properties of the blends. Although the maleated extents (graft ratios) of the compatibilizer is influential, the concentrations of the compatibilizer in the blends more sensitively affected the mechanical properties of the compatibilized blends. In summary, this study has shown that by increasing the MA contents (within the reported window) in the compatibilizer, the impact toughness could be more dramatically improved. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Thermoplastic elastomers or rubbers have been used to toughen semicrystalline polymers such as Nylon 6 since the last decade.^{1,2} A semicrystalline polymer is usually blended with an elastomer within a composition window to enhance the mechanical properties of the polymer. A compatibilizer, usually the same elastomer functionalized (grafted) with a reactive group (such as maleic anhydride), is commonly used to improve the compatibility of the blend. The molecules of the compatibilizer, thus, consist of a grafted functional group and an elastomeric main chain. The grafted group (e.g., maleic anhydride) of the compatibilizer is reactive toward the continuous polymer phase (the polyamide) of the blend, while the elastomeric main chain of the compatibilizer is soluble and entangled with the elastomer phase of the blend. In this manner, which is similar to the classical mechanism of a surfactant,

it brings about a fine dispersion of the discontinued elastomeric phase surrounded by a continuous semicrystalline polymer (polyamide) matrix. Due to like-dissolve-like behavior between the elastomer molecules and chemical bonding to the continuous matrix through the grafted MA group, excellent interactions between the two phases³ can usually be ensured.

The optimal sizes of the discrete rubber phase domains, however, may vary from one system to another.⁴ For a typical elastomer-toughened polyamide blend containing 15 weight percent (wt %) of elastomer content, the critical particle size has been reported to be about 0.7 μm .⁵ Additionally, it has been proposed that there exists a brittle/tough criterion based on the interparticle distances instead of the particle sizes.⁵ For polyamide-6 (PA-6), this distance is about 0.3 μm .^{6,7} In addition, the interfacial adhesion is another important factor determining mechanical properties. Wu⁶ suggested that the minimum adhesion required for toughening is about 1000 J/m², which is typical for van der Waals adhesion. Paul et al.⁴ found that there is a maximum adhesion from the functionalized rubber for a series

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of PA-6/SEBS blends. Moreover, they suggested that an optimal adhesion might reflect micro-mechanical effects at the interface. The compatibilizer in a semicrystalline polymer blend can also influence the forms of the crystallites as well as the crystallinity. Martuscelli⁸ showed that the increase of the vinyl-acetate content of the ethylene-vinyl acetate (EVA) copolymer promotes the γ -form crystalline structure of polyamide in the PA-6/EVA blend.

Styrene-(ethylene-butylene)-styrene (SEBS) triblock copolymer is a thermoplastic elastomer, which, together with its maleated copolymer as a compatibilizer, has been used as an impact modifier for polyamides by various researchers.^{4,9,10} Modic et al.¹⁰ showed that ternary blends of PA-6/SEBS/maleated SEBS had a higher impact toughness than binary blends of PA-6/SEBS. Paul et al.⁴ also reported that the impact toughness could be increased from 60 J/m for a binary PA-6/SEBS blend to a maximum impact toughness of about 1000 J/m for ternary PA-6/SEBS/maleated SEBS blends. Their blends contained 16.2 wt % of SEBS as the toughness modifier and 3.8 wt % of maleated SEBS as the compatibilizer. In their studies, the compatibilizer had a relatively low MA-to-SEBS graft ratio of 1.84 wt %.

The objective of this study was to further investigate what effects the maleated SEBS might have if the MA graft ratios in the compatibilizer were available at much higher levels than those that were currently available from commercial sources. Maleated SEBSs were prepared at different graft ratios of MA in the laboratory, which was used as the compatibilizer at various compositions for blends of PA6 and SEBS. The effects of the composition of the compatibilizer and the graft ratio of MA-to-SEBS on the mechanical properties as well as the morphologies of the ternary blends in terms of the interfacial interaction were studied.

EXPERIMENTAL

Preparation of MA-Graft-SEBS

Grafting of maleic anhydride (MA) onto SEBS (Kraton G-1652, Shell Chemical Co.) was conducted in benzene as the solution with dicumyl peroxide (DCP) as an initiator at an elevated temperature of 140°C under nitrogen atmosphere. At atmospheric pressure, it ordinarily would not be possible to react MA with SEBS at such a high temperature in the benzene solution. However, in this experiment, the entire reaction setup was placed inside an autoclave for pressurization. SEBS (120 g) and MA (16 to 30

g) were dissolved in benzene (500 mL) as the solution and heated to 140°C inside the pressurized autoclave. The grafting reaction was judged complete and terminated at 150 min. The initiator, DCP/benzene solution (3 g/100 mL), was added dropwise by a metering pump at a rate of 2 mL/min for the first 50 min. Upon completing the reaction at 150 min, the reaction mixture was cooled to the room temperature and the product was precipitated by adding a sufficient quantity of ethanol into the benzene solution. A white powdery product (MA-g-SEBS) was obtained by filtering and subsequently washed several times with ethanol to remove unreacted MA and/or residual initiator. After ethanol washing, the products were further washed using a Soxhlet extractor with hot water for 24 h to ensure that all the anhydride groups were hydrolyzed into acids. The product was then dried overnight in vacuum. The graft ratios of MA in the MA-g-SEBS compatibilizer were determined by elemental analysis (Heraeus, CHN-O-RAPID). The results of the elemental analysis indicated that the graft ratios of MA-to-SEBS in the maleated SEBS were 0.090, 0.110, and 0.140 g MA/g SEBS. In terms of MA wt % in the MA-g-SEBS, these graft ratios were calculated to be 8, 10, and 13 wt %, respectively.

Preparation of Ternary Blends

Polyamide-6 (PA-6) was dried in an oven at 80°C for 48 h prior to use in blending. The PA-6 (after drying), SEBS, and MA-g-SEBS were weighed and premixed at various predetermined ratios. These mixtures were then melt blended using a laboratory twin screw extruder (Ikegai, PCM 30) operating at 200 rpm. The temperature profiles along the extruder barrel were maintained at 250°C, 260°C, and 260°C, with the temperature at the die kept at 250°C. The blend extrudates after exiting the extruder were quenched in water, pelletized, and dried in vacuum for 24 h at 100°C.

Table I shows the compositions of the blends studied. All the blends studied consisted of 85 wt % PA-6 and a total of 15 wt % of the elastomers of SEBS and maleated SEBS. Of the total 15 wt % elastomers in the ternary blends, the SEBS (elastomer) was varied from 15 to 11 wt % and the maleated SEBS (the compatibilizer) varied from 0 to 4 wt %. For brevity, the ternary blends with various compositions and maleation extents were coded by using a capital letter indicating the extents of MA grafting and using an Arabic number indicating the composition of the compatibilizer in the blends. For the compatibilizer, three levels of maleation (8, 10,

Table I The Formulations and Impact Strengths of the Blends

Code	Recipe				Impact Strength (J/m)
	PA6 (wt %)	SEBS (wt %)	MA-g-SEBS (wt %)	MA Graft Ratio (wt %)	
P	100	—	—	—	4.26×10
B	85	15	—	—	1.03×10^2
L1	85	14	1	0.08	1.12×10^2
L2	85	13	2	0.08	1.54×10^2
L3	85	12	3	0.08	1.16×10^3
L4	85	11	4	0.08	1.10×10^3
M1	85	14	1	0.10	1.18×10^2
M2	85	13	2	0.10	2.02×10^2
M3	85	12	3	0.10	1.10×10^3
M4	85	11	4	0.10	8.05×10^2
H1	85	14	1	0.13	1.08×10^2
H2	85	13	2	0.13	1.50×10^2
H3	85	12	3	0.13	4.24×10^2
H4	85	11	4	0.13	2.02×10^2
P*	100	0	0	—	3.95×10
B*	80	20	0	—	6.90×10
S*	80	15	5	0.014	9.50×10^2

* Data from Ref. 4.

and 13 wt %, respectively, of MA in the maleated SEBS) in the compatibilizer (MA-g-SEBS) were used. The blends containing the compatibilizer at these three levels of maleation were designated by a capital letter prefix as following:

L—(low maleation level—8% maleation in the MA-g-SEBS),

M—(medium maleation level—10% maleation in the MA-g-SEBS), and

H—(high maleation level—13% maleation in the MA-g-SEBS).

In the code names listed in this table, the Arabic number following the alphabetic prefix indicates the weight percents of the compatibilizer (MA-g-SEBS) in the ternary blends. For example, "L2" indicates that the ternary blend contains 85 wt % of PA-6, 13 (15 less 2) wt % of SEBS as the toughness modifier, and the remaining 2 wt % of MA-g-SEBS as the compatibilizer which has a low (L—8 wt % of MA in MA-g-SEBS) maleation extent.

Scanning Electron Microscopy

The morphologies of the blends were examined using scanning electron microscopy (SEM) (JEOL, JSM-

840A). The sample for SEM had a dimension of $3 \times 3 \times 5$ mm. Only the top surface was smoothed by microtoming (LKB, Ultratome) with a diamond knife. The smoothed sample was then etched with p-xylene to remove the elastomeric (SEBS) phase. After etching, the samples were sputter-coated with gold prior to SEM examination.

Mechanical Properties

The specimens of the blends for Izod impact tests had dimensions of $6.35 \times 1.27 \times 0.317$ cm with a notch radius of 0.0254 cm machined with a notch cutter. All impact samples were stored in a desiccator before testing to avoid moisture absorption. Notched Izod impact strengths of the samples were measured at ambient temperature by following the procedures described in ASTM D-256. for tensile property tests.

The specimens for tensile tests were prepared using a commercially available laboratory injection molding machine (Arburg) and stored in a desiccator before testing to avoid moisture absorption. The specimens had the geometry of a dumbbell shape with 3 mm in thickness, 10 mm in width, and 20 mm in gauge length. The tensile tests were performed using a mechanical tester (Instron, Model 1011) at room temperature. The crosshead speed was set at 50 mm/min.

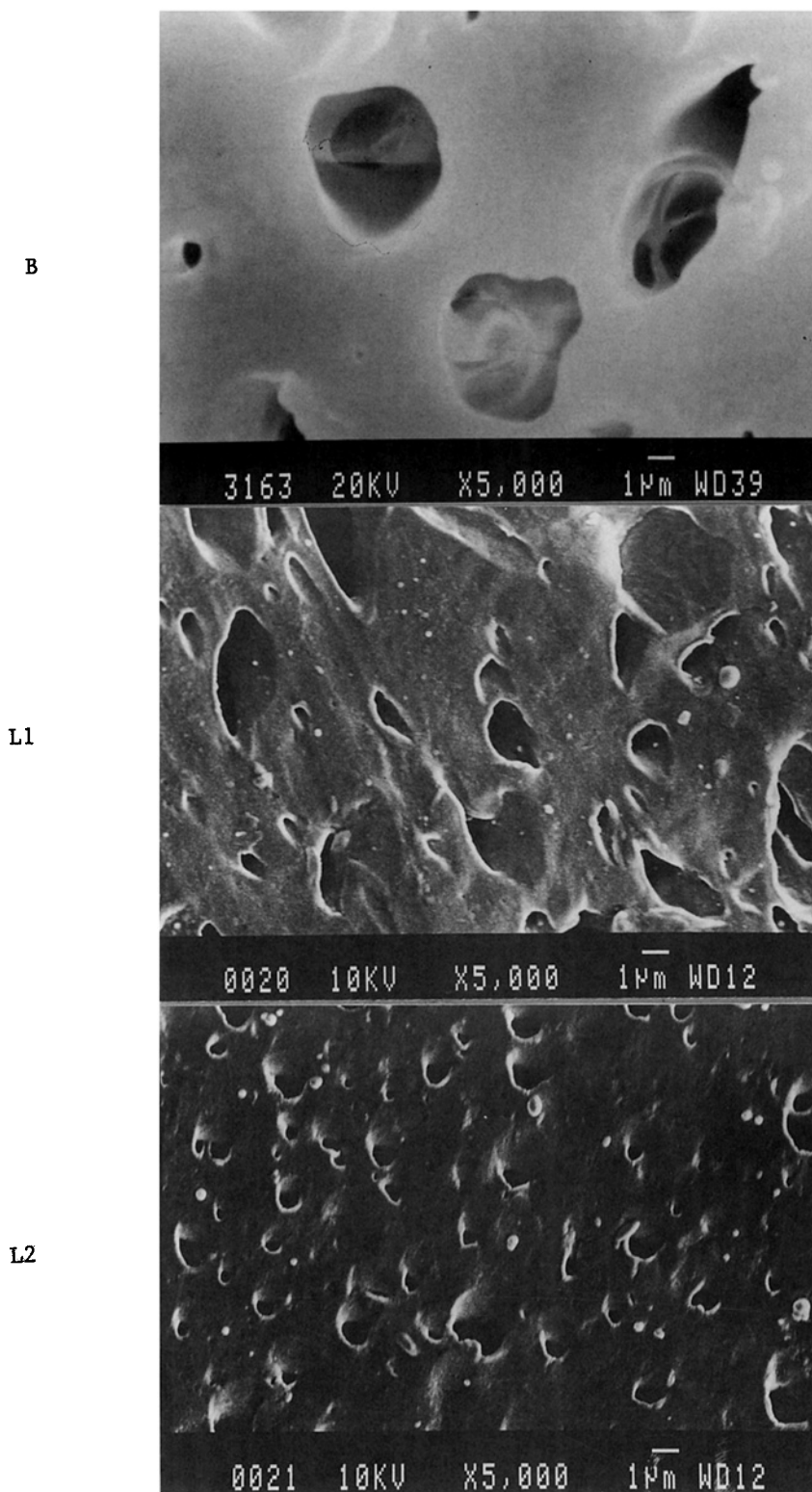


Figure 1 SEM micrographs of xylene etched surfaces of the blends compatibilized with various compatibilizer concentrations at various MA graft levels (5000 \times).

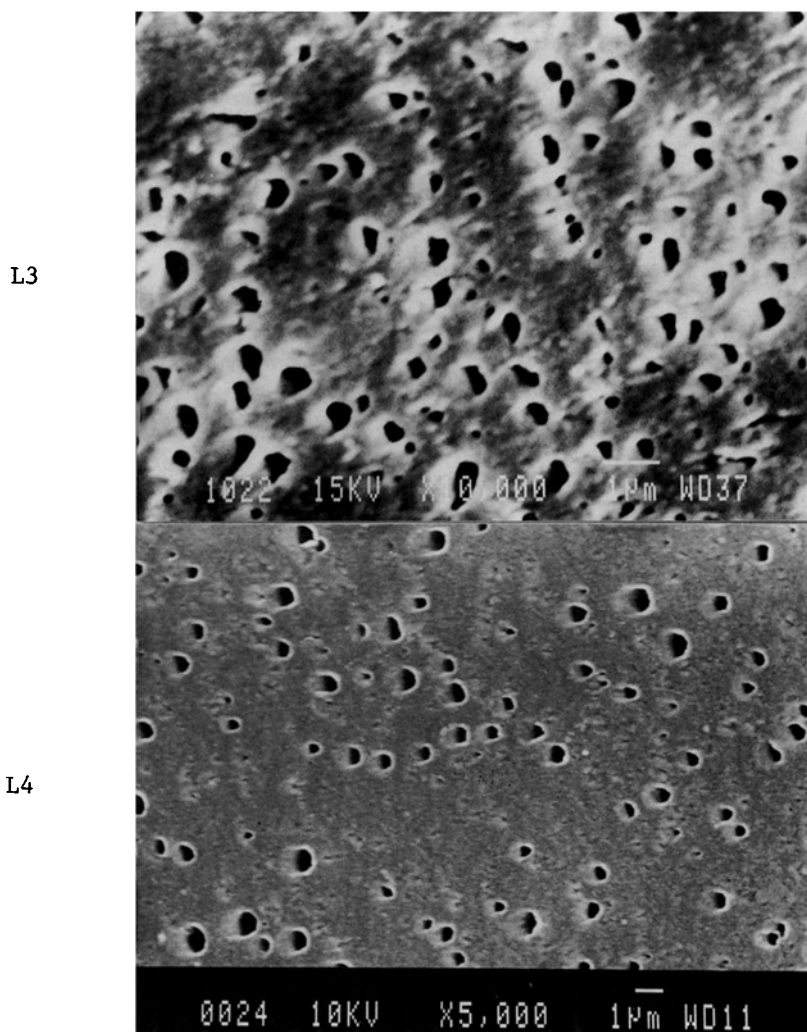


Figure 1 (Continued from the previous page)

Dynamic Mechanical and Rheological Properties

Tan δ and storage modulus G' were measured using a dynamic analyzer (Rheometrics Inc., RDA-700) at a frequency of 1 Hz. The tests were run by cooling the sample in the Rheometrics temperature chamber to -150°C using liquid nitrogen and then heated at a constant heating rate of $10^\circ\text{C}/\text{min}$ to at least 200°C .

RESULTS AND DISCUSSION

Effect of Compatibilizer on Morphology

Figure 1 shows the SEM pictures of the etched blends. The effect of the compatibilizer (MA-g-SEBS) on the morphology of the ternary blends has been demonstrated in these pictures. The holes in-

dicated that the discrete phase of SEBS in the blend had been dissolved into p-xylene during etching. Note that the shape of the holes in the binary PA-6/SEBS blend (coded "B") is different from those in the L-series of ternary blends of PA-6/SEBS/maleated SEBS. For the binary blend, there were several smaller holes of uneven sizes inside a larger hole with fairly smooth and uniform geometry. This suggested that the elastomeric domains were cleanly ripped off during etching. However, clean etching was not observed in the compatibilized ternary blends, which apparently exhibited much better interactions between the particles and the matrix, which was indicated by "protruded circular walls" similar to craters for the etched specimens of the ternary blends. Furthermore, the extents of "pull-out" effects apparently depended on the compositions and/or the MA graft ratios of the compati-

bilizer used. For instances, there were noticeable "crater walls" in the L-series containing 2 wt % of the compatibilizer (L2). On the other hand, there were neither significant "crater walls" in the binary blend, nor in the L-series containing 1 wt % the compatibilizer (L1).

The mechanism of the compatibilizer in the blends was similar to the classical mechanism of a surfactant in emulsifying two different phases. Better interactions were resulted at an optimal compatibilizer composition or at an optimal maleation extent of the compatibilizer. When p-xylene was used to etch the elastomeric domains from the continuous matrix, strong interactions between the elastomer and the matrix phases would make complete removal of the elastomers more difficult. The phenomenon of incomplete removal of the elastomeric particles was observed under the SEM as "protrusion." The "protruded objects" were actually the partially dislocated rubber particles. The difficulty in cleanly etching out the particles was due to strong interactions between the PA-6 and SEBS phases with the compatibilizer acting as the "bridges."

Utilizing the Schwartz-Saltykov method,¹¹ the corrected particle size distributions (CPSD) of the holes could be estimated. Figure 2 indicates the CPSD of the holes varied from about 0.2 to 5.0 μm for the L-series ternary blends. The results showed that the shape and size distribution of the holes varied not only with the compatibilizer concentrations in the blends but also with the graft ratios of MA of the compatibilizer. At a given graft ratio, the higher the compatibilizer concentration, the smaller the size and the narrower the distribution. At a given compatibilizer concentration, the effect of the graft ratios of MA in the compatibilizer was not obvious at low compatibilizer concentrations. At compatibilizer concentrations greater than 2%, a trend was clearly observed, which was that as the MA graft levels increase, particle sizes became smaller.

Figure 3 shows the particle size distribution for the ternary blends (H-series blends) compatibilized with the highly maleated MA-g-SEBS. Most of the particles were below 0.5 μm . Additionally, as a result of stronger and more uniform dispersion by the highly maleated compatibilizer, the particle size distribution became smaller.

For comparison of crystallinities of the blends, Figure 4 shows the wide angle X-ray (WAXS) spectrum of the neat PA-6, binary blend of PA-6/SEBS, and the L-series ternary blends. The WAXS of the neat PA6 and binary blend showed a characteristic diffraction peak of the γ -form crystalline structure

at $2\theta = 21.5^\circ$, while those of the L-series blends showed three diffraction peaks at about $2\theta = 20^\circ$, 23° , and 21.5° , which were the characteristic diffraction patterns of the α - and γ -form crystalline structures.^{12,13} It should be noted that the α -form crystalline structure was the major one in the L3 and L4 blends. The relative proportions of the α - and γ -form crystalline structures in the L1 and L2 blends were not so much different. It suggested that the introduction of the compatibilizer was favored for the formation of the α -form crystallites. The degrees of crystallinity of all the blends were also estimated from the WAXS to be between 37 and 41%. Apparently, due to complete immiscibility between the rubber and the semicrystalline polymer, the compatibilizer affected little on the degree of crystallinity.

Mechanical/Impact Properties

The notched impact strengths of the blends were measured and the results are summarized in Table I. The impact strength of the uncompatibilized binary blend of PA-6/SEBS exhibited about 2.5-fold increase when compared to the neat PA-6. Note that all three series (L, M, H) of ternary blends showed even more improved impact strengths. The improvement on the impact strength of the ternary blends became more obvious as the compositions of the compatibilizer were greater than 2 wt %. Both the L- and M-series blends containing 3 wt % of maleated SEBS (L3 and M3) attained a 30-fold increase in the impact strengths over that of the neat PA-6. This impact strengths of the ternary blends were about 10 times that of the binary blend.

Graphically, the trends of variation of the impact strengths for the three series of blends (L-, M-, and H-) are shown in Figure 5. At the highest maleation extent (H series, or 13 wt % MA in MA-g-SEBS), the impact strengths of the H-series ternary blends were not as significantly improved as those of the other two series (L and M) of blends. Hence, a significant improvement on the impact strength of the blend could be obtained only if the blend consisted of an optimal concentration of the compatibilizer. In addition, for the compatibilizer, there existed an optimal maleation extent for it to be most effective in compatibilizing the blends. In earlier study by Paul et al., a maximum impact toughness of about 1000 J/m for ternary PA-6/SEBS (16.2%)/maleated SEBS (3.8%) blends was reported. In this study, the ternary blends contained only about a total of 15 wt % of total elastomers. However, our study has proven that the impact toughness could

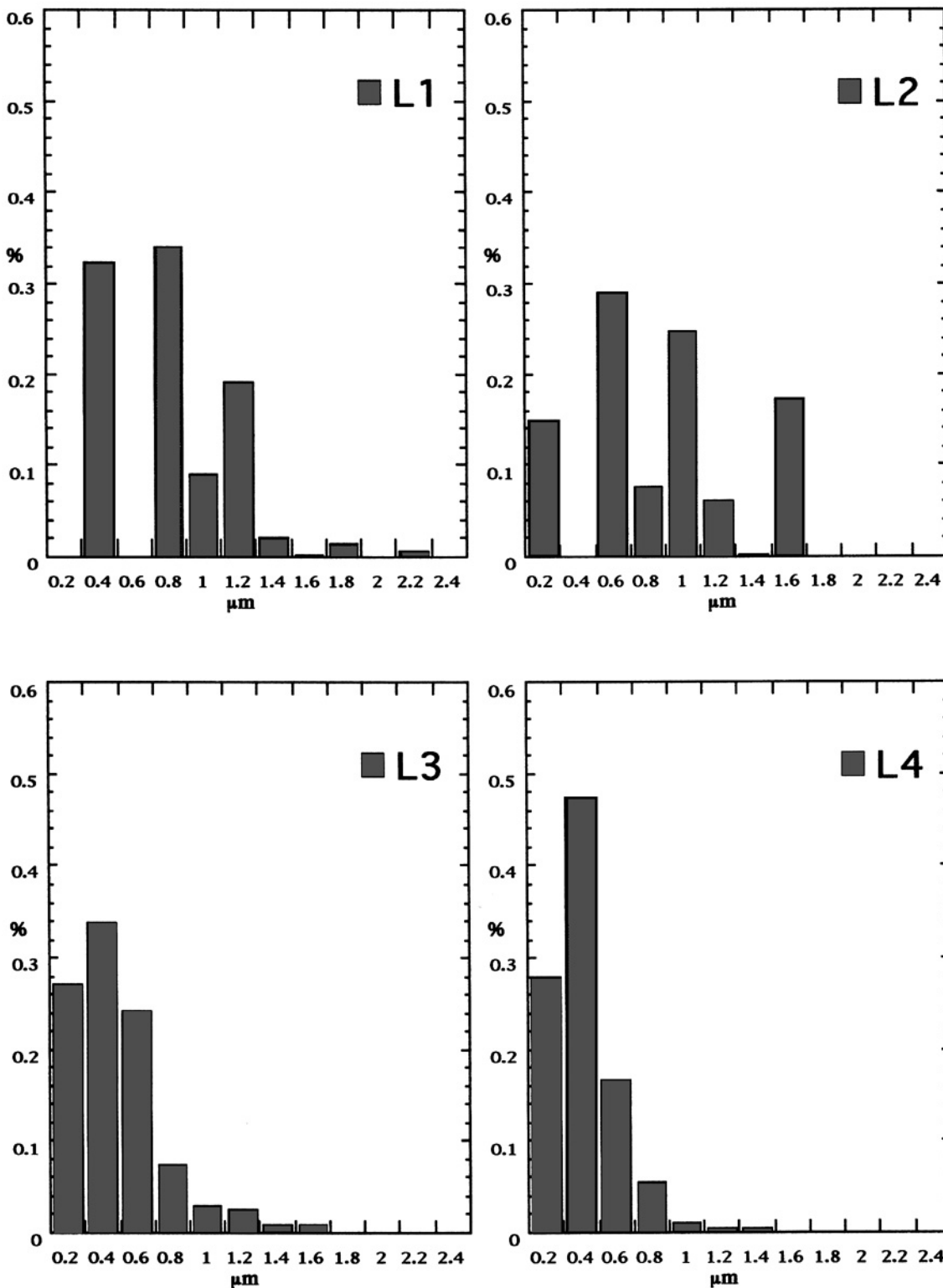


Figure 2 The corrected size distributions of the SEBS particles in the L-series ternary blends.

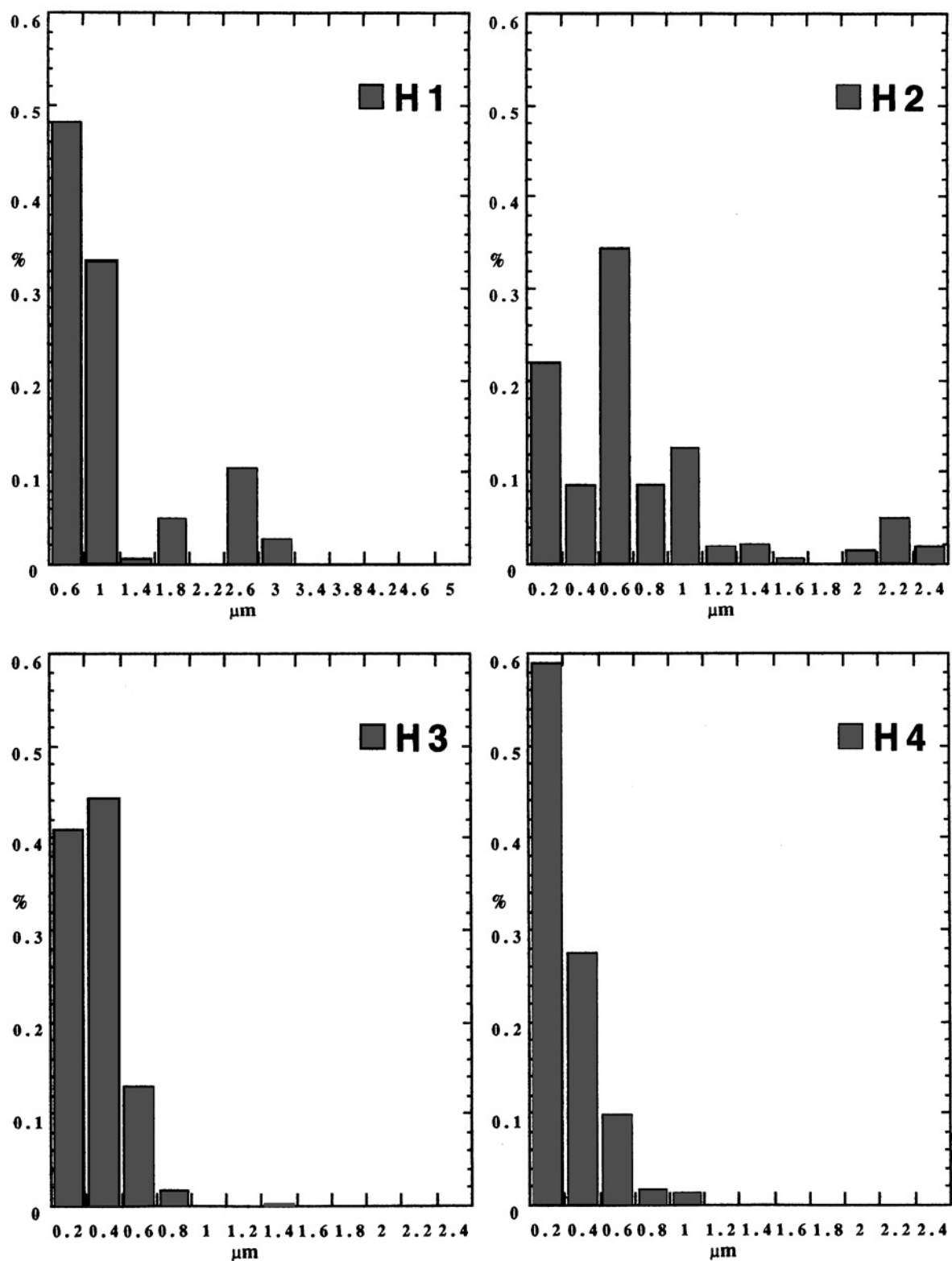


Figure 3 The corrected size distributions of the SEBS particles in the H-series ternary blends.

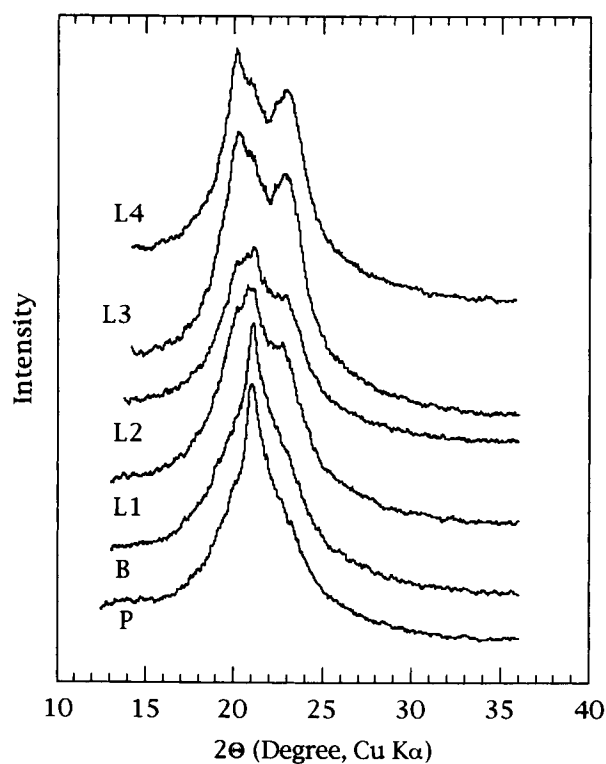


Figure 4 Wide Angle X-ray diffraction scans of the blends: (PA6/SEBS/MA-g-SEBS): 4-A, P (100/0/0); 4-B, B (85/15/0); 4-C, L1 (85/14/1); 4-D, L2 (85/13/2); 4-E, L3 (85/12/3); 4-F, L4 (85/11/4).

be more dramatically improved to well above 1000 J/m for most of the blends compatibilized by the more extensively maleated SEBSs that were successfully synthesized in the laboratory.

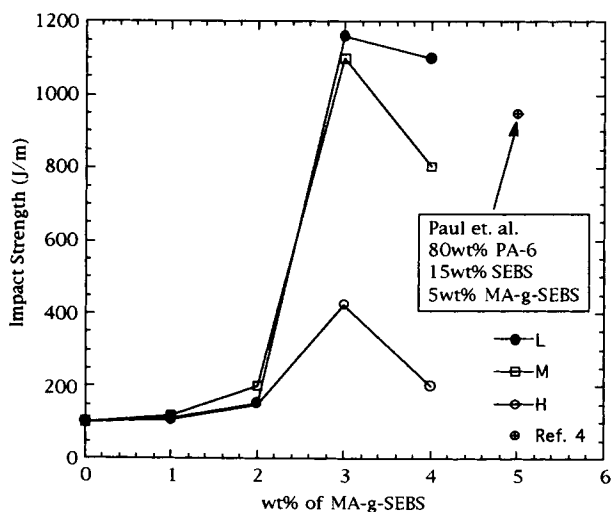


Figure 5 Impact strengths for all L-, M-, and H-series ternary blends as functions of compatibilizer compositions at various graft levels.

Tensile properties could also provide some information about the effectiveness of the compatibilizer in the ternary blends. The tensile properties of the blends reported here were obtained from the average of 5 to 10 specimens. Figure 6 illustrates the typical stress-strain curves for the L-series ternary blends (L1 to L4) in comparison with the binary blend of PA-6/SEBS. The other ternary blends all showed trends similar to the L-series ternary blends. The stress-strain behavior of the blends apparently varied with the compatibilizer compositions in the blends. The compatibilizer, up to 4 wt % of the blends, clearly promoted impact toughness of the blends, as indicated by the increased area under the stress-strain curves. The yield stress of the blend dropped to the magnitude between the volume fraction of the neat polyamide (0.82) and the predicted value (0.62) from the Ishiai and Cohen equation.¹⁵ Similar results have been reported in literature.⁴ For the uncompatibilized blend of PA-6/SEBS, note that there were apparently several “kicks” (peaks and valleys) in the cold-drawing region just prior to final failure. However, as the compatibilizer compositions increased, the kicks gradually diminished. At the higher compatibilizer contents (L3 and L4),

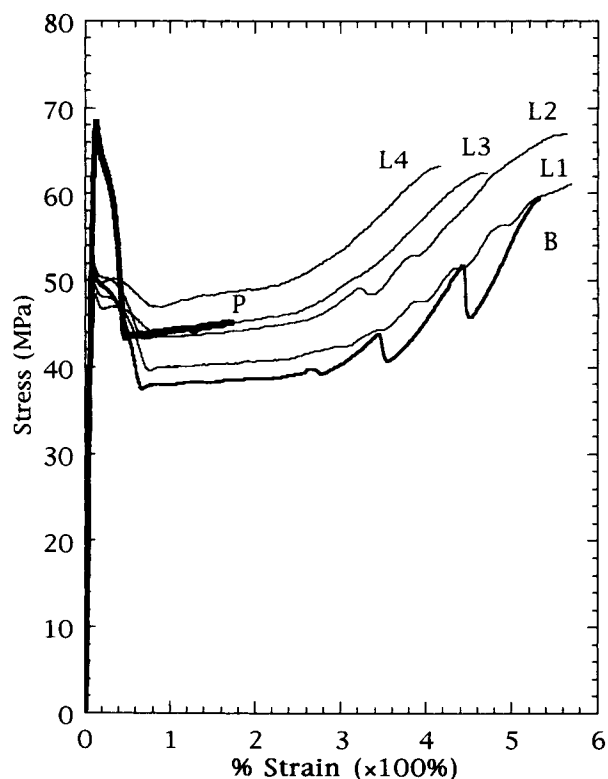


Figure 6 The stress-strain behaviors of the compatibilized blends.

the kicks disappeared completely. Apparently, the "kicks" might be associated with less-than-perfect interactions between the rubber particles and the matrix. During cold drawing, the polyamide chains were being extended from the spherulites and the crystalline area. These chains were then aligned along the force direction. Subsequently, they exerted a stress on the dispersed rubber particles among them. If the rubber particle had a relatively large size and lacked strong enough interactions with the polyamide surroundings, the particle would slide along the force direction or collapse to smaller particles. Both behaviors would release the stress and resulted in the additional yields. On the other hand, the blend containing the compatibilizer had finer rubber particles and strong interactions, which restricted such behaviors. Therefore, it resulted in a relatively smooth cold drawing curve. The cold drawing stress increases as the increase of the compatibilizer in the blend. It may be ascribed to (1) shifting of the dominant crystalline form from the γ form to the more stable α form whose interactions between the crystalline chains are greater than those in the γ form, and (2) a stabilization effect provided by the compatibilizer.

Dynamic Mechanical Property

Information about the compatibility of the blends could also be obtained by examining the dynamic

mechanical properties of the compatibilized ternary blends. Figure 7 shows the three G' curves, respectively, each for the neat PA-6, SEBS, the binary blend (B), and the L-series compatibilized ternary blends (L1 thru L4). A higher impact strength of the blend was always accompanied by a smaller G' .

Figure 8 shows the $\tan \delta$ curves each for the neat PA-6 and SEBS, the binary blend, and the ternary blends (L1 thru L4). All blends showed multiple transitions, which could be clearly discerned as the two α -transitions (polystyrene block and polybutadiene block) of SEBS, the primary and secondary transitions in PA-6. The distinctly different T_g transitions indicates that PA-6 and SEBS in the L-series blends are not miscible by nature, as expected. At low temperatures, the G' and $\tan \delta$ of all the blends did not differ much. However, as the temperature approached T_g of PA-6, the G' of all the blends started to deviate from each other. In the temperature range between T_g and 150°C , the effects of the elastomer modifier and compatibilizer became more apparent. These sensitive effects were a result of the high maleation level of the compatibilizer.

Table II summarizes the effect of the graft ratios (MA contents in MA-g-SEBS) of the compatibilizer on $\tan \delta$ of the blends. At a given compatibilizer composition, M4 and L4 gave a relative greater $\tan \delta$ than the others. By carefully examining the results in Table II, it could be observed that a clear trend of variation in $\tan \delta$ of the blends agreed quite well

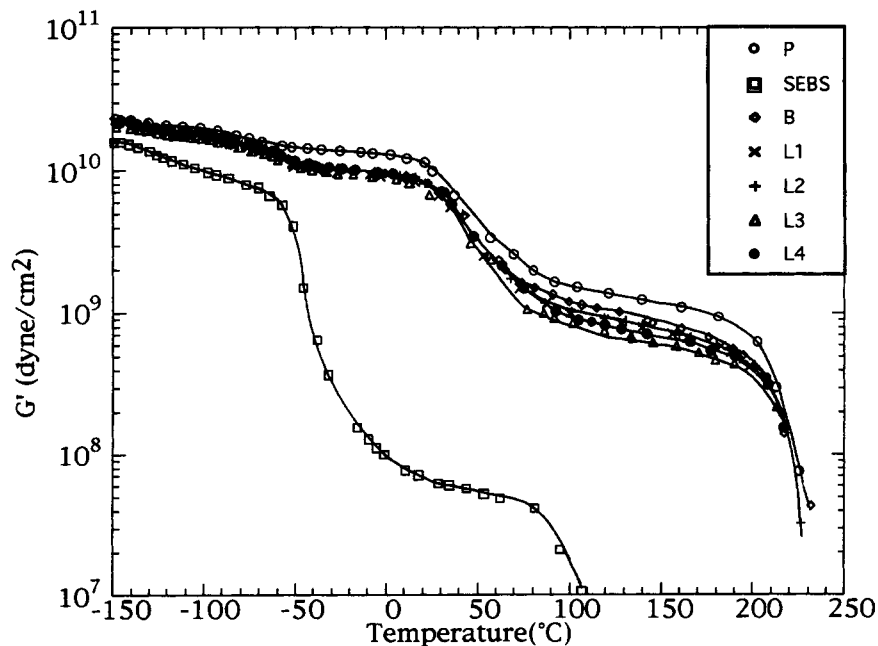


Figure 7 The storage modulus (-150 – 200°C) of ternary blends in comparison with binary blends and neat PA-6 and SEBS.

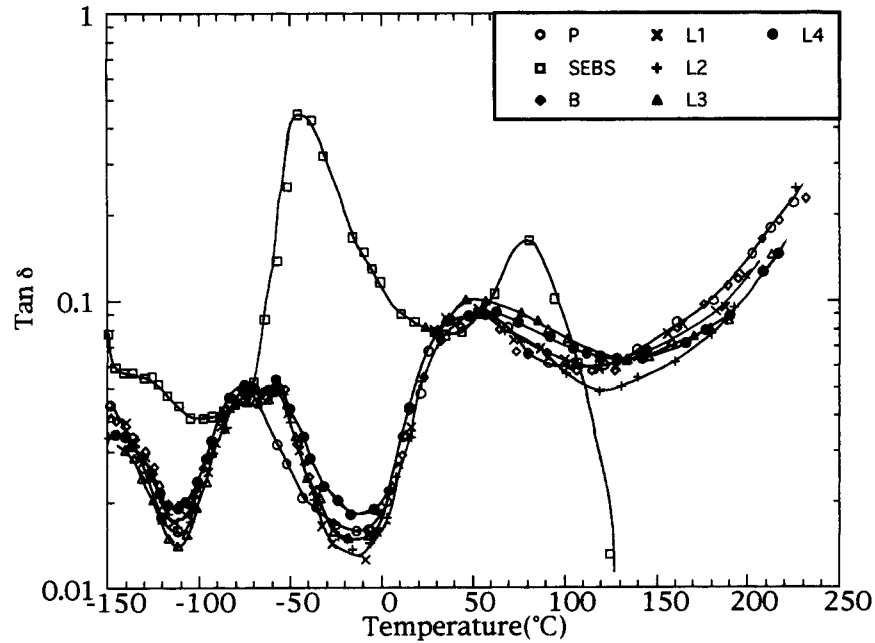


Figure 8 The loss tangent (-150 – 200°C) of ternary blends in comparison with binary blends and neat PA-6 and SEBS.

with that of the Izod impact strengths summarized in Table I. This suggested that, at the same rubber contents, a greater damping ($\tan \delta$) meant better interactions between the elastomeric and matrix phases in the ternary blends.

CONCLUSION

Maleated SEBS elastomer were found to be quite effective in enhancing the compatibility between a semicrystalline polyamide, PA-6, and an elastomer, SEBS. Commercially available MA-g-SEBS typically contained relatively low MA contents (about

1.8 wt %). To investigate effect of MA grafting densities on effectiveness of compatibility, higher MA levels (8 and 14 g/100 g SEBS) were grafted onto SEBS by laboratory synthesis. The results showed that the effectiveness of compatibility was significantly raised by increasing the MA graft densities. At high MA graft levels, the effectiveness could also become lower if the MA grafting densities in the compatibilizer kept increasing. Just as there existed an optimal window of compatibilizer compositions in order to achieve optimal particles, there existed an optimal maleic anhydride grafting densities in order to achieve strongest interactions.

The morphology and the impact strengths of the compatibilized ternary blends were determined for blends containing various wt % of compatibilizers with various MA grafting densities. Depending on the maleated extents, the compatibilizer influenced significantly the properties of the blends. Both the maleated extents (graft ratios) of the compatibilizer and the compositions of the compatibilizer in the blends strongly affected the mechanical properties of the compatibilized blends. This study has shown that by increasing the MA contents in the compatibilizer, the impact toughness could be more effectively improved.

Table II $\tan \delta$ at the PA-6 Glass Transition Peak Maximum

Code	$\tan \delta$
B	0.087
L1	0.089
L2	0.090
L3	0.098
L4	0.094
M2	0.092
H2	0.087
L4	0.094
M4	0.093
H4	0.088

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