

# Compatibilization of Polyethylene Terephthalate/Polypropylene Blends with Styrene–Ethylene/Butylene–Styrene (SEBS) Block Copolymers

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**ABSTRACT:** Blends of polyethylene terephthalate (PET) and polypropylene (PP) at compositions 20/80 and 80/20 were modified with three different styrene–ethylene/butylene–styrene (SEBS) triblock copolymers with the aim of improving the compatibility and in particular the toughness of the blends. The compatibilizers involved an unfunctionalized SEBS and two functionalized grades containing either maleic anhydride (SEBS-*g*-MAH) or glycidyl methacrylate (SEBS-*g*-GMA) grafted to the midblock. The effects of the compatibilizers were evaluated by studies on morphology and mechanical, thermal and rheological properties of the blends. The addition of 5 wt % of a SEBS copolymer was found to stabilize the blend morphology and to improve the impact strength. The effect was, however, far more pronounced with the functionalized copolymers. Particularly high toughness combined with rather high stiffness was achieved with SEBS-*g*-GMA for the PET-rich composition. Addition of the functionalized SEBS copolymers resulted in a finer dispersion of the minor phase and clearly improved interfacial adhesion. Shifts in the glass transition temperature of the PET phase and increase in the melt viscosity of the compatibilized blends indicated enhanced interactions between the discrete PET and PP phases induced by the functionalized compatibilizer, in particular SEBS-*g*-GMA. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 241–249, 1997

**Key words:** polymer blend; polypropylene; polyethylene terephthalate; compatibilization; styrene-ethylene/butylene-styrene block copolymer

## INTRODUCTION

Blending of two or more polymers offers an interesting route to modify the properties of thermoplastics. The aim can be, for example, to improve the properties of commodity thermoplastics or to lower the cost of engineering high-performance polymers. Upgrading of recycled polymer scrap, which often contains more than one polymer, is also a challenging task, because most thermoplastics are immiscible with each other and the prop-

erties of their mechanical blends unsatisfactory. Especially, the impact strength is often poor due to the immiscibility and lack of interfacial adhesion between the discrete polymer phases. Addition of suitable block or graft copolymers as compatibilizers for such immiscible polymer blends is thus necessary to improve the compatibility and properties of the blends. Such compatibilization often results in stabilized morphology with a fine dispersion of the minor phase, which affects the macroscopic properties of the blends.<sup>1–6</sup>

The properties of polyolefins may be improved by blending with, for example, thermoplastic polyesters or polyamides. Thermoplastic polyesters are of particular interest, because they generally exhibit lower moisture absorption compared to

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polyamides. Polyethylene terephthalate (PET) and polypropylene (PP) are incompatible due to differences in chemical nature and polarity. Therefore, their blends exhibit a clear two-phase morphology, where the dispersed phase forms relatively large spherical droplets and no particular adhesion between the phases exists. Generally, the strength and stiffness of their blends increases with increasing PET content almost linearly, but owing to the incompatibility, the blends exhibit very poor impact strength. Hence, appropriate compatibilization is needed to achieve better adhesion between the two phases and to overcome the brittleness.<sup>7-9</sup>

A-B-A type block copolymers consisting of styrene endblocks and butylene, isoprene, or ethylene/butylene midblocks are thermoplastic elastomers exhibiting physical properties typical for rubbers but similar melt processability to conventional thermoplastics. These properties arise from the fact that styrene is thermodynamically incompatible with the elastomeric midblock and, therefore, micro-phase separation of the material occurs. The hard polystyrene microdomains act as physical crosslinks between the elastomeric sequences providing high strength. On the other hand, thanks to the soft midblocks elasticity similar to conventional vulcanized rubbers is achieved. These materials have been successfully used as impact modifiers for several thermoplastics like polystyrene (PS), polyphenylene ether (PPE), polycarbonate (PC), polyamides (PA), and polyolefins. In addition, they have been shown to act as compatibilizers for different polymer blends, especially for those of polystyrene or polyesters with polyolefins, where they bridge the blended polymers through physical or chemical interactions. For this purpose the versatility of SEBS block copolymers can be significantly improved by grafting to the midblock such functionalities like maleic anhydride or epoxy groups that can react, for example, with the end groups of polyamides or polyesters.<sup>10-17</sup>

In earlier studies we have found that SEBS- or polyolefin-based compatibilizers containing maleic anhydride or epoxy functionalities are effective in improving the properties of blends of polar engineering polymers like polyamides, polyesters, or polyester-type LCPs with nonpolar polymers like polyolefins. The interactions involving reactions between the functional groups of the compatibilizer and, for example, amine or carboxylic acid end groups of polyamides or polyesters, respectively, have remarkably stabilized the morphology and improved the properties of the

blends. DMTA, FTIR, and rheological analyses indicated that these reactions took place during melt blending in an extruder.<sup>3-6</sup>

In this work the effects of three SEBS triblock copolymers used as compatibilizers for PET/PP blends have been studied. One of the copolymers was unfunctionalized (SEBS) and two others contained either maleic anhydride (SEBS-*g*-MAH) or epoxy functionalities (SEBS-*g*-GMA) grafted to the elastomeric midblock. Because the noncompatibilized PET/PP blends generally consist of two discrete phases with the minor phase as relatively large spherical droplets resulting in poor impact strength, the main aim of this study was to find out if these block copolymers can markedly improve the toughness of these blends.

## EXPERIMENTAL

### Materials

The polypropylene (PP) used in the experiments was an isotactic homopolymer VA40 20E produced by Borealis Polymers. According to the manufacturer it has a melt index of 0.4 g/10 min (2.16 kg, 230°C). The polyethylene terephthalate (PET) was a medium-viscosity extrusion grade Arnite D04 300 produced by DSM. According to the manufacturer it has an intrinsic viscosity of 0.82 g/dl (tetrachloroethane/phenol). The materials were chosen so that their melt viscosities were close to each other in the actual blending conditions.<sup>18,19</sup>

The function of three styrene-ethylene/butylene-styrene block copolymers were studied as potential compatibilizers for PET/PP blends. The unfunctionalized copolymer (hereafter referred to as SEBS) was Kraton G1652 exhibiting low relative molecular weight, styrene/rubber ratio of 30/70, and a glass transition temperature ( $T_g$ ) at -42°C. Two functionalized copolymers were also used. Kraton FG 1901 X is functionalized with 2 wt % of maleic anhydride (referred to as SEBS-*g*-MAH). According to the manufacturer, the relative molecular weight of the triblock is low, the styrene/rubber ratio is 28/72, and the  $T_g$  of the material is -42°C. Both SEBS and SEBS-*g*-MAH are produced by Shell Chemicals. The other functionalized grade studied contained epoxy groups in the form of grafted glycidyl methacrylate (SEBS-*g*-GMA) and it was a developmental product generously submitted to us by Asahi Petrochemicals.

The blend compositions studied were PET/PP

20/80 and 80/20. The amount of the compatibilizer added (5 wt %) was taken from both phases, so that in the compatibilized blends the exact contents of the major blend components were 17.5 and 77.5 wt %.

### Blending and Injection Molding

Before blending PET was dried in a dehumidifying dryer (3 h at 120°C + 4 h 160°C). Melt blending of the dry-mixed materials was done in a Werner & Pfleiderer ZSK 25 M9 corotating twin-screw extruder. The temperature profile from 1.barrel to die was 270–270–275–275–275–275°C. The screw speed was 200 1/min and throughput 6 kg/h. The hot extrudate was immediately quenched in a water bath and pelletized.

The blends were dried in a dehumidifying dryer (16 h at 80°C) and injection molded to tensile and flexural test bars with an Engel ES 200/40 injection molding machine. The temperature profile from 1.barrel to die was 280–280–285–285°C and the mold temperature was 50°C.

### Characterization of Mechanical Properties

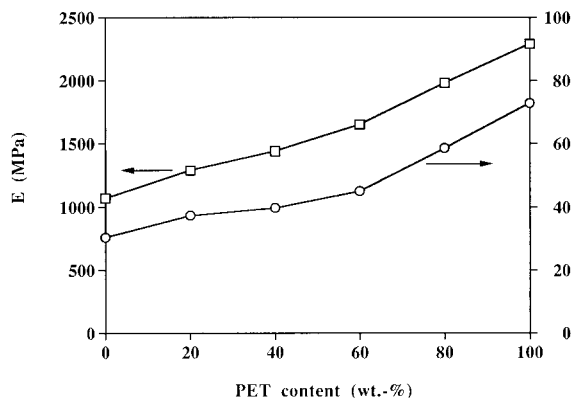
Before testing of mechanical properties the test bars were conditioned for 48 h at 23°C and 50% relative humidity. Tensile and flexural tests were made with an Instron 4204 universal testing machine according to the standards ISO 527 and ISO 178, respectively. Charpy impact strength was determined of both notched and unnotched specimens with a Zwick 5102 pendulum-type testing machine according to the standard ISO 179/1A.

### Morphology

Morphology of the blends was characterized from the cross-sections of cryogenically fractured surfaces of the twin screw extruded strands by using a JEOL JXA-840A scanning electron microscope (SEM). The samples were fractured after dipping in liquid nitrogen and the fracture surfaces were plated with a thin layer of gold before scanning.

### Rheological Properties

Melt viscosities of both the neat polymers and the blends were measured with a Göttfert Rheograph 2002 capillary viscosimeter over a shear rate range from 100 to 10,000 1/s. The measuring temperature was 280°C and a die with length to diameter ratio ( $L/d$ ) of 30/1 was used. The measurements were done to determine the viscosity



**Figure 1** Flexural modulus ( $E$ ) and strength ( $\sigma$ ) vs. PET content of noncompatibilized PET/PP blends.

ratio of PET and PP, and to observe the possible effects of compatibilization on the blend viscosity. All measurements include Rabinowitsch correction, but Bagley correction was not made.

### Dynamic-Mechanical Properties

Dynamic-mechanical properties of the blends were studied with a Perkin–Elmer 7 DMTA equipment using the three-point bending method with the aim to evaluate the possible changes in glass transition temperatures induced by compatibilization. The temperature range studied was from –25 to 150°C, the heating rate 4°C/min, and the frequency 1 Hz.

## RESULTS AND DISCUSSION

### Mechanical properties

Flexural strength and modulus of the noncompatibilized 80/20 and 20/80 (PET/PP) blends were between those of the neat PP and PET showing only slight negative deviation from the addition rule (Fig. 1). The level of notched impact strength of both neat polymers was rather poor and due to the incompatibility, their noncompatibilized blends exhibited impact strengths even inferior to those (Table I). Compositions 80/20 and 20/80 were chosen for the compatibilization studies based on earlier studies to be able to see the effects of the copolymers added on the blend morphology, in particular on the particle size of the minor phase.<sup>5</sup>

Generally, as it was hoped, the addition of 5 wt % of a SEBS-based compatibilizer resulted

in improved impact strength of the blends. In 80/20 (PET/PP) blends the effect of neat SEBS was negligible, but SEBS-*g*-MAH gave three times and SEBS-*g*-GMA five times as high impact strength as the noncompatibilized blend. In the PP-rich blends the addition of neat SEBS led to twice as high impact strength as the noncompatibilized blend. With functionalized compatibilizers the improvement was again much greater; both of them increased the impact strength fourfold. Hence, significant toughening of PET/PP blends was observed with both the functionalized SEBS grades studied.

Owing to the elastomeric nature of these compatibilizers the level of flexural strength and modulus of the blends was lowered as expected. In PP-rich blends SEBS decreased the strength and modulus only slightly less than SEBS-*g*-MAH and SEBS-*g*-GMA. On the other hand, in PET-rich blends the difference between the effects of the unfunctionalized and functionalized SEBS grades was more pronounced. This was probably due to greater amount of chemical reactions that had taken place between the functionalized compatibilizers and the carboxylic acid end groups of PET in the PET-rich compositions. The unfunctionalized SEBS is located most probably in the PP phase, which is already the softer component in the blend. Reactions between the functionalized SEBS grades and PET favor mixing between the PP and PET phases leading to a smaller dispersed particle size. When present at relatively small amounts (below 20 wt %) PET can, therefore, no longer act as a reinforcement for the blend.

### Morphology

SEM micrographs in Figures 2(a) and 3(a) show that the noncompatibilized blends exhibited clear two-phase morphology and poor adhesion between the two phases. The average particle size of the PET-rich blend was about 6–8  $\mu\text{m}$ , with small deviations. The PP-rich blend, in turn, exhibited a finer dispersion of the minor phase with PET domains of the order of 1–2  $\mu\text{m}$ . This difference in particle size of the minor phase was related to the slightly lower viscosity of PET at low shear rates, such as applied in blending. However, although not shown in Figure 3(a), some larger agglomerated PET particles were found as well.

SEM micrographs of the PET/PP (80/20) blends with and without the compatibilizers are presented in Figure 2. Addition of neat SEBS to the PET-rich blend did not reduce the average particle size of PP, but the adhesion between the

phases was slightly improved. Both functionalized SEBS grades, in turn, clearly reduced the average particle size and improved the interfacial adhesion between PP and the PET matrix. In the case of SEBS-*g*-GMA, the reduction in the particle size was even more pronounced, resulting in an average size of about 1–3  $\mu\text{m}$  for the blend exhibiting the highest impact strength (see Table I). As mentioned above, the noncompatibilized PP-rich blend exhibited PET domains of the order of 1–2  $\mu\text{m}$ , but showed poor impact strength. This shows that in addition to optimal particle size, good interfacial adhesion is needed to achieve toughening.

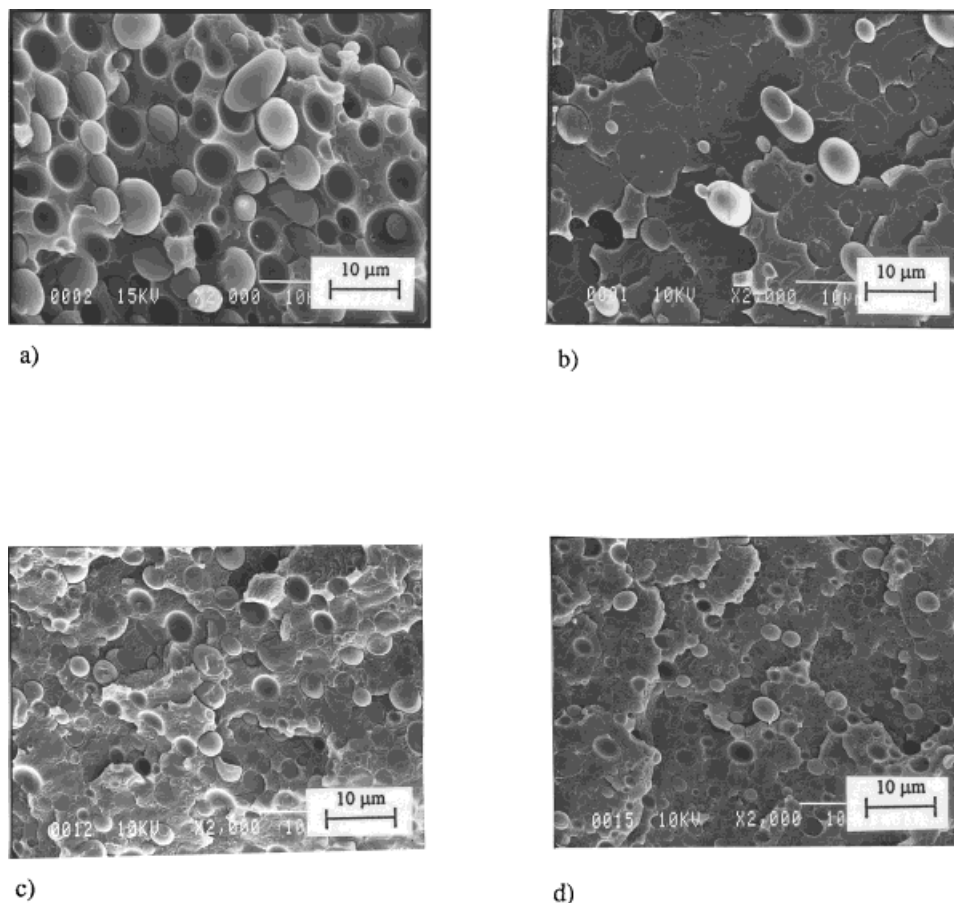
In blends where PP formed the matrix (see Fig. 3) addition of the unfunctionalized SEBS did not change the size of the PET particles (1–3  $\mu\text{m}$ ), which, however, seemed to be better attached to the PP matrix. It is thus possible that the unfunctionalized SEBS may locate at the interfaces and act as a compatibilizer by increasing physical interactions between the phases. Both functionalized SEBS grades instead reduced the average particle size significantly to a submicron level [note the different magnifications in Figs. 3(a) and 3(b) vs. 3(c) and 3(d)] and the dispersed PET droplets seemed to be well attached to the PP matrix. Such a small particle size combined with good interfacial adhesion led to high toughness as shown by earlier studies as well.<sup>5</sup>

### Thermal Properties

DMTA analysis was made to study the possible shifts in glass transition temperatures ( $T_g$ ) of the PET and PP phases. The  $T_g$  values of the PET phase in different blend compositions determined from the peaks of  $\tan \delta$  curves are shown in Figure 4. The PP phase is not discussed, because it showed only small peaks without any clear changes in their location.

In PET/PP (80/20) blend the  $\tan \delta$  peak of the PET phase was located at 78°C. The addition of SEBS or SEBS-*g*-MAH did not affect the  $T_g$  of PET, but SEBS-*g*-GMA shifted the peak four degrees towards that of neat PP (at 6°C). This is an indication of enhanced interactions between the PET and PP phases induced by SEBS-*g*-GMA. The result is in good agreement with the impact properties and morphology of the blends discussed above.

The noncompatibilized PP-rich blend and that containing neat SEBS exhibited almost similar values of  $T_g$  for the PET phase, 75 and 76°C, respectively. The blends compatibilized with SEBS-



**Figure 2** SEM micrographs of the noncompatibilized and compatibilized PET-rich blends. (a) PET/PP (80/20), (b) PET/PP/SEBS, (c) PET/PP/SEBS-*g*-MAH, and (d) PET/PP/SEBS-*g*-GMA (magnification  $\times 2000$ ).

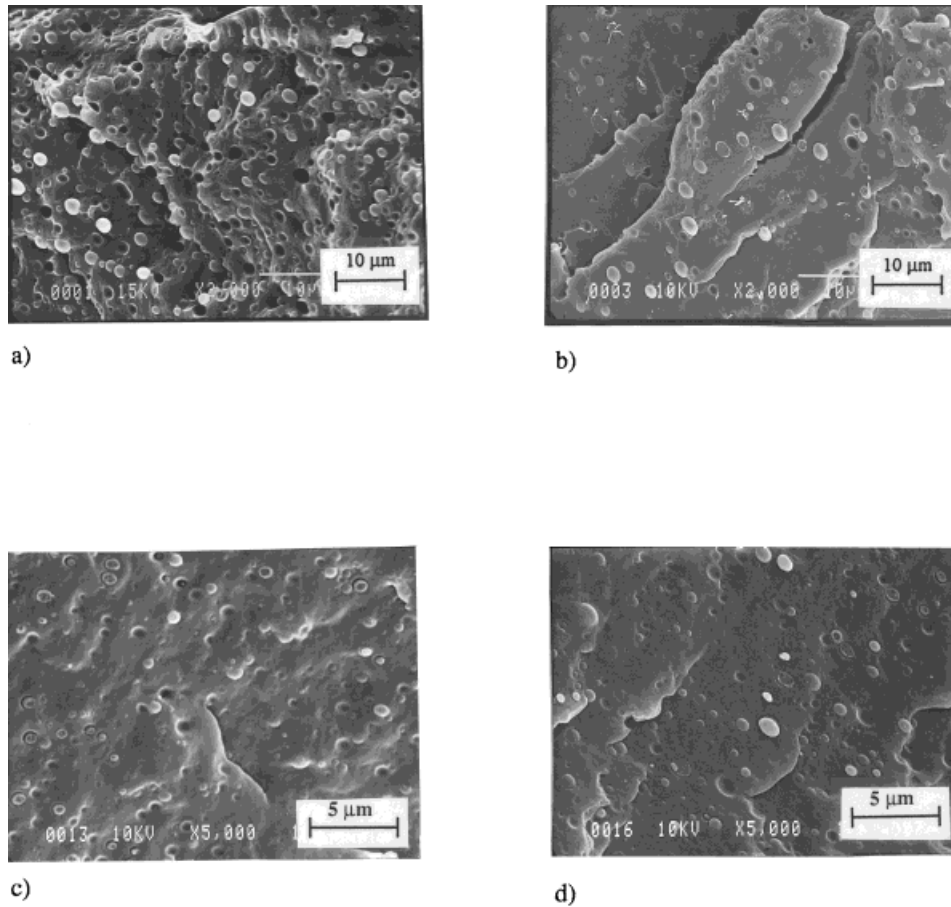
*g*-MAH (72°C) and SEBS-*g*-GMA (71°C), in turn, showed significant shifts in the  $\tan \delta$  peak of the PET phase towards that of PP. These interactions induced by the functionalized SEBS grades shown by DMTA analysis support the findings made in the impact tests and the morphology characterization.

### Rheological Properties

Melt viscosities of neat PET and PP were measured to evaluate the possible effects of the viscosity ratio on the blend morphology. According to our earlier studies,<sup>18,19</sup> these materials were chosen so that their viscosities were close to each other in the blending conditions. As mentioned above, PET exhibited, however, a slightly lower viscosity at low shear rates, which explained the smaller size of the dispersed PET phases in the noncompatibilized PP-rich blend.

Melt viscosities of all blends measured at the temperature of blending (280°C) are shown in Figure 5. Addition of 5 wt % of SEBS or SEBS-*g*-MAH lowered the viscosity of the PET/PP (80/20) blend significantly, which was expected due to the low melt viscosity of these polymers at the high temperature applied (280°C). The blend containing SEBS-*g*-GMA, in turn, exhibited a viscosity close to the level of the noncompatibilized blend, although SEBS-*g*-GMA itself has a low viscosity [Fig. 5(a)]. The high viscosity of this blend compared to the other ones, in combination with its fine morphology, is a further indication of strong interactions between the blend components most probably involving reactions between the end groups of PET and the epoxy functionalities in SEBS-*g*-GMA. Similar findings have been made earlier with other related blend systems.<sup>5,20</sup>

All blends where PP formed the matrix exhibited almost similar viscosities and more pro-



**Figure 3** SEM micrographs of the noncompatibilized and compatibilized PP-rich blends (note the different magnifications): (a) PET/PP (20/80) ( $\times 2000$ ), (b) PET/PP/SEBS ( $\times 2000$ ), (c) PET/PP/SEBS-*g*-MAH ( $\times 5000$ ), and (d) PET/PP/SEBS-*g*-GMA ( $\times 5000$ ).

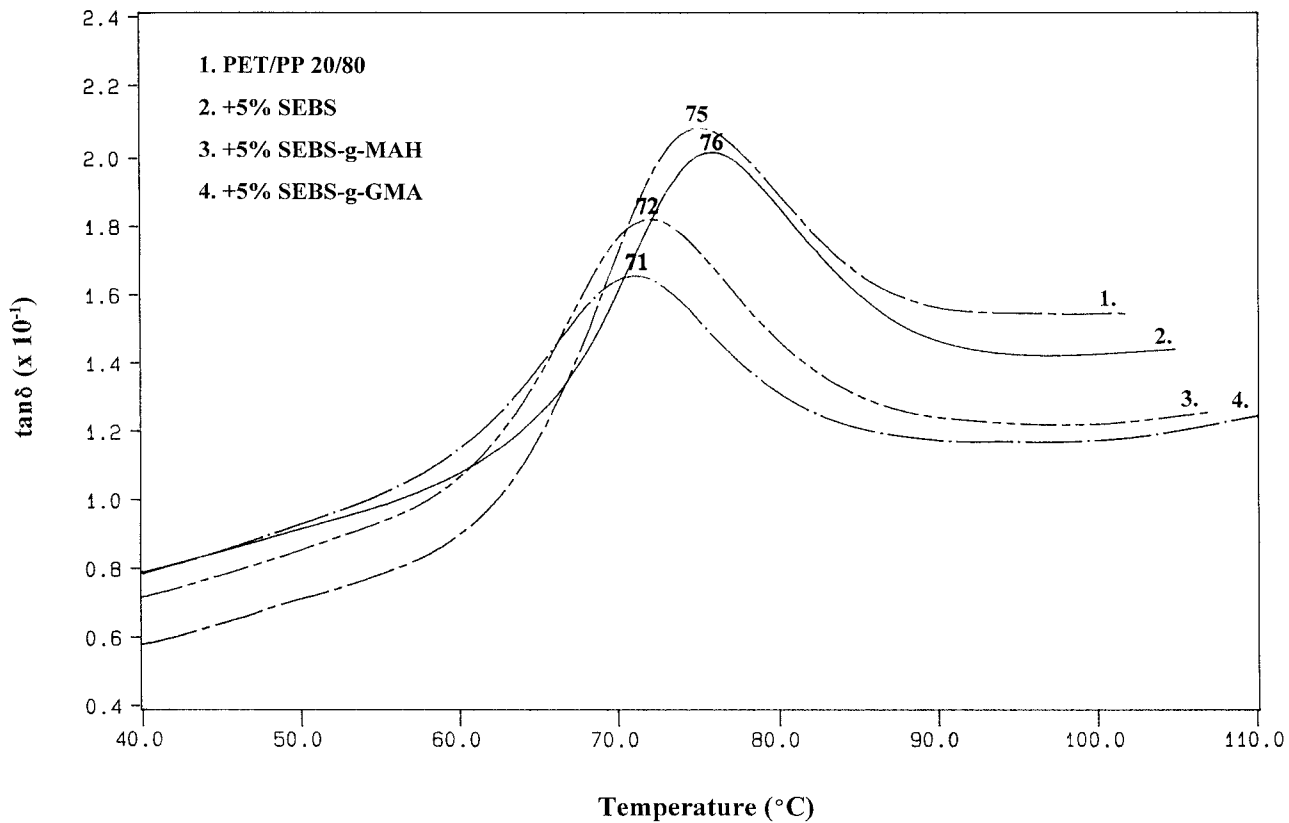
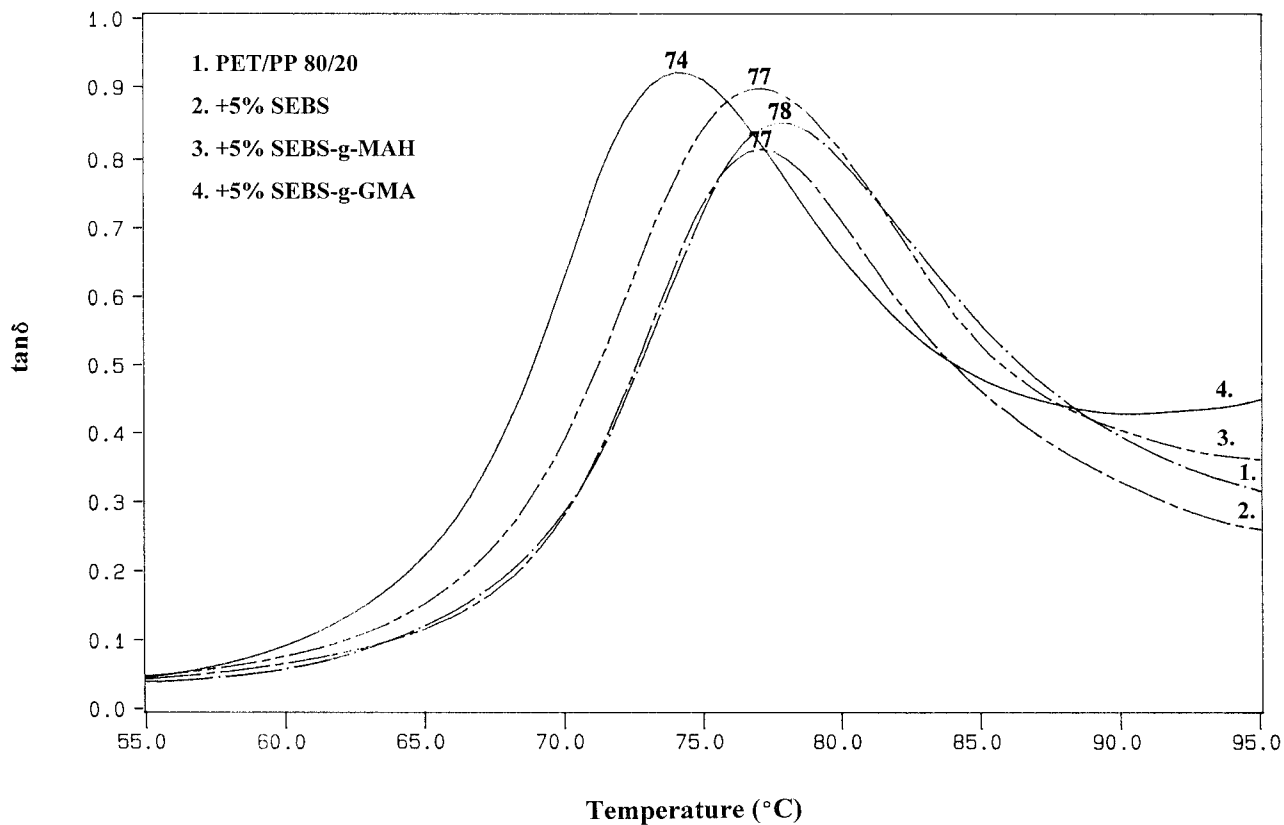
nounced shear thinning behavior, which is typical for PP [Fig. 5(b)]. Probably the small amount of PET in the blend could not provide sufficient

amount of reactions to affect the blend viscosity and thus the viscosities of the blends were controlled by the PP matrix.

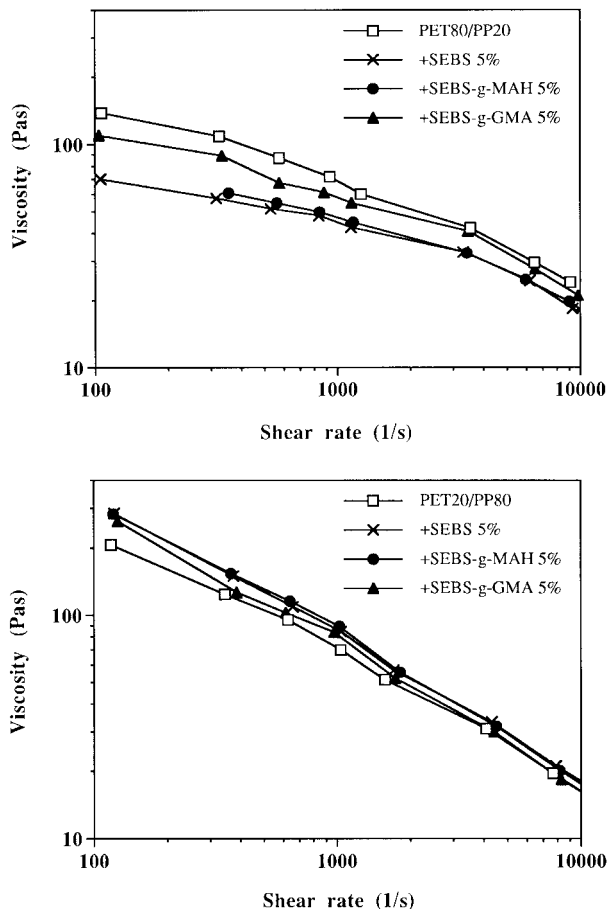
**Table I** Mechanical Properties of the PET/PP/Compatibilizer Blends

Blend	Flexural Modulus MPa	Flexural Strength MPa	Charpy Impact Strength (kJ/m <sup>2</sup> )	
			Unnotched	Notched
PP	1070 (10)	30 (1)	NB	4.1 (0.3)
PET/PP 20/80	1290 (30)	37 (1)	42 (6)	2.5 (0.3)
PET/PP/SEBS 17.5/77.5/5	1000 (20)	31 (1)	70 (8)	5.2 (0.3)
PET/PP/SEBS- <i>g</i> -MAH 17.5/77.5/5	920 (40)	28 (1)	NB	10.1 (1.0)
PET/PP/SEBS- <i>g</i> -GMA 17.5/77.5/5	880 (10)	26 (1)	NB	10.3 (1.0)
PET/PP 80/20	1980 (40)	59 (1)	45 (7)	2.5 (0.1)
PET/PP/SEBS 77.5/17.5/5	1720 (50)	56 (1)	NB	2.6 (0.1)
PET/PP/SEBS- <i>g</i> -MAH 77.5/17.5/5	1380 (50)	45 (1)	NB	8.4 (0.7)
PET/PP/SEBS- <i>g</i> -GMA 77.5/17.5/5	1430 (30)	46 (1)	NB	12.6 (2.8)
PET	2290 (60)	73 (1)	NB	3.1 (0.1)

NB = not broken.



**Figure 4** Tan  $\delta$  curves of PET/PP blends at (a) PET-rich and (b) PP-rich compositions.



**Figure 5** Melt viscosities at 280°C of the PET/PP/compatibilizer blends at: (a) PET-rich and (b) PP-rich compositions.

## CONCLUSIONS

Three SEBS block copolymers, an unfunctionalized (SEBS) and two functionalized grades (SEBS-*g*-MAH and SEBS-*g*-GMA), were evaluated as potential compatibilizers for PET/PP blends. Generally, the addition of 5 wt % of any of these copolymers was found to modify the morphology and to improve the impact strength of the blends. The compatibilizing effect was, however, far more pronounced with the functionalized copolymers, and glycidyl methacrylate (GMA) was found to be more effective functionality than maleic anhydride (MAH). This was observed in particular for the PET-rich blends, which showed significantly improved toughness combined with relatively high values of strength and modulus. Owing to the softness of the elastomeric compatibilizers the flexural strength and modulus of the blends were, however, slightly lowered. Further upgrading of the strength and stiffness of the

blends is possible, for example, through the addition of fillers or reinforcements such as talc or glass fibers.

The compatibilized blends containing either SEBS-*g*-GMA or SEBS-*g*-MAH showed synergistic behavior in impact strength measured for notched samples at compositions with PET/PP ratio of 20/80 and 80/20. The toughening was based on a stabilized morphology consisting of very fine dispersion of the minor phase with droplets well embedded in the matrix. Hence, not only the small particle size, but the improved adhesion between the PET and PP phases caused by the compatibilizers was of great importance in the toughening. The function of the functionalized copolymers was related to good mixing of their ethylene/butylene midblocks with the PP phase and strong interactions of the functional groups with the end groups of PET. The shifts in the glass transition temperature of the PET phase towards that of PP found by DMTA and the high melt viscosity of the compatibilized PET-rich blends are indications of such interactions. Most probably, the functional groups of the compatibilizer, in particular the epoxy groups in SEBS-*g*-GMA, reacted with the end groups of PET. The results thus indicate that the highly incompatible PET/PP blends can be effectively compatibilized with functionalized SEBS block copolymers, especially with the new SEBS-*g*-GMA.

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## NOMENCLATURE

DMTA	dynamic-mechanical thermal analysis
FTIR	Fourier transform infrared spectroscopy
L/d	length to diameter ratio
LCP	liquid crystalline polymer
$M_w$	weight average molecular weight
PC	polycarbonate
PET	polyethylene terephthalate
PP	polypropylene
PPE	polyphenylene ether
SEBS	styrene - ethylene/butylene - styrene triblock copolymer
SEBS- <i>g</i> -GMA	SEBS grafted with glycidyl methacrylate
SEBS- <i>g</i> -MAH	SEBS grafted with maleic anhydride
SEM	scanning electron microscopy
$\tan \delta$	loss modulus ( $E''$ )/storage modulus ( $E'$ )
$T_g$	glass transition temperature