

# Styrene Maleic Anhydride and Styrene Glycidyl Methacrylate Copolymers as *In Situ* Reactive Compatibilizers of Polystyrene / Nylon 6,6 Blends

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The reactive type copolymers styrene maleic anhydride (SMA) and styrene glycidyl methacrylate (SG) are used as *in situ* compatibilizers in polyblends of polystyrene (PS) and nylon 6, 6 (N66). Both copolymers can react with N66 to form copolymers as effective compatibilizers to reduce interfacial tension and increase phase adhesion. However, the toughness of the compatibilized blends is significantly lower than of the corresponding noncompatibilized blends. Only a small fraction of SMA is actually reacted in a typical melt blending, and SG copolymer seems to be more reactive than SMA. The unreacted copolymers are expected to be distributed mostly in the PS phase because of their structural similarity. The reacted copolymers are not exclusively distributed along the interface; some may distribute in both matrices. SMA is known as a very brittle polymer, and the way it is distributed can greatly influence the toughness of the resulting blends. PS is also very brittle relative to N66, and moreover a high amount of SMA in the N66 phase is detrimental since N66 is responsible for the toughness of PS/N66 blends. The better compatibilized blends have the tendency to bring more SMA and reacted SMA into the N66 phase. The relative detrimental effect on the inherent toughness of N66 is much more severe than in case of PS, if they contain the same amount of SMA. This study demonstrates that polyblends with good compatibilizers do not guarantee toughness improvement. The way the compatibilizers affect the inherent properties of the matrix needs also to be taken into consideration.

## INTRODUCTION

The use of polymer blends to achieve price and property advantage has been a rapidly expanding field of research. Except for a few binary blends that are known to be thermodynamically miscible, most polyblends are immiscible to certain degrees with complex phase morphologies that depend on the chemical character of the constituents and their individual rheological properties. The immiscible systems are actually more desirable because each component retains its own properties. However, in a typical immiscible system, satisfactory overall physicochemical behavior critically depends on proper interfacial tension to generate a small phase size and strong interfacial adhesion to transmit applied force effectively between the component phases (1).

Methods to reduce interfacial tension and to improve phase adhesion between two immiscible phases have been the subject of considerable research activity, often of proprietary nature. The syn-

thesized block and graft copolymers as compatibilizers have successfully turned several otherwise incompatible blends into compatible, useful blending materials. The choice of a block or graft copolymer is based on the miscibility of its segments with the blend components, and such a copolymer tends to concentrate at the interface as emulsifier.

Block and graft copolymers usually require a separate preparation step, however and certain block copolymers, such as polycarbonate polyesters, are difficult to obtain. Therefore, considerable research and development efforts have focused on compatibilizers formed *in situ*. Examples and selections of *in situ* compatibilization up to now are concentrated mostly on polyblends of nylons and maleic anhydride (MA) grafted polyolefins (2-15) and relatively less often on other systems (16-22). Blends involving the *in situ* compatibilizer copolymer containing glycidyl methacrylate (GMA) are even fewer, but become important because of its potential applications in other blend systems (23-25). A few studies

on polyblends of polystyrene (PS) and nylon 6 with styrene maleic anhydride (SMA) as a compatibilizer have been previously reported (2, 26, 27). In this study, we purposely selected these two types of *in situ* reactive compatibilizers, MA- and GMA-containing copolymers, in polyblends of polystyrene and nylon 6,6 and examined their specific miscibility and correlation with their physical properties.

## EXPERIMENTAL

Figure 1 shows the complete experimental steps that have been carried out in this study.

### Materials

Polystyrene: Maxiglac 100, BC Chem. Corp. of Taiwan, MI = 16 (3.8 kg, 230°C).  $M_w = 307,000$ ;  $M_n = 102,500$  by gel permeation chromatography (GPC).

Nylon 6,6: Zytel 101L, general-purpose grade from Du Pont. MI = 44.7 (2.16 kg, 275°C).

SMA copolymer: (1) Dylark 232 from Arco Chem. Co., random copolymer with 11 wt% MA, MI = 10 (3.8 kg, 230°C).  $M_w = 224,000$ ;  $M_n = 86,700$  (by GPC). (2) Low-molecular-weight SMA (SMA2) with  $M_n = 1900$ , 75% styrene content, from Aldrich Chem. Co.

Styrene glycidyl methacrylate copolymer (SG): This copolymer was prepared by suspension polymerization of 97 parts of styrene and 3 parts of GMA at 75°C for 9 h using 2 parts of BPO as initiator.

MI = 110 (3.8 kg, 230°C).  $M_w = 11,000$ ;  $M_n = 48,500$  (by GPC).

### Melt Blending

The blends were prepared using 2.0 cm Welding Engineers twin-screw extruder with  $L/D = 48$  and counterrotating intermeshing screws. The blended pellets were molded into 0.32 cm test specimens on an Arburg 3 oz injection-molding machine. To study the effects of flow direction on impact properties, plaques of  $15.2 \times 6.4 \times 0.32$  cm were also prepared. Standard Izod impact (ASTM-D256), tensile (ASTM-D638), and flexural (ASTM-D790) tests were carried out at ambient conditions.

### Other Tests

Rheological properties: capillary rheometer, model Rheograph 2001, Göttfert, Germany.

Differential scanning calorimetry (DSC): Model Seiko I SSC-5000 from Seiko Co. of Japan.

Fourier transform infrared spectroscopy (FTIR): Model Nicoklet 520 from Nicklet Co. of U.S.A.

Scanning electron microscopy (SEM): Model S-570, Hitachi Co., Japan.

Transmission electron microscopy (TEM): Model Jeol 2000, Jeol, Japan. Samples were stained with  $\text{OsO}_4$  solution.

Impact fracture mechanics: For procedures, see Refs. 28 through 30.

## RESULTS AND DISCUSSION

### SEM and TEM of Perpendicularly Fractured Surface Morphologies

Figure 2 shows the micrographs of the blends of PS/N66:5/5 with and without 5 phr of various compatibilizers. The presence of 5 phr SMA results in blurring of the phases (blends 4b and 4c, Table 2). The presence of 5 phr SMA2 (low-molecular-weight SMA, blend 4c) clearly results in smaller domain size. The higher MA content and lower molecular weight of SMA2 are responsible for the observed better compatibilization. The best compatibilization is seen in the blend with 5 phr SG copolymer (blend 4g, Fig. 2d), which shows the smallest phase domains and total blurring of the phase boundaries. The presence of even 1 phr SG (blend 4e, micrograph not shown here) causes a significant change in morphology. The other blends all show similar trends; the presence of more SMA or SG copolymer causes further reduction in domain size and phase contrast. Figures 3a and 3b show the TEM micrographs of the blends 3 (PS/N66:7/3) and 4b (PS/N66/SMA:5/5/0.5), in which the darker phase is PS. This could be derived from Fig. 3a, where the nylon is present as the minor component and as the dispersed phase. Even in the presence of SMA, both matrix phases are clearly separated. The extremely brittle properties due to severe fibrillation made it almost impossible to microtome blend PS/N66:5/5 for TEM. Therefore, we were unable to compare the

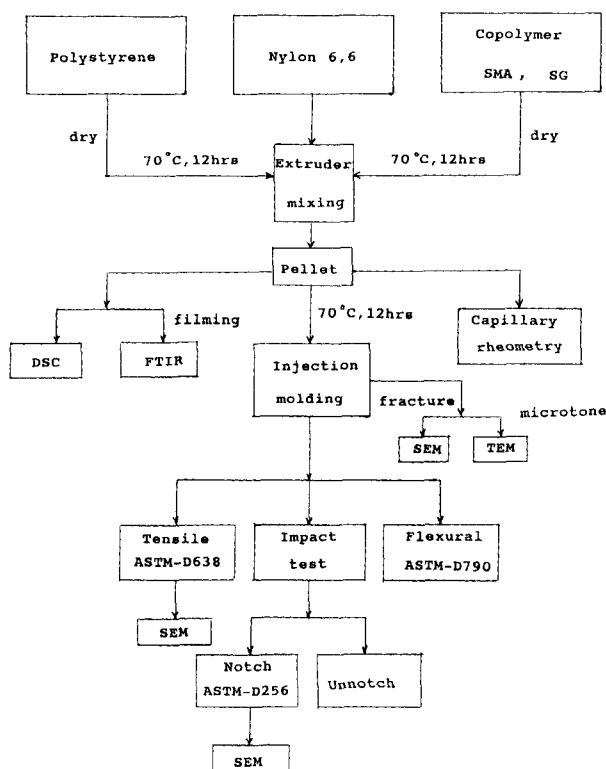


Fig. 1. Diagrams of experimental steps.

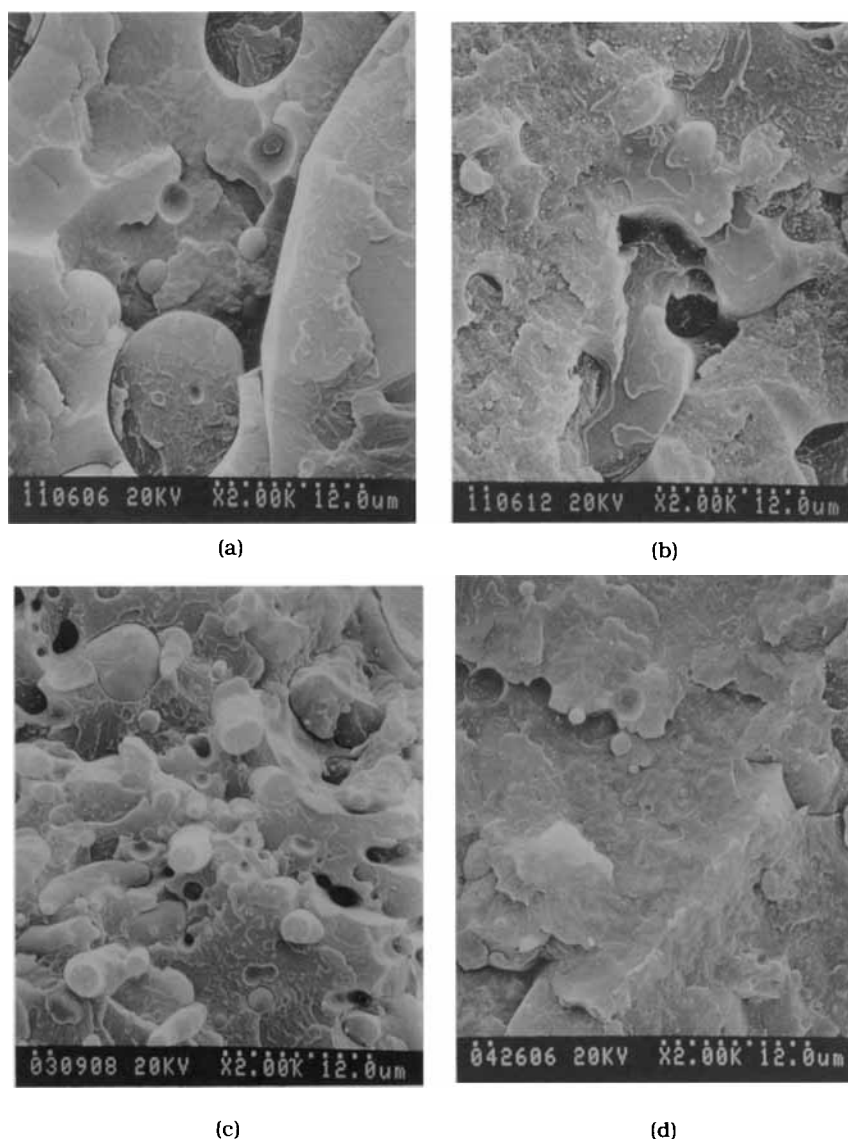


Fig. 2. SEM micrographs perpendicular to flow direction: (a) PS/N66/5/5, (b) PS/N66/SMA:5/5/0.5, (c) PS/N66/SMA2:5/5/0.5, (d) PS/N66/SG:5/5/0.5.

TEM micrographs for the above blend with and without compatibilizer.

#### SEM of Parallel Fractured Surface Morphologies

In any melt process such as extrusion or injection molding, the converging flow into the die followed by melt stretching and elongation of the dispersed phase into long fibrils oriented in the direction of flow will be locked in by rapid solidification. This fibrillation is so severe for the noncompatibilized PS/N66 blends that it can be visually detected. Such fibrillation is significantly reduced after compatibilization with SMA or SG copolymer.

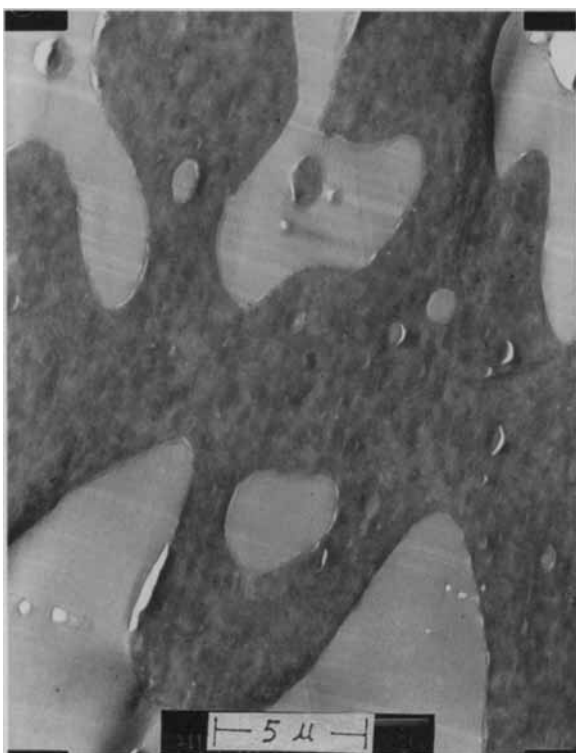
Figure 4 shows higher magnification of the fracture surfaces parallel to the flow direction for blends PS/N66:5/5 containing various compatibilizers and different methods of processing. The noncompatibilized blend PS/N66:5/5 shows the elongated and

dispersed lamellae with diameters of around  $20 \mu\text{m}$  (Fig. 4a), while the lamellae from the one-step blending (method A) with 5 phr SMA have been reduced to about  $7 \mu\text{m}$  (Fig. 4b).

Figures 4c and 4d have the identical composition as Fig. 4b except that blending was carried out in two stages with different order of addition. Method B is defined as blending the reactive compatibilizer (here SMA) with reactive component (here N66) first, followed by addition of the nonreactive component (here PS) and the resulting morphology is shown in Fig. 4c. Method C is defined as blending the reactive compatibilizer with the nonreactive PS first, after which the reactive component is added. The results are shown in Fig. 4d. The difference in morphology between Figs. 4b and 4d is insignificant, which indicates that SMA is more miscible with PS than with N66 and, therefore, the chance of SMA reacting



(a)



(b)

Fig. 3. TEM micrographs perpendicular to flow direction: (a) PS/N66:7/3, (b) PS/N66/SMA:5/5/0.5.

with N66 to generate SMA-N66 copolymer is limited. Figure 4c shows that the elongated lamellae have completely disappeared. Method B (preblending SMA and N66) provides better contact opportunity to form the PS-N66 copolymer as a compatibilizer.

The effect of 5 phr SG copolymer (one-step mixing method A (Fig. 4e)) seems to be more efficient in breaking down domain size than the corresponding addition of SMA (Fig. 4b). The reactivity difference is believed to be more important than the miscibility difference, because the SG copolymer contains 97% styrene and should therefore be more compatible with PS than SMA is. Besides the reactivity difference, the melt viscosity difference between SMA and SG (MI 10 versus 110) is another reason that SG is more efficient than SMA in compatibilizing PS/nylon blends.

The effect of compatibilizers on phase morphology is related to the interfacial tension. Agglomeration depends on the Taylor number,  $k/R \cdot \eta \cdot \dot{\gamma}$ , where  $k$  is the interfacial tension,  $R$  is the phase dimension, and  $\dot{\gamma}$  is the deformation rate (8, 26, 31). Therefore, blends with higher interfacial tension give coarse phase morphologies that are unstable and tend to coalesce. The tendency of the melt to coalesce is depressed by the compatibilizers that may concentrate along the interface and act as emulsifiers by reducing the interfacial tension.

#### Rheological Properties of Pure Polymers and Their Blends

The shear viscosity versus shear rate behavior of PS, N66, and PS/N66:5/5 blends with and without compatibilizer is shown in Fig. 5 and is very similar to the PS/N6 blends previously reported (26). The higher viscosity of the compatibilized blends indicates better miscibility and molecular weight increase due to copolymer formation. SMA was previously reported to be more favorable to nylon 6 than to PS, based on the distinguishable dispersed particles found only in the SMA/P6 blend (26). We feel that the unreacted SMA is more favorable to PS than nylon 6,6 based on structural similarity and our morphological results. After the formation of SMA-N66 copolymer, it may or may not switch to the interface or the N66 phase. The viscosity increase due to the addition of SG and SMA2 copolymers is higher than that due to SMA, which correlates well with the morphological properties mentioned above.

#### Differential Scanning Calorimetry

DSC results are summarized in Table 1 and Figs. 6 and 7. Blends of PS/N66 indicate essentially no movement of the glass-transition temperature ( $T_g$ ) of PS and the melt temperature ( $T_m$ ) of N66. A blend of PS/SMA only shows a slight shift of  $T_g$ s of PS and SMA, indicating partial miscibility. Slight miscibility between PS and SMA is understandable because their structural similarity. Blends of N66/SMA show significant changes in  $T_g$  of SMA, and  $T_m$  and  $\Delta H$  of

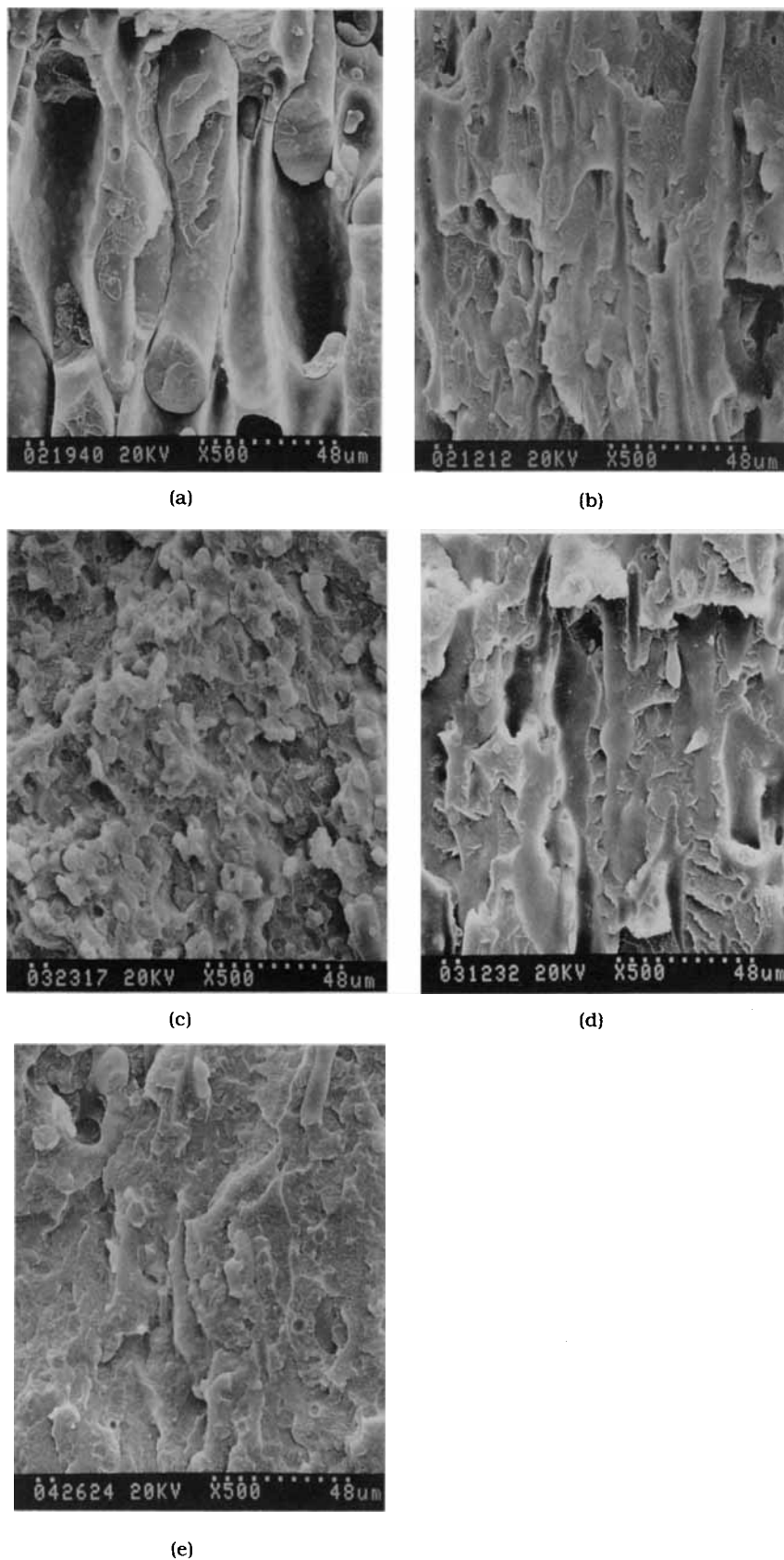


Fig. 4. SEM micrographs parallel to flow direction: (a) PS/N66:5/5, (b) PS/N66/SMA:5/5/0.5, (c) PS/N66/SMA:5/5/0.5 (method B), (d) PS/N66/SMA:5/5/0.5 (method C), (e) PS/N66/SG:5/5/0.5.

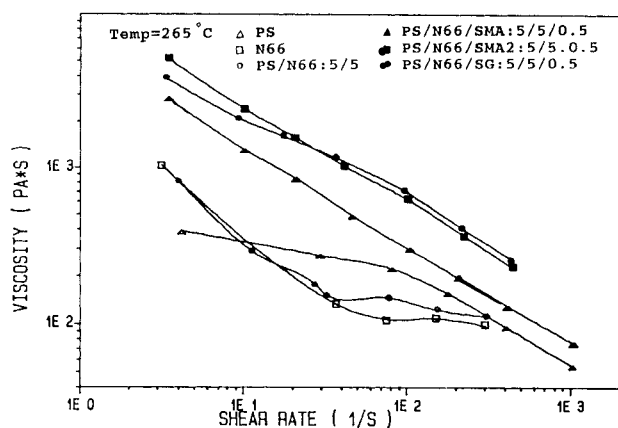


Fig. 5. Plots of shear rate versus viscosity.

N66, which must be related to the formation of N66-SMA copolymer.

### Impact, Tensile and Flexural Properties

Little literature exists on polyblends of PS and nylon with compatibilizers and most of it emphasizes morphology, DSC, and rheology with scarce mention of the resultant mechanical properties (2, 26, 27). Attempts to blend PS and nylon to impart the desirable properties of each in a composition have not been entirely successful because these materials are incompatible. Fibrillation usually found in extruded or injection-molded objects made of PS/nylon blends is caused by a splitting at the interfaces of the noncompatible resins. An early U.S. patent (27) claimed that SMA was able to reduce the fibrillation problem in PS/nylon blends, but no data were given. Ide and Nasegawa (2) reported that the mechanical properties of the compatibilized PS/N6 blends (using SMA) were not improved over their noncompatibilized blends even though good phase dispersity was achieved.

Mechanical properties of matrices and blends from our work are summarized in Table 2. Nylon is known to readily absorb moisture, and the resulting mechanical properties depend on moisture content. It

was very difficult to control moisture content of the blends in this study, and the mechanical properties obtained are not totally consistent, as predicted. However, the general conclusion from Table 2 is that the addition of compatibilizer makes the blends stiffer (higher modulus) and less tough (lower impact strength, fracture energy, and elongation to break). Figure 8 indicates that the presence of SMA reduces impact strengths of PS/N66 blends. Figure 9 shows that the compatibilized blends have higher flexural moduli. Figure 10 shows that the fracture energies ( $G_c$ ) of PS/N66 blends vary as does the Izod impact strength. Figure 11 shows example plots relating fracture energy ( $G_c$ ) to impact fracture mechanics; the results clearly point out that the higher the amount of compatibilizer, the lower is the fracture energy. Essentially, all the compatibilized blends show better dispersity and probably stronger adhesion; however, they do not clearly show improved mechanical properties over the corresponding noncompatibilized blends.

The observed below-average mechanical properties of the incompatible PS/nylon blends are not surprising and actually expected. However, the overall below-average performance from this compatibilized PS/N66 system relative to other blend systems requires more than the conventional interpretations. At first, we suspected that the better mechanical properties of the noncompatibilized blends with highly oriented fibrils could simply be explained by the fact that most mechanical tests are done against the strong direction tending to fracture the fibrilled structure. If this is true, the compatibilized blends with better adhesion and dispersity should perform better than the corresponding noncompatibilized blends in the weak direction of the specimens. Specimens cut into parallel and perpendicular directions from a large injection-molded plaque were employed to approach the problem. The directional properties of notched Izod impact strengths are shown in Table 3. Since the degree of orientation in these plaques (parallel to flow direction) is not as high as in the smaller bars, a lower

Table 1. Summarized DSC Data.

Sample	$T_g$ (°C)	$T_m$ (°C)	Total $\Delta H$ (mJ/mg)	$\Delta H$ for N66 (mJ/mg)
PS	98.3	—	—	—
SMA	118.5	—	—	—
N66	—	265.6	83.1	83.1
PS/N66:9/1	96.8	262.7	7.8	78
PS/N66:7/3	98.2	265.0	20.4	68
PS/N66:5/5	97.3	263.8	36.0	74.3
PS/N66:3/7	—	265.6	56.4	80.6
PS/N66:1/9	—	265.1	71.1	78.6
PS/N66/SMA:5/5/0.5	99.5	263.3	35.4	74.3
N66/SMA:3/7	121.4	262.1	23.6	78.6
N66/SMA:5/5	120.1	263.8	36.4	72.8
N66/SMA:7/3	117.4	264.5	48.8	69.7
PS/SMA:5/5	101.4, 116.5	—	—	—

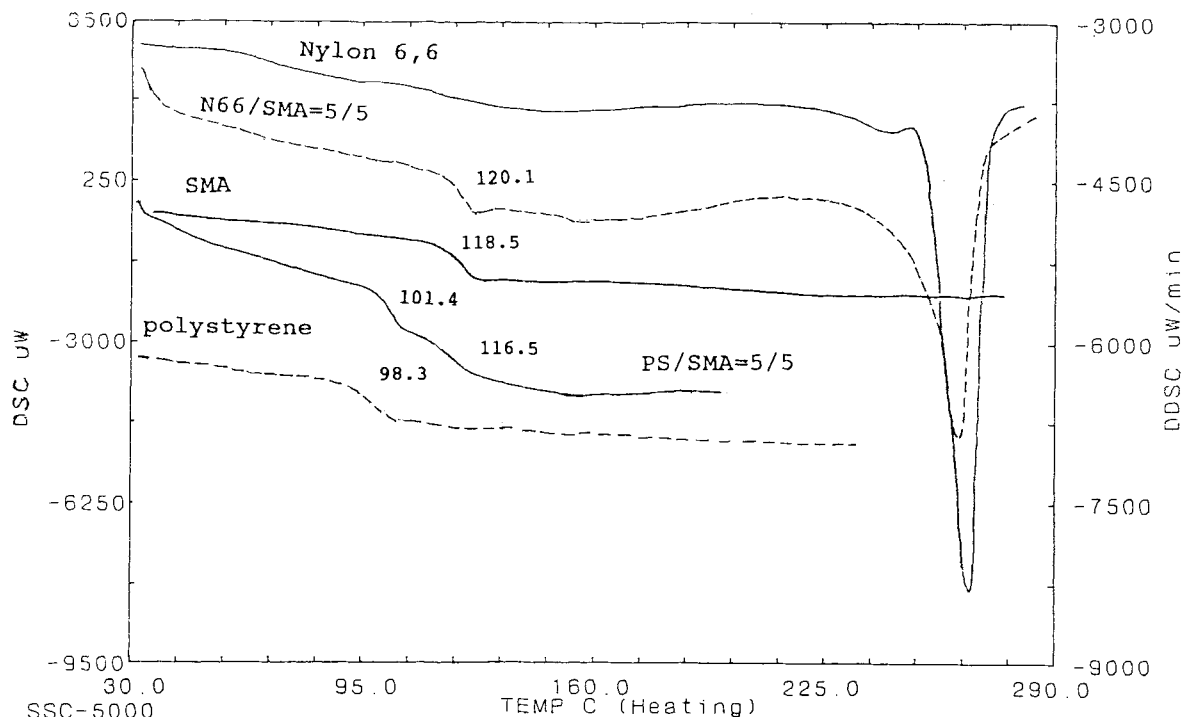


Fig. 6. DSC of PS, N66, SMA, and N66/SMA blend.

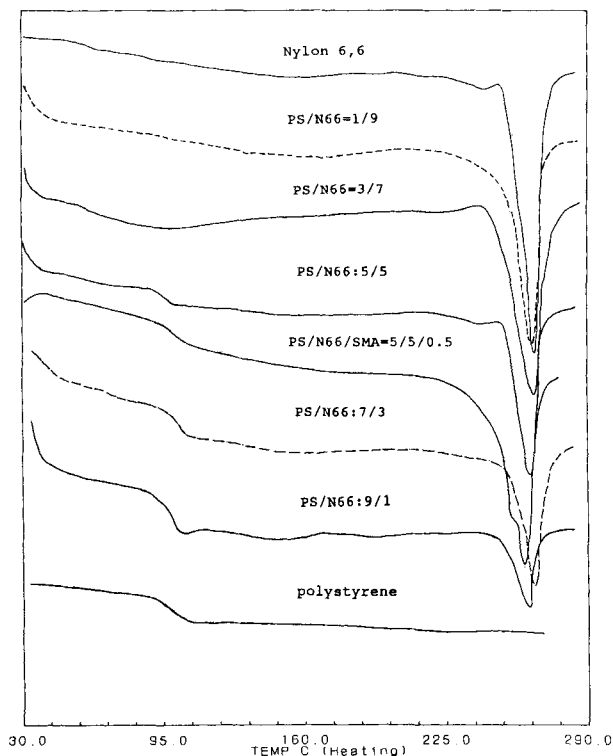


Fig. 7. DSC of PS, N66, and their blends with various compositions.

impact strength is expected (22.9 versus 37.2 J/m from PS/N66:5/5 blend). The weak direction impact strength of 18.7 J/m compared with 22.9 J/m from strong direction is also expected. The blends with

compatibilizers show that the differences in impact strength between the two directions have been reduced, which is also expected. It is surprising to see that the impact strength of the weak direction in the compatibilized blends does not improve as expected; it actually decreases. Thus, the improvements of adhesion and dispersity in any immiscible polyblend do not guarantee an improvement of its performance (at least in impact). Our interpretation based on our proposed model will be given later.

### Chemistry, Reactivity, and Characterization of Copolymer Formation

The reaction between nylon endgroups with anhydride groups of SMA under melt conditions is well-known and has been extensively reported. Infrared spectroscopic verification of the copolymer resulting from imide or amide formation proved to be extremely difficult because of low concentrations (32). To study the extent of this reaction, the solvent-non-solvent fractionation method (Soxhlet extraction with benzene) previously reported (33) was employed to separate the unreacted SMA from N66 and SMA-N66 copolymer from a N66/SMA blend. FTIR spectra of the benzene-extracted solution (after solvent removal) from the N66/SMA blend are essentially identical to those of pure SMA showing only negligible evidence of the N66 characteristic peaks at 3302, 1636, and 1540  $\text{cm}^{-1}$ . These findings mean that the copolymer, if formed, will not be soluble in benzene. After repeated extractions, we obtained 11.26 g of residue from 20.00 g of the N66/SMA:5/5 blend. So, a maximum of 1.26 g of SMA has been

Table 2. Summarized Data of the Mechanical Properties of the Blends.

Sample Number	Composition by Weight	Impact (J/m Notch/Non)	Y. str. (MPa)	Elong. (%)	Flex. mod. (MPa)	Impact $G_c$ (J/m <sup>2</sup> )
1	polystyrene	13.9/142	41.6*	2.5	2949	740
2	PS/N66:9/1	8.8/87.2	33.9*	3.8	2969	180
2a	PS/N66/SMA:9/1/0.5	7.8/83.2	34.5*	3.6	3018	—
3	PS/N66:7/3	22.2/125.4	41.0*	4.7	2705	770
3a	PS/N66/SMA2:7/3/0.5 <sup>†</sup>	11.8/88.2	32.6*	3.9	2832	—
3b	PS/N66/SMA:7/3/0.5	10.8/104.4	43.0*	4.6	2754	—
4	PS/N66:5/5	37.2/176.5	43.0*	7.3	2423	2680
4a	PS/N66/SMA = 5/5/0.2	31.4/167.6	56.8*	7.2	2479	—
4b	PS/N66/SMA = 5/5/0.5	21.6/140.1	46.1*	7.1	2508	1630
4b(B)	PS/N66/SMA = 5/5/0.5	19.6/79.4	47.0*	5.2	2244	—
4b(C)	PS/N66/SMA = 5/5/0.5	26.5/112.7	52.9*	5.8	2734	—
4c	PS/N66/SMA2 = 5/5/0.5 <sup>†</sup>	18.5/106.8	48.7*	4.2	3038	—
4d	PS/N66/SMA = 5/5/1	17.6/134.3	47.9*	5.8	2048	780
4e	PS/N66/SG = 5/5/0.1	27.7/120.2	61.9*	7.8	3279	—
4f	PS/N66/SG = 5/5/0.3	26.4/114.6	61.4*	7.5	3211	—
4g	PS/N66/SG = 5/5/0.5	31.3/152.0	60.3*	8.1	3156	—
5	PS/N66 = 3/7	33.3/421.4	47.0	39.0	2500	—
5a	PS/N66/SMA = 3/7/0.5	25.0/228.3	59.1*	6.8	2685	—
6	PS/N66 = 1/9	45.4/—	67.1	81.0	2617	4040
6a	PS/N66/SMA = 1/9/0.5	36.3/819.	80.9	17.0	2705	—
7	Nylon 6,6	72/—	65.6	332.0	3233	4720
8	N66/SMA = 7/3	17.6/96.3	47.6*	151.0	2234	1650
9	N66/SMA = 5/5	10.8/27.0	56.6*	12.7	2557	1590
10	N66/SMA = 3/7	9.8/13.9	62.6*	6.9	2763	560
11	PS/SMA = 5/5	—/—	—	—	—	—
12	SMA	9.8/10.9	40.5*	4.1	3214	—

\*ultimate breaking stress, no yielding.

<sup>†</sup>SMA2, low molecular weight SMA,  $M_n = 1900$ .

(B) method B blending, copolymer mixed with N66 first then PS.

(C) method C blending, copolymer mixed with PS first then N66.

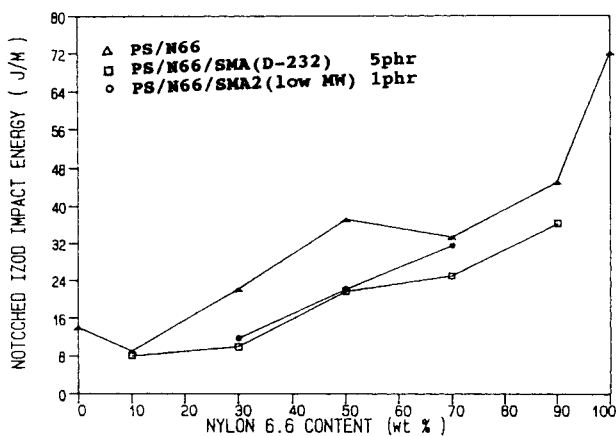


Fig. 8. Izod impact strengths of PS/N66 blends with and without SMA compatibilizer.

converted into SMA-N66 copolymer by the reaction between the terminal amine functionality and the anhydride moiety in a typical extruder mixing. Figure 12 shows FTIR spectra of the extracted residue from the P66/SMA:5/5 blend and of N66 and SMA for direct comparison. The extracted residue (assuming complete extraction) contains SMA characteristic peaks, which can be easily identified from Fig. 12, even though we are unable to tell whether they come from the original SMA or the SMA-N66 copolymers. Without catalyst, the copolymer formation rate is considered to be fairly slow in the one-step three-component PS/N66/SMA system. Since

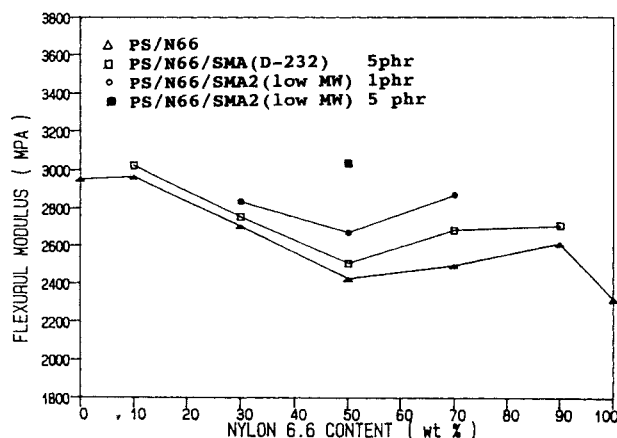


Fig. 9. Flexural moduli of PS/N66 blends with and without SMA compatibilizer.

SMA is probably more likely to reside in the PS phase, the chance of SMA contacting and reacting with N66 is considerably less in the one-step blending process compared with the premixing method B. Thus, only a very small fraction of SMA reacted in the one-step blending, and even less reaction is expected in case of method C (blending SMA and PS first, then with N66). The best compatibilization results obtained from method B (blending SMA and N66 first, then with PS) can be now understood. The reaction between epoxide groups with amine or carboxylic acid is also a well-known chemistry and will not be discussed here.



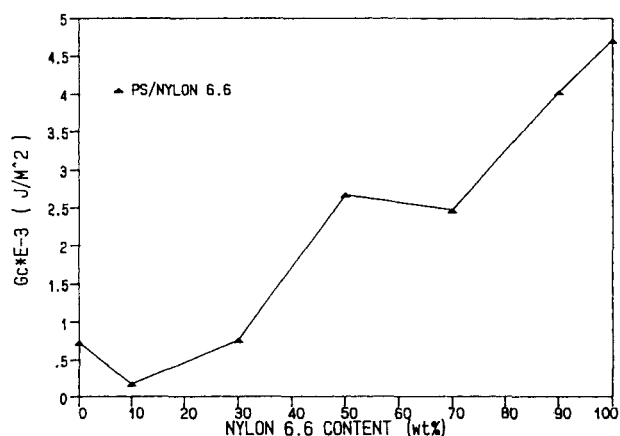
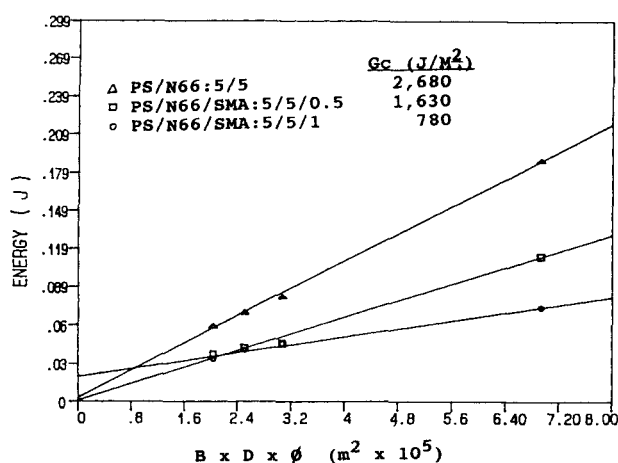

 Fig. 10. Fracture energy ( $G_c$ ) of PS/N66 blends.

 Fig. 11. Plots of impact energy versus  $B \cdot D \cdot O$  for blends PS/N66:5/5 with and without SMA.

Table 3. Izod Impact Strengths Measured Parallel and Perpendicular to Injection-Molding Directions.\*

Sample Number	Composition by Weight	Parallel (J/m)	Perpendicular (J/m)	Perp.-Para. (J/m)
3	PS/N66 = 7/3	9.3	15.1	5.8
4	PS/N66 = 5/5	18.7	22.9	4.2
6	PS/N66 = 3/7	16.1	22.0	5.9
4b	PS/N66/SMA = 5/5/0.5	11.1	13.9	2.8
4c	PS/N66/SMA2 = 5/5/0.5	11.1	13.0	1.9
4g	PS/N66/SG = 5/5/0.5	11.1	13.0	1.9

\*Specimens were cut from large injection-molded plaques (6.0 × 2.5 × 0.125 inch) parallel and perpendicular to flow.

### Copolymer Distribution and Its Effect on Mechanical Properties

To give a reasonable interpretation of why the compatibilized PS/N66 blending system loses its toughness even with improvement in both adhesion and dispersity, we have to look to the effect of the compatibilizer copolymer distribution and its subsequent influence on matrix properties. PS and N66

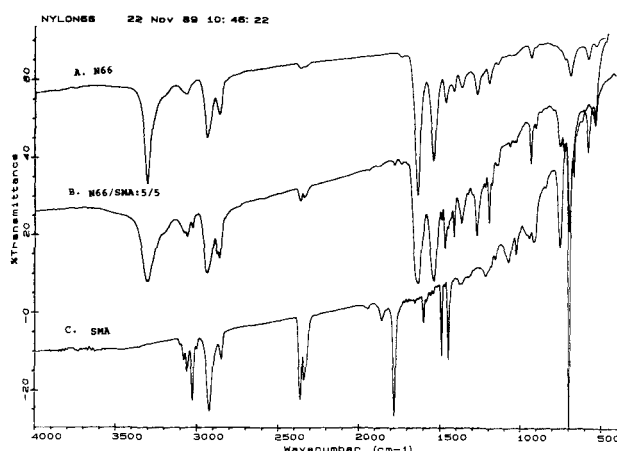


Fig. 12. FTIR spectra: (a) N66, (b) extracted residue from N66/SMA:5/5 blend, (c) SMA.

are highly immiscible with poor interfacial adhesion and mutual solubility. N66 is much tougher than PS (impact strength 72 versus 13.9 J/m), and N66 contributes most to the toughness in the PS/N66 blends. SMA is a very brittle polymer with an impact strength of only 9.8 J/m. Blending PS or N66 with an equal small amount of SMA will result in a detrimental toughness loss in the case of N66, but not so significant in the case of PS.

If SMA were a nonreactive copolymer, it most likely would stay in the PS phase (due to their structural similarity), with little or no change in interfacial adhesion, resulting in the least decrease of the PS/N66:5/5 blend toughness. Blend 4b(C)—prepared by method C with probably the least SMA-N66 copolymer formation because SMA and PS are pre-blended before N66 is added—provides the closest possible situation, and indeed this blend retains 71% of toughness (26.5 versus 37.2 J/m). The blend 4b(B)—prepared by method B with the expected highest SMA-N66 copolymer concentration—retains merely 53% of toughness (19.6 J/m). When more SMA-N66 copolymer is formed, the SMA (reacted or unreacted) concentration in the N66 phase will be increased. The toughness improvements due to adhesion increase and better dispersity appear to be insufficient to compensate for the toughness loss due to the higher concentration of SMA in N66. Therefore, the addition of an efficient compatibilizer to a binary system does not assure improvement in toughness.

This point of view has been virtually neglected in the literature, probably because not many examples have been discovered yet. The third component, especially as a compatibilizer, will affect not only the morphology and adhesion but also the inherent toughness of the other two components. If the third component (a good compatibilizer) improves, or at least does little damage to the two components individually, the improvement of interfacial adhesion and better phase dispersity certainly will result in a

toughness increase, and this is what most literature has reported. When the third component has a detrimental effect on either or both blend components, the resultant toughness is determined by the competition between these two factors.

Chen, *et al.* (26), proposed models of binary blends with compatibilizing agents. According to the models, compatibilizer distribution can be one of the following three possible cases: along the interface, in both blend components, and at the interface as well as in both components. Since SMA is a random copolymer not containing a MA block, the reacted SMA-N66 copolymer may distribute along the interface and in both matrices (26). A model similar to Chen's model based on 100 imaginary SMA molecules in a PS/N66:5/5 blend prepared by three blending procedures is shown in Fig. 13. Of the original SMA, assume 10% is converted to SMA-N66 copolymer by method A, 30% by method B, and 5% by method C. SMA is also assumed to be more soluble in PS than in N66. All the assumptions were indirectly based on results from this study without definite evidence. Figure 13b shows the best compatibilized blend with the highest concentration of SMA (as original SMA and SMA-N66 copolymer) in the N66 phase and along the interface. As mentioned earlier, the disadvantage of the detrimental effect on the N66 matrix is much greater than the possible advantage achieved from strong interfacial adhesion and dispersity (not shown in the model). Figure 13c is the blend with probably the least SMA-N66 copolymer formation and, therefore, the smallest number of SMA molecules will reside in N66 and along the interface. The presence of SMA in the brittle PS will have less of an influence on the inherent toughness of PS and let N66 maintain most of its inherent toughness. This proposed model, though without direct evidence, is able to explain why the better compatibilized blends have less toughness than the noncompatibilized or less compatibilized blends.

### SUMMARY

Polyblends of polystyrene and nylon 6,6 are immiscible and incompatible with poor interfacial adhesion and large phase domains. SMA or SG copolymer itself does not function as a compatibilizer, but will become one after reacting with nylon 6,6 during melt blending. The toughness of the compatibilized blends decreases, even with the expected improvement of interfacial adhesion and the observed finer phase dispersity. The compatibilizers do not reside exclusively along the interface. Some compatibilizer dissolves in both blend components depending on several factors such as chemical structure, processing method, molecular weight, type of copolymer, and many more. The compatibilizer distributed in the blend components certainly will alter the inherent toughness of these components. In the case of detrimental effects, the resultant blend may increase or decrease in toughness depending on the

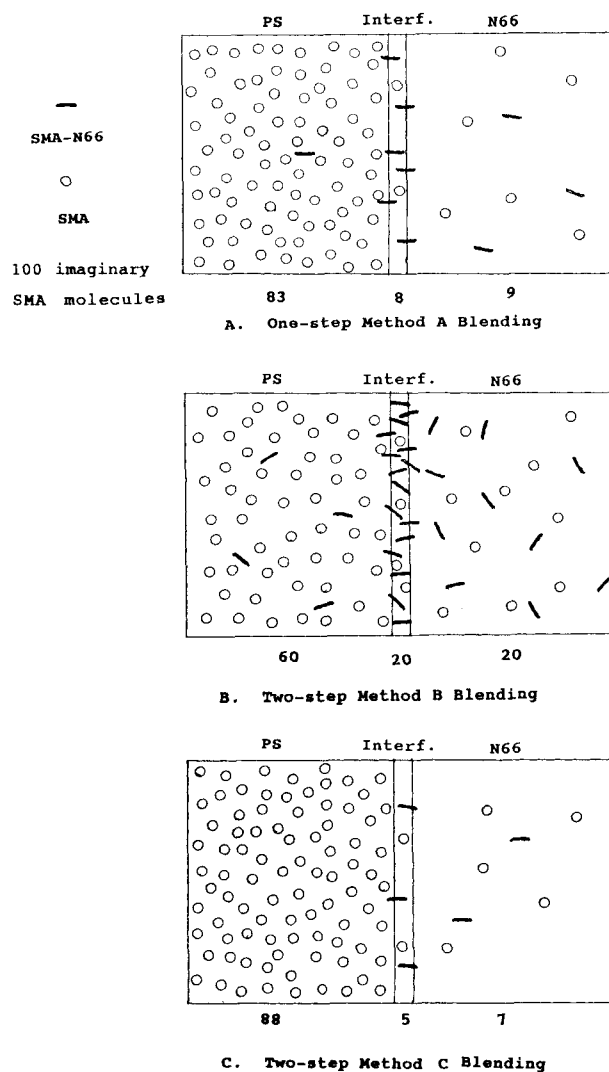


Fig. 13. Model for compatibilizer distribution of binary blend with in situ type compatibilizer: (a) method A, one-step blending; (b) method B, two-step blending, first with reactive component then with nonreactive component; (c) method C, two-step blending, first with nonreactive component then with reactive component.

competition between the advantages due to better adhesion and dispersity and the disadvantage due to the loss of inherent toughness of blend components. Therefore, a good compatibilizer in a binary blend does not assure improvement in its toughness, and this point of view has been virtually neglected previously. In the present blending system, the brittle SMA causes severe damage by residing in the nylon phase rather than in the PS phase. The blend becomes better compatibilized, but in addition the SMA concentration in the nylon phase is high. It appears that the loss of toughness due to the N66 phase embrittlement outweighs the increase of toughness due to better adhesion and dispersity. The proposed model is able to explain why a blend with expected better adhesion and observed better dispersity can show a decrease in toughness.

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