Compatibilization and Elastomer Toughening of Polyamide-6 (PA6)/Poly(phenylene ether) (PPE) Blends

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ABSTRACT: In the elastomer-modified (polyamide-6/poly(phenylene ether) (PA6/PPE) = 50/50 blends, poly(styrene-*co*-maleic anhydride) (SMA) was demonstrated to be an efficient reactive compatibilizer. The G1651 elastomer was shown to be an effective impact modifier to result in superior toughness and heat-deflection temperature (HDT) than is the 1901X elastomer for the SMA-compatibilized blends because G1651 particles exclusively reside within the dispersed PPE phase but 1901X particles tend to distribute in the PA6 matrix and/or along the interface. The apparent average diameter of the dispersed PPE phase is insignificantly dependent on the elastomer content in the G1651-modified blend, whereas it increases with increase of the elastomer content in the 1901X-modified blend. Moreover, there exists a critical elastomer content, 15 phr, for the ductile–brittle transition of the G1651-modified SMA-modified PA6/PPE blends. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 23–32, 1999

Key words: PA6; PPE; SMA; toughness; compatibilizer; impact modifier

INTRODUCTION

The great profit of polymer blends and alloys from different available polymers is the most effective and convenient route to create new and useful materials with greater versatility and flexibility than is the development of new polymers. However, from the thermodynamics point of view, most of polymer pairs are immiscible and incompatible at the molecule level, which results in poor interfacial strength and inferior mechanical properties. Hundreds of polymer blends have been attempted[1–3]; only very few of them have been successfully commercialized and the most important one is the HIPS/poly(phenylene ether) (PPE) blend.[4–6] The common route to overcome the incompatible obstruction of a polymer blend is to add a suitable compatibilizing agent, usually a block or graft copolymer, to lead to a great improvement of the mechanical properties of the blend.[7–12]

For polymers in engineering applications, the fracture toughness of a polymer becomes crucial in the material selection. Therefore, there has been great interest in developing toughened polymers and polymer blends during the last two decades. There have been a great number of successful examples by adding elastomers to various polymers to toughen the originally brittle or notch-sensitive polymers.[13–28] Many variables can influence the degree of toughening achieved and some debate about underlying mechanisms exit.[18,19,29–34] However, there is general agreement that the morphology of the blend, more specifically, the particle size and the elastomer distribution, is an influential factor. The optimized elastomer size distribution depends mainly upon the viscosity ratio, interfacial tension, involved deformation mechanisms, and other possible factors.

Table I   Summary of Different Kinds of Elastomers

Designation	Material (Trademark)	Composition	Molecular Weight	Source
G1651	Styrene/ethylene–butylene/styrene (Kraton G1651)	29% Styrene	$M_w = 29{,}000$ Styrene block $= 29{,}000$ EB block $= 116{,}000$	Shell Chemical Co. (Houston, TX)
1901X	Styrene/ethylene–butylene/styrene (Kraton FG-1901X)	29% Styrene 2% MA	$M_w = 20{,}000$	Shell Chemical Co. (Houston, TX)

Both polyamide-6 (PA6) and PPE [poly(2,6-dimethyl-1,4-phenylene ether)] are important engineering plastics, each providing outstanding performance in various applications. Nevertheless, they possess some negative aspects and PA6/PPE blends are expected to complement each other's deficiencies while maintaining the good properties of each polymer. However, PA6 and PPE are thermodynamically immiscible and incompatible in the whole composition range. To modify this blend with potential commercial interest, the combination of a compatibilizer and an impact modifier is necessary. During the last decade, extensive research has been carried out in areas of compatibilization and/or impact toughening of the nylon (PA6 and PA6,6)/PPE blends. Ghidoni et al.[35] reported that the modified PPE, PPE functionalized with N-methyl-4-nitro-phthalimide, was allowed to react with the amine end group of PA6 to produce a transimidation copolymer as the compatibilizer and then this blend was further toughened with a suitable rubber to improve the Izod impact strength. Chiang et al.[36–40] utilized various reactive compatibilizing agents to enhance the interfacial strength and subsequently promote the mechanical properties of the incompatible PA6/PPE blends. Hobbs et al.[41] utilized a proprietary coupling agent as a compatibilizer and a styrene–butadiene–styrene (SBS) block copolymer as an impact modifier to develop a high-impact PA6,6/PPE blend. There are several patents[42–46] reporting polyamide–PPE blends compatibilized by adding maleic anhydride (MA) directly or by a copolymer precompounded PPE with MA and toughened with a rubber impact modifier. This study attempted to improve the toughness of PA6/PPE blends by incorporating both a compatibilizer and impact modifiers.

EXPERIMENTAL

Materials

PA6, trademark 1010C2, with a relative viscosity of 2.3 was obtained from the Mitsubishi Kasei Co. Ltd. (Yokohama, Japan). PPE, trademark Blendex HPP-820, with intrinsic viscosity of 0.4 dL/g was purchased from the General Electrical Co. (Dallas, TX). The poly(styrene-co-maleic anhydride) (SMA), trademark Dylark 232, with 8% MA and an $M_w = 2 \times 10^5$, was supplied by Arco Chemical Co. (Tokyo, Japan). Two different types of elastomers, G1651 and 1901X, were employed in this study as shown in Table I. Both G1651 and 1901X have styrene end-blocks and a hydrogenated butadiene midblock resembling an ethylene/butylene copolymer. However, 1901X was grafted with 2% wt MA along the olefin midblock.

Sample Preparation

All the blends were prepared on a corotating 30-mm twin-screw extruder ($L/D = 36$, Sino-Alloy Machinery Inc.) with a rotational speed of 250 rpm. The barrel temperatures were set from 210 to 290°C. The standard ASTM $\frac{1}{8}$-in. testing specimens were prepared by an Arburg 3-oz injection-molding machine. The temperatures of the injection molding were from 280 to 295°C.

Characterization

Standard tensile tests (ASTM-D638) were carried out at a crosshead speed of 5 mm/min. Standard flexural tests (ASTM-D790) were carried out at a crosshead speed of 1.2 mm/min and with a span length of 50 mm. Notched Izod impact tests were carried out at ambient conditions according to the ASTM-D256 standard method. The heat-deflection temperature (HDT) was determined under a load of 66 psi for the $\frac{1}{8}$-in. specimens according to
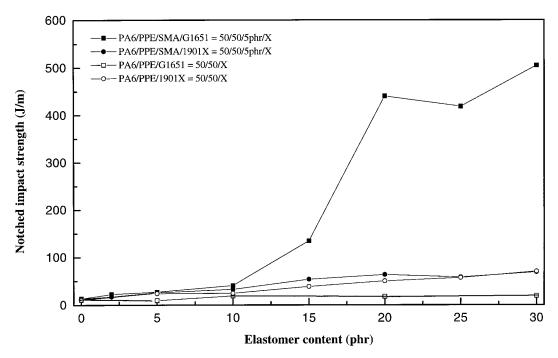
Figure 1 Effect of two different elastomers on the notched impact strength of the uncompatibilized and compatibilized PA6/PPE = 50/50 blends.

the ASTM-D648 standard method. The procedures of the previously developed method to determine the impact critical strain energy release rate (G_c) were carried out at ambient conditions by varying the depth of a notch.[47]

Morphological studies were carried out by transmission electron microscopy (TEM). Sections were microtomed using a Reichert-Jung Ultracut E to section molded specimens perpendicular to the flow direction and then stained with 0.5 wt % ruthenium tetraoxide (RuO_4). The thin sections were laid on top copper grids and examined using a JEM-E1200 EXII (or JEOL 200CX) TEM operating at an accelerating voltage of 90 kV. Dynamical mechanical analysis (DMA) was carried out with a single-cantilever clamp mode, on a TA Instrument DMA 2980, at a frequency of 10 Hz and a heating rate of 3°C/min. Samples were cut into a size of 40 × 15 × 4 mm from the molded specimens.

RESULTS AND DISCUSSION

Mechanical Properties

In general, the assessments of the material's mechanical properties can be roughly classified into two categories: toughness and strength. The Izod impact strength and tensile elongation are considered as the material toughness, while the tensile strength and modulus are considered as the material strength. Modification of a polymeric material seldom results in improving both material strength and toughness simultaneously. In other words, one property is usually improved while the other suffers.

Figure 1 illustrates the effect of two different elastomers on the notched impact strengths of the uncompatibilized and compatibilized PA6/PPE = 50/50 blends. At low elastomer content (≤10 phr), there is insignificant difference between the impact strength of all the blends. The SMA-compatibilized G1651-modified blend is the only blend in which its impact strength is drastically increased and results in ductile failure when the elastomer content is 15 phr or higher. The 1901X-modified blends, uncompatibilized or compatibilized, do not give high-impact ductile failure even if the elastomer content is increased to 30 phr. However, their impact strengths are always higher than those of the uncompatibilized G1651-modified blends because the MA of 1901X can react with the amine end group of PA6 to form an *in situ* copolymer as a compatibilizer. Therefore, SMA actually plays a key role as a compatibilizer to improve the interfacial adhesion and to reduce
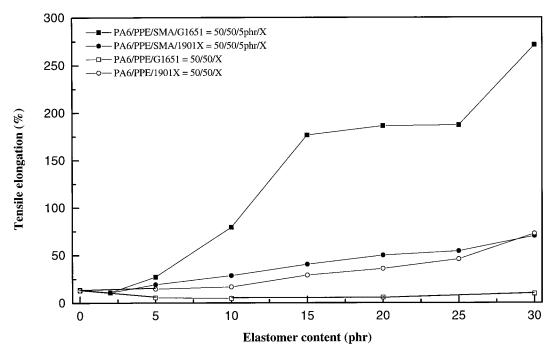
Figure 2 Effect of two different elastomers on the tensile elongations of the uncompatibilized and compatibilized PA6/PPE = 50/50 blends.

the size of the disperse phase in the G1651-modified blends. The effects of two different elastomers on the tensile elongations of the uncompatibilized and the compatibilized PA6/PPE = 50/50 blends are shown in Figure 2. The trend in tensile elongation is similar to the notched impact strength as shown in Figure 1. The G1651-modified blend has a higher flexural modulus than that of the 1901X-modified blend at the same elastomer content as shown in Figure 3, because G1651 always resides in the dispersed PPE phase, whereas most 1901X reside in the PA6 matrix.

Morphologies

The effect of a compatibilizer upon the mechanical properties of a polymer blend can be elucidated by the particle-size distribution of the dispersed phase and its interfacial strength. However, the base morphology of a system and the level of interfacial bonding are dictated by the amount of compatibilizer formed and/or added and processing conditions.[41] In toughening a polymer, the elastomer particle size and its interfacial adhesion are important factors in dictating the toughness of the resultant blend. Figure 4 gives transmission electron microscopy (TEM) micrographs of uncompatibilized and compatibilized

PA6/PPE = 50/50 blends. The PA6 is the matrix (light region) and the PPE is the dispersed phase (gray region) in this system due to relatively lower PA6 viscosity. The dispersed phase size of the blend becomes smaller and the interface contrast becomes blurred after compatibilization. The *in situ*-formed PA6-*g*-SMA at the interface is an effective compatibilizer of the PA6/PPE blend. TEM micrographs of elastomer-modified compatibilized blends are shown in Figures 5 and 6 where elastomers are stained by RuO$_4$. Figure 5 shows that G1651 particles exclusively reside in the dispersed PPE phase since they are more compatible. From the higher magnification [Fig. 5(c)], the G1651 particles are distributed within the PPE phase where the microstructures of polystyrene (PS) and poly(ethylene-*co*-butylene) (PEB) show phase separation between plastic PS and rubbery PEB. On the contrary, most 1901X particles reside in the PA6 matrix and/or exist along the interface due to the reaction between the MA of 1901X and the amine end group of PA6 as shown in Figure 6. 1901X elastomers distributed along the interface compete with SMA-*g*-PA6 copolymers, but the latter is a more effective compatibilizer than is the former. Therefore, the presence of more 1901X elastomers results in lower compatibility of the PA6/PPE/SMA blend. The pres-
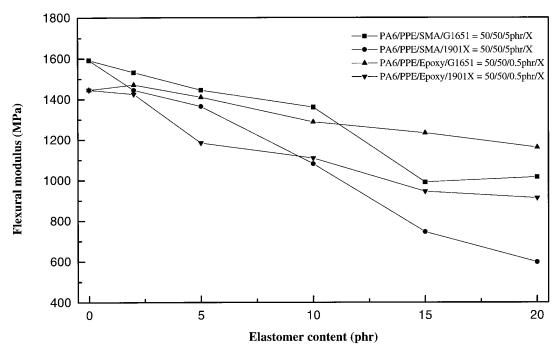
Figure 3 Effect of two different elastomers on the flexural moduli of the SMA-compatibilized PA6/PPE = 50/50 blends.
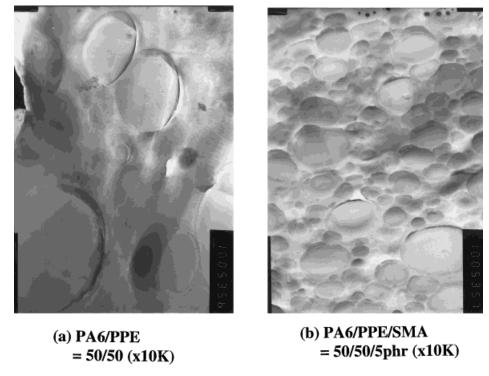

(a) PA6/PPE
= 50/50 (x10K)

(b) PA6/PPE/SMA
= 50/50/5phr (x10K)

Figure 4 TEM micrographs of uncompatibilized and compatibilized blends.

(a) PA6/PPE/SMA/G1651
= 50/50/5phr/10phr (x10K)

(b) PA6/PPE/SMA/G1651
= 50/50/5phr/20phr (x10K)

(c) PA6/PPE/SMA/G1651
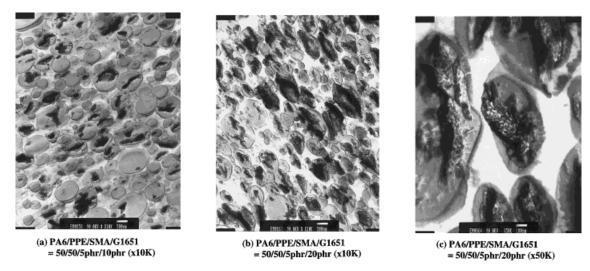= 50/50/5phr/20phr (x50K)

Figure 5 TEM micrographs of G1651-modified compatibilized blends.

ence of the 20 phr 1901X elastomer [Fig. 6(b)] results in a larger dispersed PPE phase domain size than that with the 10 phr 1901X elastomer [Fig. 6(a)]. Therefore, the 1901X elastomer actually decreases the effectiveness of the SMA compatibilizer in this PA6/PPE blend and results in less improvement in the toughness.

From the morphological results, the apparent average diameters of the dispersed PPE phase are summarized in Table II. The diameter of the dispersed PPE phase in the compatibilized PA6/PPE blend is about one-third relative to the uncompatibilized blend. Additionally, the diameter of the dispersed PPE phase is less dependent upon the elastomer content in the G1651-modified blend but increases in the 1901X-modified blend.

For the PA6/PPE/G1651 = 50/50/5 phr blend, the diameter of the dispersed PPE phase is larger than that of the uncompatibilized blend due to the coalescence of the dispersed PPE phase induced by G1651. The diameter of the dispersed PPE phase of the PA6/PPE/1901X = 50/50/10 phr blend is similar to that of the uncompatibilized blend, whereas it is three times that of the PA6/PPE/SMA/1901X = 50/50/5 phr/5 phr blend. Therefore, SMA is a more effective compatibilizer than is 1901X in the PA6/PPE blend.

From the results of the mechanical properties and morphologies, it can be concluded that the 1901X elastomer has a certain compatibilizing ability but it will also interfere with the compatibilizing ability of the already existing SMA. If the
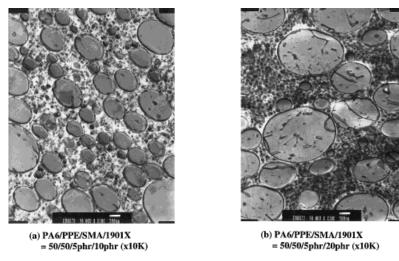

(a) PA6/PPE/SMA/1901X
= 50/50/5phr/10phr (x10K)

(b) PA6/PPE/SMA/1901X
= 50/50/5phr/20phr (x10K)

Figure 6 TEM micrographs of 1901X-modified compatibilized blends.

Table II   Summary of Various Diameters and Size Distribution of the Dispersed PPE Phase

Composition	Number-Average Particle Diameter, dn (nm)	Weight-Average Particle Diameter, dw (nm)	Dispersity Index (n)
PA6/PPE = 50/50	1794	2255	1.26
PA6/PPE/SMA = 50/50/5 phr	648	871	1.34
PA6/PPE/G1651 = 50/50/5 phr	2274	2999	1.32
PA6/PPE/1901X = 50/50/10 phr	1807	2239	1.24
PA6/PPE/SMA/G1651 = 50/50/5 phr/5 phr	559	781	1.40
PA6/PPE/SMA/G1651 = 50/50/5 phr/10 phr	551	679	1.23
PA6/PPE/SMA/G1651 = 50/50/5 phr/15 phr	590	732	1.24
PA6/PPE/SMA/G1651 = 50/50/5 phr/20 phr	616	817	1.33
PA6/PPE/SMA/G1651 = 50/50/5 phr/25 phr	648	815	1.26
PA6/PPE/SMA/G1651 = 50/50/5 phr/30 phr	714	885	1.24
PA6/PPE/SMA/1901X = 50/50/5 phr/5 phr	600	733	1.22
PA6/PPE/SMA/1901X = 50/50/5 phr/10 phr	729	915	1.26
PA6/PPE/SMA/1901X = 50/50/5 phr/20 phr	951	1405	1.48
PA6/PPE/SMA/1901X = 50/50/5 phr/30 phr	743	1164	1.57

amount of 1901X reaches a critical value, its compatibilizing ability precedes its interference, so that the diameter of the dispersed PPE phase becomes smaller, for example, PA6/PPE/SMA/1901X = 50/50/5 phr/30 phr. Hence, G1651 distributed in the dispersed PPE phase is more effective than is 1901X distributed in the PA6 matrix to toughen the PA6/PPE blends. In our previous study,[48] it was also discovered that the final elastomer destination is a determinative factor to toughen the PC/PET blend. A core–shell elastomer distributed in the PC phase is more effective than that distributed in the PET phase for toughening the PC/PET blend.

Dynamical Mechanical Properties and Thermal Analysis

SMA is a reactive compatibilizer for the immiscible and incompatible PA6/PPE blend. The reaction and the extent of segmental mixing between SMA with PA6 and PPE will affect the glass transition temperatures of PA6 and PPE. Nanasawa et al.[12] reported that the α, β, and γ transitions of PPE are 210, 50, and $-100°C$, respectively. Figure 7 presents plots of tan δ versus temperature for the uncompatibilized and compatibilized PA6/PPE blends. The uncompatibilized blend gives only the T_g of PA6 (37.15°C) and the γ transition of PPE ($-91.4°C$). The T_g of PPE cannot be detected since the glassy transition temperature of PPE ($T_g = 208.79°C$) and the melting point ($T_m = 210.84°C$) of PA6 are too close to be distin-

guished. There are two obvious T_g peaks in the compatibilized PA6/PPE blend where the main T_g peak of the PA6 remains unchanged except for the appearance of a minor peak at 75°C. We suspect this minor peak may come from the PA6-g-SMA copolymer. The peak at 171°C is probably the miscible mixture of PPE and the unreacted SMA because it has been reported that the SMA copolymer with 8% MA is fully miscible with PPE.[49–50] The effects of the elastomer content on the heat-deflection temperature (HDT) of the compatibilized blends are shown in Figure 8. The HDT of the G1651-modified blend is less dependent on the elastomer content because the elastomer particles are distributed in the dispersed PPE phase. The HDTs of the 1901X-modified blends decrease substantially since 1901X particles reside mostly in the PA6 matrix and result in the reduction of the matrix modulus.

Strain-Energy Release Rate

Linear elastic fracture mechanics (LEFM) is frequently utilized to characterize polymer fracture behavior. The stress-intensity factor, K, or the strain-energy release rate, G, represents the fracture toughness of a polymer in LEFM. According to the LEFM theory, when K or G reaches its critical value (K_c or G_c), fracture of a brittle polymer will occur. Even for a limited-yielding polymer, a modified LEFM is still applicable. However, the fracture toughness of a ductile polymer characterized by LEFM becomes difficult because
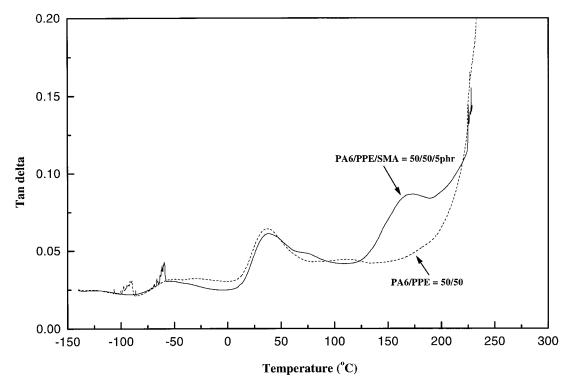
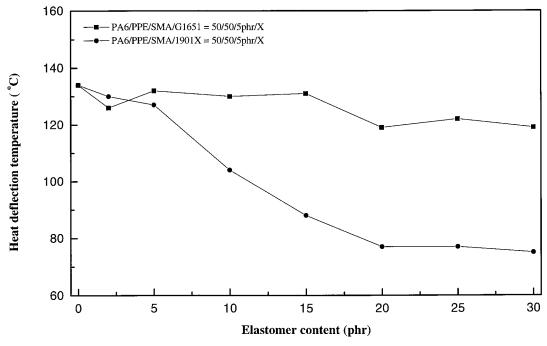**Figure 7** Tan δ versus temperature for the uncompatibilized and compatibilized PA6/PPE = 50/50 blends.

Figure 8 Effect of two different elastomers on the HDTs of the compatibilized PA6/PPE = 50/50 blends under 66 psi.
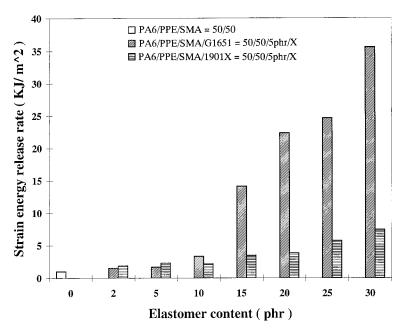
Figure 9 Effect of two different elastomers on the strain-energy release rates of the uncompatibilized and the compatibilized PA6/PPE = 50/50 blends.

the fracture toughness to yield strength ratio is high. The polymer blend with a large plastic zone prior to crack initiation violates the limitation of small-scale yielding, which ensures the validity of LEFM. Therefore, for the uncompatibilized blends or the blends with low elastomer content, they can still be characterized by LEFM in the compatibilized PA6/PPE blends.

The aim of the Izod impact test on the mechanical performance of plastics and polymer blends is to give a basic understanding of the behavior of such materials under impact loading and, hence, provides a reliable criterion for materials selection. However, although it is easy to perform, the impact test is difficult to analyze clearly since it involves the dynamic response of structures, stress waves in the solids, and nonequilibrium situations. Besides, the impact behavior depends upon the basic properties of materials, conditions of use, processing conditions, and product design. From the practical point of view, most polymers and polymer blends are sensitive to the notch radius, temperature, and strain rate.

Figure 9 illustrates the effect of two different elastomers on the strain-energy release rates of the compatibilized PA6/PPE = 50/50 blends. The improvement of the G_c of the compatibilized blend progressively increases with increasing elastomer content. At the low elastomer content, the G_c of the 1901X-modified blend is higher than

that of the G1651-modified blend owing to that 1901X can play a dual role as an interfacial agent and an impact modifier. However, there is an inverse trend at high elastomer content since the G1651 particles distributed in the dispersed PPE phase are able to promote the fracture mechanisms more effectively. When the G1651 elastomer content is greater than 10 phr, G_c dramatically increases. The blends with large-scale yielding and corresponding fracture mechanisms, will be reported in the next article.

CONCLUSIONS

SMA was demonstrated to act as an efficient reactive compatibilizer in the elastomer-toughened PA6/PPE blends. The G1651 elastomer is a more effective impact modifier and results in superior toughness and HDT than those of the 1901X elastomer for the SMA-compatibilized blend since G1651 particles are exclusively distributed in the dispersed PPE phase while 1901X particles are distributed in the PA6 matrix and/or along the interface. Besides, as an impact modifier, the 1901X elastomer also acts as an interfacial agent along the interface. However, its presence tends to interfere with the effectiveness of the SMA compatibilizer and results in relatively poor performance. The apparent average size of the dis-

persed PPE phase is less dependent upon the elastomer content in the G1651-modified blend while it increases with increase of the elastomer content in the 1901X-modified blend. Moreover, there exists a critical elastomer content, 15 phr, for the ductile–brittle transition of the G1651-modified SMA-compatibilized PA6/PPE blends. Quantitative measurements of the fracture toughness, critical elastomer diameter, and corresponding fracture behavior and mechanisms will be reported later.

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