

Reactive Mixing of PET and PET/PP Blends with Glycidyl Methacrylate-Modified Styrene-*b*-(Ethylene-*co*-Olefin) Block Copolymers

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ABSTRACT: Styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene (SEBS) and styrene-*b*-(ethylene-*co*-propylene) (SEP, SEPSEP) block copolymers with different styrene contents and different numbers of blocks in the copolymer chain were functionalized by melt radical grafting with glycidyl methacrylate (GMA) and employed as compatibilizers for PET-based blends. Binary blends of PET with both functionalized (SEBS-*g*-GMA, SEP-*g*-GMA, SEPSEP-*g*-GMA) and neat (SEBS, SEP, SEPSEP) copolymers (75 : 25 w/w) and ternary blends of PET and PP (75 : 25 w/w) with various amounts (2.5–10 phr) of both modified and unmodified copolymers were prepared in an internal mixer, and their properties were evaluated by SEM, DSC, melt viscosimetry, and tensile and impact tests. The roles of the chemical structure, grafting degree, and concentration of the various copolymers on blend compatibilization was investigated. The blends with the grafted copolymers showed a neat improvement of

phase dispersion and interfacial adhesion compared to the blends with nonfunctionalized copolymers. The addition of grafted copolymers resulted in a marked increase in melt viscosity, which was accounted for by the occurrence of chemical reactions between the epoxide groups of GMA and the carboxyl/hydroxyl end groups of PET during melt mixing. Blends with SEPSEP-*g*-GMA and SEBS-*g*-GMA, at concentrations of 5–10 phr, showed a higher compatibilizing effect with enhanced elongation at break and impact resistance. The effectiveness of GMA-functionalized SEBS was then compared to that of maleic anhydride-grafted SEBS. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2201–2211, 2005

Key words: block copolymers; compatibilization; functionalization of polymers; polyesters; poly(propylene) (PP)

INTRODUCTION

The blending of polyolefins and poly(ethylene terephthalate) (PET) offers some important advantages over its pure components in cost/performance for industrial applications (packaging, automotive, textiles, etc.) as well as for recycling technology. However, because of the different chemical nature of these polymers, appropriate compatibilization is needed to improve the phase interactions and thus the physical/mechanical properties of the blends.¹

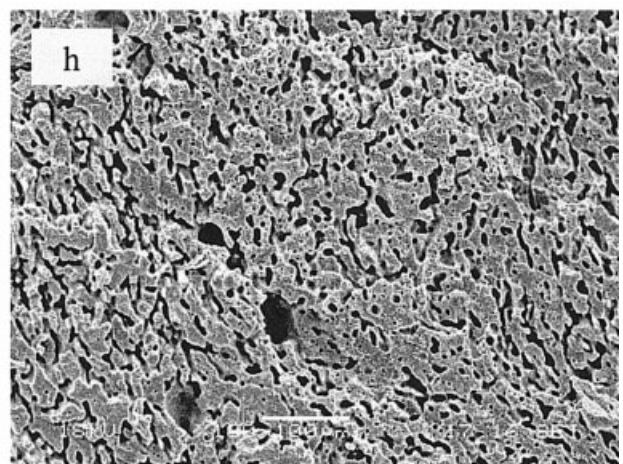
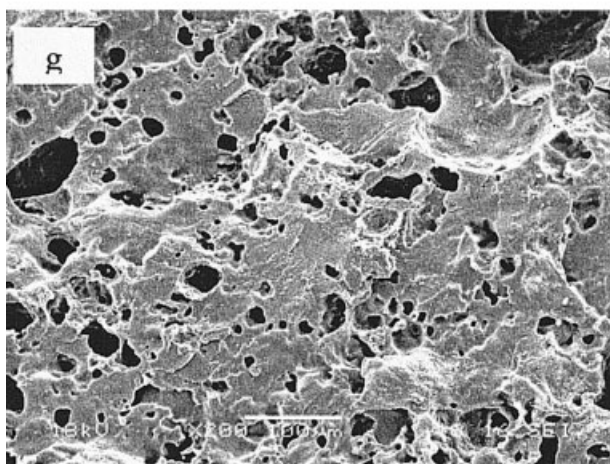
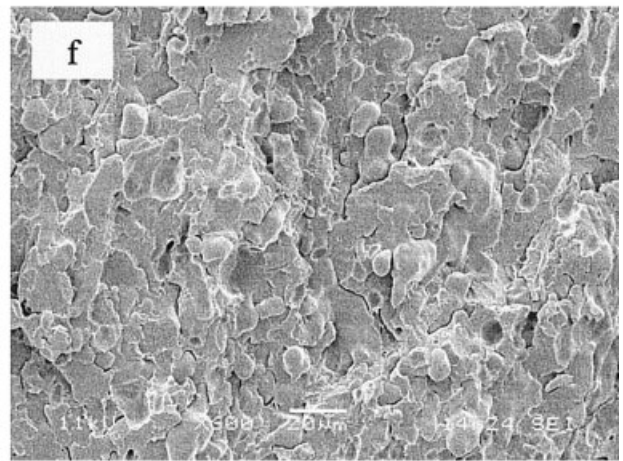
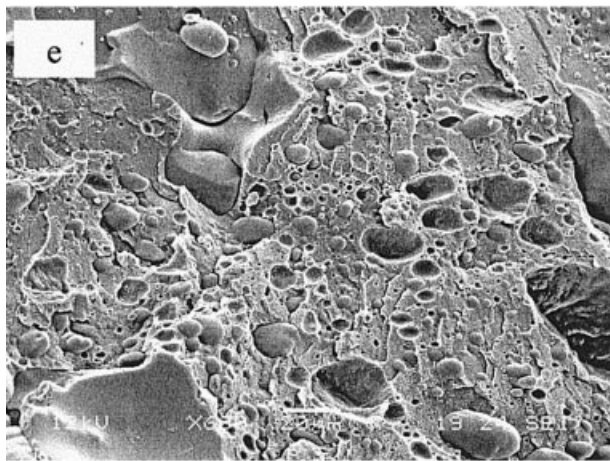
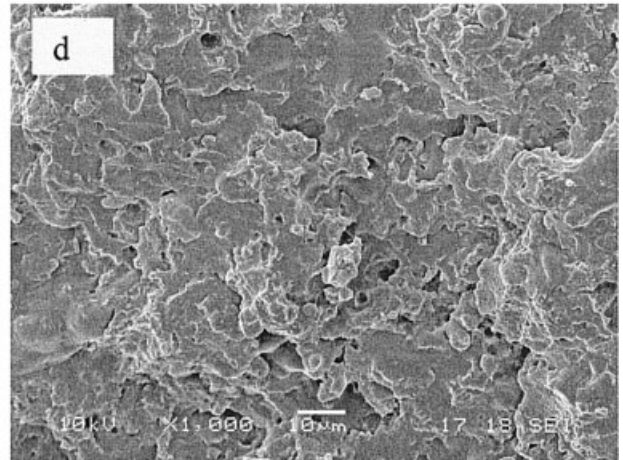
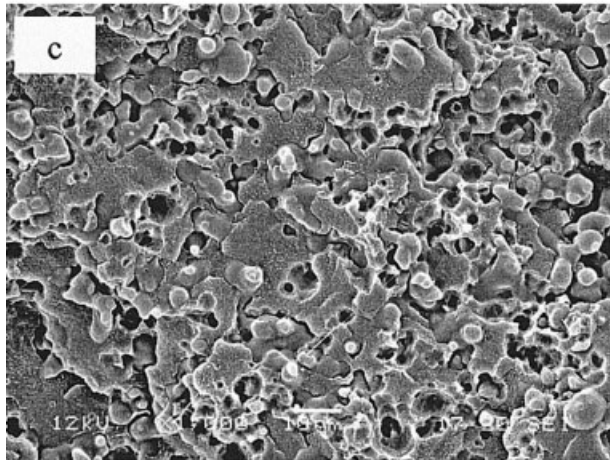
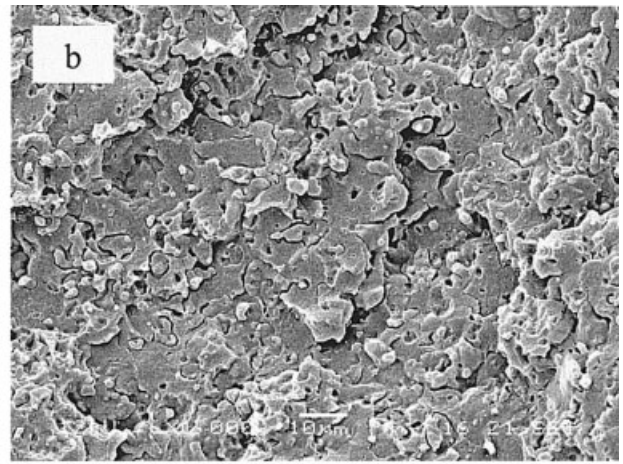
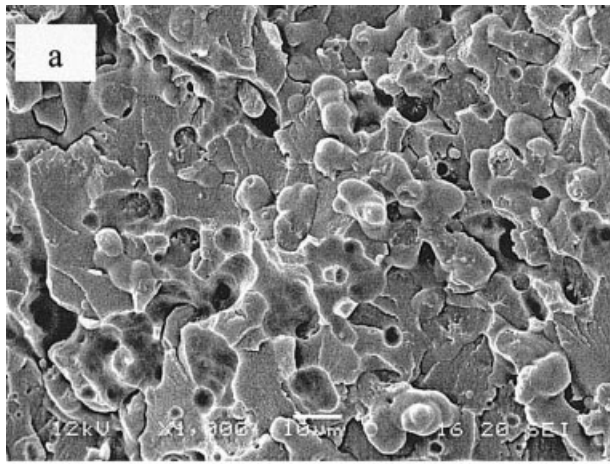
In situ compatibilization of blends of polyolefins and polyesters can be efficiently achieved by suitable modification of polyolefin chains with reactive groups (i.e., carboxyl, anhydrides, epoxides, etc.) able to give rise during melt blending to chemical reactions with the functional groups of the polar component.^{1–3} Improvement of phase dispersion and adhesion at the interface has been reported for such systems and attributed to chemical/physical interactions between

the grafted functional groups and the polyester end groups.^{4–6} Thermoplastic elastomers with different types and numbers of rubber blocks in the chain also have been used as compatibilizers for various polymer blends,^{7–10} and it has been shown that the morphology and properties of these blends can be markedly enhanced through the chemical modification of the block copolymers with functional groups like maleic anhydride (MAH) or glycidyl methacrylate (GMA).^{11–13}

GMA is a suitable functional unsaturated monomer that can be easily grafted onto polyolefins and advantageously exploited for the compatibilization of blends with polyamides or polyesters, as the epoxide group of GMA can react with amino, carboxyl, and hydroxyl end groups. In some cases, the reactivity of GMA-functionalized polyolefins has been reported to be higher than that found for MAH- and AA-grafted polyolefins.^{4,6}

In a previous article¹⁴ we described the GMA radical grafting reactions of styrene-*b*-(ethylene-*co*-butylene) (SEBS) and styrene-*b*-(ethylene-*co*-propylene) (SEP, SEPSEP) copolymers with different numbers of blocks and styrene content. The effect of monomer

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concentration, radical initiator, and reaction procedures on the grafting yield was investigated, and the properties of grafted copolymers were then compared with those of neat copolymers. It was found that the grafting degree (3–6 wt % GMA) was influenced by the styrene content and by the structure of the elastomer block in the copolymers. In the present work, SEBS, SEP, and SEPSEP block copolymers functionalized with GMA were employed for reactive blending with PET and PET/PP blends. The study was aimed at examining the role of the chemical structure of the copolymers and of GMA functional groups in the compatibilization of the blends. For this purpose the morphological, thermal, rheological, and mechanical properties of compatibilized blends were examined and compared with those of blends containing non-functionalized copolymers. PET/PP blends mixed with a commercial SEBS-g-MAH sample also were analyzed in order to compare the compatibilizing effectiveness of the two different functional groups.

EXPERIMENTAL

Materials

Isotactic PP (Novolen 1100 N, Targor, GmbH, Germany) with a melt flow rate (MFR) of 12 g/10 min (230°C, 2.16 kg) and PET (SINCO Engineering) with an intrinsic viscosity of 0.74 dL/g were used throughout. Before use, the materials were carefully dried under vacuum in order to reduce the moisture content: PET samples were heated to 170°C for 4 h, and PP was dried at 80°C.

Commercial samples of styrene-olefin block copolymers, kindly supplied by Shell Italia (Milan, Italy)—SEBS (Kraton G1652), SEP01 (Kraton G1701X), SEP02 (Kraton G1702 X), and SEPSEP (Kraton G1730 M)—were employed as compatibilizers. SEBS (30 wt % PS, viscosity = 1.4 Pa s, MFR = 10 g/10 min) is a linear triblock copolymer with two polystyrene (PS) end blocks; SEP01 (37 wt % PS, viscosity > 50 Pa s, MFR = 0.6 g/10 min) and SEP02 (28 wt % PS, viscosity > 50 Pa s) are linear diblock copolymers; and SEPSEP (21 wt % PS, viscosity = 0.62 Pa s, MFR = 11 g/10min) is a linear tetrablock copolymer. Polymer viscosities were measured in 20% toluene solution at 25°C; melt flow rates were recorded at 230°C/5 kg. For SEBS and SEP01 copolymers number-average molecular weights of about $6.6 \cdot 10^4$ and $9.0 \cdot 10^4$, respectively, have been reported.

The GMA-grafted copolymers (SEBS-g-GMA, SEP01-g-GMA, SEP02-g-GMA, SEPSEP-g-GMA) were

obtained by melt radical grafting of the copolymers with GMA monomer (Aldrich, 97% purity) and, as radical initiator, bis-[1-(tert-butylperoxy)-1-methylethyl]benzene (Aldrich, Milan, Italy) in a Brabender internal mixer at 200°C according to the procedure described by Pracella and Chionna.¹⁴ The grafting products were purified by dissolution in boiling xylene and precipitated with ethanol to remove the unreacted monomer and homo-polymerized GMA. The amount of grafted GMA was then determined by titration and FTIR spectroscopy. The grafting degree (wt GMA per 100 g polymer) was 3.3 for SEP01-g-GMA, 4.4 for SEBS-g-GMA, 5.2 for SEP02-g-GMA, and 5.8 for SEPSEP-g-GMA. A commercial sample of SEBS grafted with 1.7 wt % maleic anhydride (SEBS-g-MAH), purchased by Shell (Kraton FG 1901 X, MFR = 20–25 g/10 min), also was used as compatibilizer for the PET/PP blends.

Blending

Binary blends of PET with functionalized and non-functionalized block copolymers (75 : 25 w/w), as well as ternary blends of PET and PP (75 : 25 w/w) with various amounts (2.5–10 phr) of both unmodified and modified copolymers, were prepared by melt blending in a Brabender Plasticorder internal mixer (Duisburg, Germany) at 260°C with a roller speed of 50 rpm under a nitrogen stream by using a two-step mixing procedure. PET was first melted in the mixer for 2 min, then PP and the compatibilizers were added with continuous mixing for an additional 5 min. Ternary blends containing SEBS-g-MAH were obtained using the same mixing procedure. Furthermore, binary blends of PP with neat block copolymers (SEP, SEPSEP, SEBS) with a composition of 75 : 25 (w/w) were prepared in the internal mixer at 180°C. The chosen composition matched the highest ratio between PP and the copolymers in the ternary blends.

PET/PP blends containing 5 and 10 phr of functionalized copolymers also were prepared in a laboratory corotating twin-screw extruder (D = 25 mm, L/D = 33, two-venting zone), assembled by the CBiMM-PAN research group (Lodz, Poland). The extrusion was carried out at a rotation speed of 50–60 rpm using a temperature profile of 250°C, 260°C, 270°C, 270°C, and 265°C, with a residence time of about 7 min and a yield of 1 kg/h. The blends, extruded in a cool air flow, were pelletized and saved in plastic bags in a dry place.

Figure 1 SEM micrographs of binary blends (75 : 25): (a) PET/SEP01, (b) PET/SEP01-g-GMA, (c) PET/SEP02, (d) PET/SEP02-g-GMA, (e) PET/SEPSEP, (f) PET/SEPSEP-g-GMA, (g) PET/SEBS (etched surface), (h) PET/SEBS-g-GMA (etched surface).

Microscopy

Blend samples were fractured at the temperature of liquid nitrogen, sputter-coated with gold, and examined by scanning electron microscopy (SEM) using a Jeol 5600 LV microscope (Tokyo, Japan). The average size of the dispersed phase in the blends was determined by measuring a consistent number of particles (200–400) from each sample using the semiautomatic Scion Image analysis program. Selective extraction of the elastomer components also was carried out on binary and ternary blends. The freeze-fractured samples were soaked in acetone and/or xylene at room temperature for 12 h; after drying in vacuum, the etched samples were coated with gold and the surface analyzed by SEM. The morphology at the phase boundary of the compatibilized samples also was investigated by atomic force microscopy (AFM) in tapping mode with a Nanoscope III microscope (Santa Barbara, CA).

Calorimetry

The thermal behavior of the blends was examined with a Perkin–Elmer DSC-2 differential scanning calorimeter equipped with data station 3700 and with a Perkin–Elmer Pyris Diamond StepScan instrument (Shelton, CT). Heating and cooling scans were carried out on 5–10 mg of material under a nitrogen flow in a temperature range of 30°C–290°C at a standard rate of 10°C/min. The samples were first melted to 290°C (first run) to erase the previous thermal history, then cooled to 30 °C and reheated to 290°C (second run). The phase-transition temperatures were determined at the maximum of the melting peak (T_m) or at the minimum of the crystallization peak (T_c). The values of the enthalpies of melting (ΔH_m) and crystallization (ΔH_c) were calculated from the areas of the respective peaks. Indium was employed as a standard for temperature and enthalpy calibration. The degree of crystallinity of the polymer components in the blends was calculated from the ratio of the observed ΔH_m on the second heating run and the melting enthalpy of 100% crystalline polymers (136 J/g for PET and 189 J/g for PP).¹⁵

Rheology

The melt viscosities of the grafted copolymers and blends were measured by a CEAST capillary viscometer (Torino, Italy) over a shear rate in the range of 10¹–10³/s. A measuring temperature of 260 °C and a die length-to-diameter ratio (L/d) of 40 : 1 was used. All measurements included the Rabinowitsch correction.

Mechanical testing

Measurement of elastic modulus and tensile strength was performed at room temperature by an Instron

tensile machine (model 4302, Lancombe, England) according to standard conditions using a speed of 5%/min. Samples of extruded ternary blends were prepared by injection molding in a Battenfeld 30-g injection machine (Germany) and by compression molding according to standards (ASTM D638). At least five specimens of each blend were tested. Impact strength was determined on an injection-molded impact bar in the Izod test with a Resil 5.5 instrumented impact hammer (Ceast, Torino, Italy). Notched type A samples were used.

RESULTS AND DISCUSSION

Binary blends of pet with block copolymers

Morphology

SEM micrographs of binary blends PET/SEP, PET/SEPSEP, and PET/SEBS (75 : 25 w/w) and of blends PET/SEP-g-GMA, PET/SEPSEP-g-GMA, and PET/SEBS-g-GMA (75 : 25 w/w) are shown in Figure 1. In the blends with nonfunctionalized copolymers [Fig. 1(a,c,e,g)], the elastomer phase is poorly dispersed, with the appearance of irregular and interconnected domains. The coarse morphology is mainly a result of the difference in the nature of PET (polar) and elastomers (apolar) and, furthermore, is very unstable to coalescence. The higher interfacial tension in the nonreactive blends and the high melt viscosity of the copolymer component favored coalescence into large particles. For all blends with grafted copolymers [Fig. 1(b,d,f,h)], clear improvement in dispersion and adhesion between the phases was observed. The decrease in domain size may be attributed to a decrease in the interfacial tension because of chemical interactions between the epoxy groups and the chain ends of PET, reducing the tendency toward coalescence.^{16–17} To provide better evidence of the dispersion and morphology of the polymer phases, the surfaces of fractured samples were etched with a selective solvent for the copolymers. SEM micrographs of the PET/SEBS and PET/SEBS-g-GMA binary blends after etching with acetone are shown in Figure 1(g,h), respectively. The etched samples revealed a marked change in the size and morphology of the dispersed phase when the grafted copolymer was employed. The observed nonspherical morphology could originate from crosslinking reactions, which can take place during the compatibilization process.¹⁸ Loyens and Groeninckx¹⁷ proposed a scheme of possible crosslinking reactions occurring in blends of PET with ethylene–GMA copolymers (PET/EPR/E-GMA) and discussed the mechanisms of phase morphology development. The crosslinking reactions may involve the secondary hydroxyl groups on the graft interchain copolymer formed at the interface, as well as both functional (carboxyl and hydroxyl) end groups of PET capable of

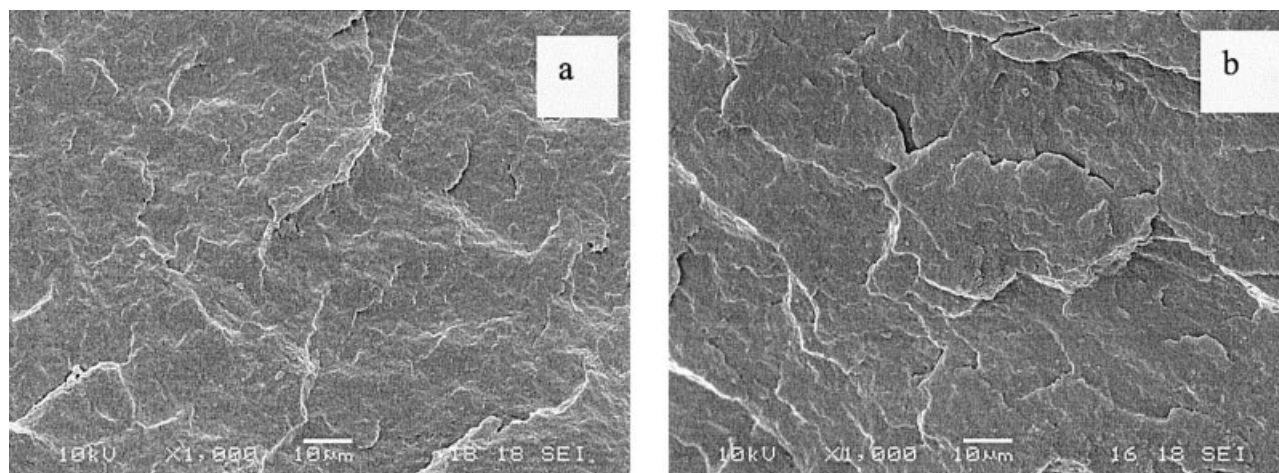


Figure 2 SEM micrographs of binary blends (75 : 25): (a) PP/SEBS, (b) PP/SEPSEP.

reacting with the epoxide of GMA. Because of these additional reactions, melt viscosity increased and the particles became less deformable, giving rise to coarse morphologies.

Binary blends of PP with block copolymers were also examined by SEM in order to assess the compatibility of the two polyolefin components. Because of the chemical structure of the elastomer block, the copolymers were expected to have a good affinity with PP. Exemplary SEM micrographs of the PP/SEP (75 : 25) and PP/SEBS (75 : 25) binary blends are shown in Figure 2. Other than that found for the blends with PET, the blends with polyolefin matrix showed a finely dispersed copolymer phase with nearly homogeneous morphology, in agreement with that reported by Bassani et al.¹⁹ for similar systems.

Rheological behavior

Torque measurement was carried out to monitor the viscosity changes of the blends during the mixing process and to support the compatibilization reactions. Chemical reactions occurring in reactive blending generally result in increased blend viscosity when compared to that of the nonreactive system. The torque values, recorded at the end of the mixing process in the Brabender mixer, are shown in Figure 3 for blends of PET with nonfunctionalized and functionalized copolymers. All blends with grafted copolymers showed a marked increase in torque relative to those with unmodified copolymers and to plain PET (about 2.7 Nm). The torque ratios of grafted to pure copolymer blends were 3.1 for SEPSEP-*g*-GMA, 2.5 for SEBS-*g*-GMA and SEP01-*g*-GMA, and 1.9 for SEP02-*g*-GMA. The higher torque values that were observed for the blends with SEP copolymers (4.4–4.8 Nm) likely can be ascribed to the higher melt viscosity of these copolymers as compared to that of SEBS and SEPSEP.

The rheological behavior of the binary blends and pure PET was examined with capillary rheometry at 260°C, and the viscosity values are plotted in Figure 4 as a function of the shear rate. The melt viscosity of PET was lower than that of the neat block copolymers in the whole examined range. Blends with grafted copolymers always displayed higher viscosity than those with unmodified ones, with the largest variation recorded for the blend with SEPSEP-*g*-GMA, which displayed the highest degree of grafting. Such an increase of viscosity mainly can be accounted for by the chemical interactions between PET end groups and the functional groups of the compatibilizer, likely leading to the formation of a graft copolymer at the interface.¹⁷ According to Han and Chuang,²⁰ when the discrete phase is anchored onto the continuous phase, it would be expected that the deformation of such particles would require much greater forces than those that are freely suspended. It would also be expected that the greater the chemical reaction between the discrete and the continuous phase, the less likely it would be for the discrete phase to deform because of stronger interfacial adhesion.

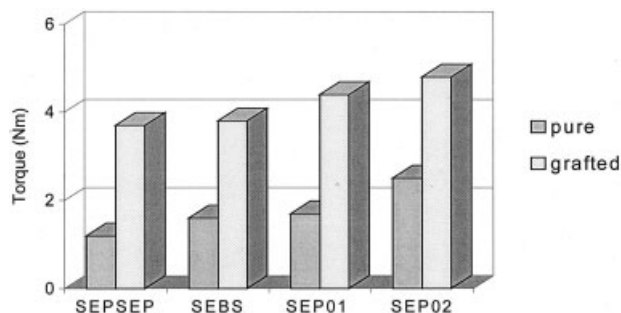


Figure 3 Torque values of binary blends of PET with neat and grafted copolymers.

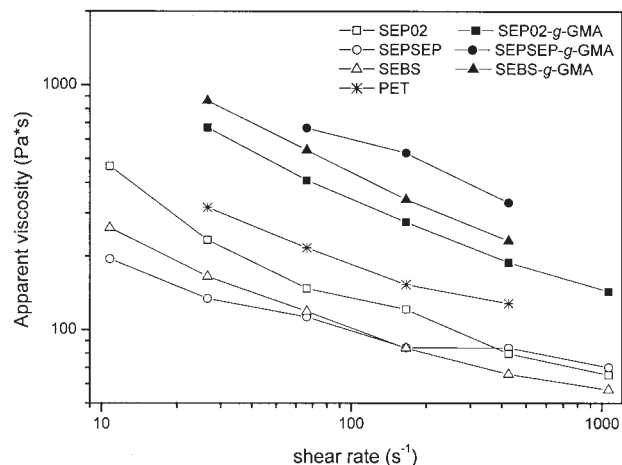


Figure 4 Apparent melt viscosity of binary blends of PET with neat and grafted copolymers as a function of shear rate.

Thermal behavior

The phase-transition parameters of binary blends of PET with the various copolymers recorded on the cooling and second heating runs in DSC are listed in Table I. The thermograms of the samples in all cases displayed single crystallization and melting peaks of the PET phase. A shift of the crystallization (T_c) and melting (T_m) temperatures toward lower values, relative to the pure PET, was observed in all blends. The effect was more pronounced for the blends with functionalized copolymers. The T_c of PET decreased from 183°C to about 177°C in the blends with SEBS-g-GMA, SEPSEP-g-GMA, and SEP01-g-GMA and to 174.7°C in the blend with SEP02-g-GMA. In parallel, the melting enthalpy (ΔH_m) and the crystallinity degree (X_c) of the blends were found to be lower than those of pure PET.²¹

As shown in Figure 5, the second heating–melting curves of the binary blends with neat copolymers displayed the multiple melting behavior of the PET

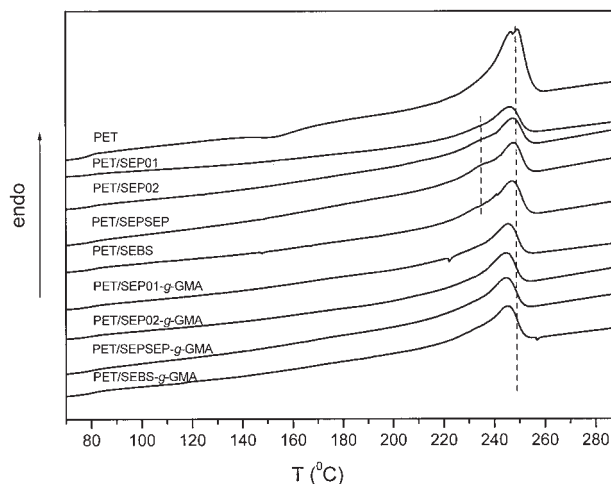


Figure 5 DSC melting thermograms (second heating: 10°C/min) of PET and its blends with neat and functionalized copolymers.

matrix, which can be ascribed to recrystallization phenomena of less perfect and stable crystals during the heating run.¹⁵ The broad shoulder at a lower T_m (about 235°C), which is related to the melting of crystals formed on cooling from the melt, almost disappeared in the blends with functionalized copolymers. The peak at higher T_m , a result of the melting of reorganized crystals, occurred in the functionalized systems at temperatures ($\sim 245^\circ\text{C}$) below those of non-functionalized ones. These effects, and the changes of thermodynamic parameters, indicate that the crystallization process of the polyester matrix from the melt was influenced by the interfacial interactions with the functional groups of the copolymers, which likely hindered the growth and reorganization of the crystals. Similar results have been reported for PA6/SEBS-g-MAH blends²² and for PET/PP blends compatibilized with SEBS-g-MAH.¹¹

TABLE I
DSC Transition Temperature (T_c , T_m), Enthalpy (ΔH_c , ΔH_m), and Crystallinity Degree (X_c) of PET in Binary Blends with Neat and Functionalized Block Copolymers

Blend	Cooling ^a		Second heating ^a		
	T_c (°C)	ΔH_c (J/g PET)	T_m (°C)	ΔH_m (J/g PET)	X_c (%)
PET	183.2	33.7	249.5	38.0	21.4
PET/SEP01	178.2	31.3	246.9	32.0	18.0
PET/SEP01-g-GMA	177.0	32.6	244.7	32.5	18.3
PET/SEP02	178.1	33.1	247.3	32.9	18.5
PET/SEP02-g-GMA	174.7	33.6	244.6	31.9	17.9
PET/SEPSEP	182.2	32.4	247.5	34.1	19.1
PET/SEPSEP-g-GMA	177.0	33.1	245.4	34.0	19.1
PET/SEBS	181.9	29.1	247.3	29.5	16.6
PET/SEBS-g-GMA	176.7	32.3	245.3	31.2	17.5

^a Cooling and heating rate: 10°C/min.

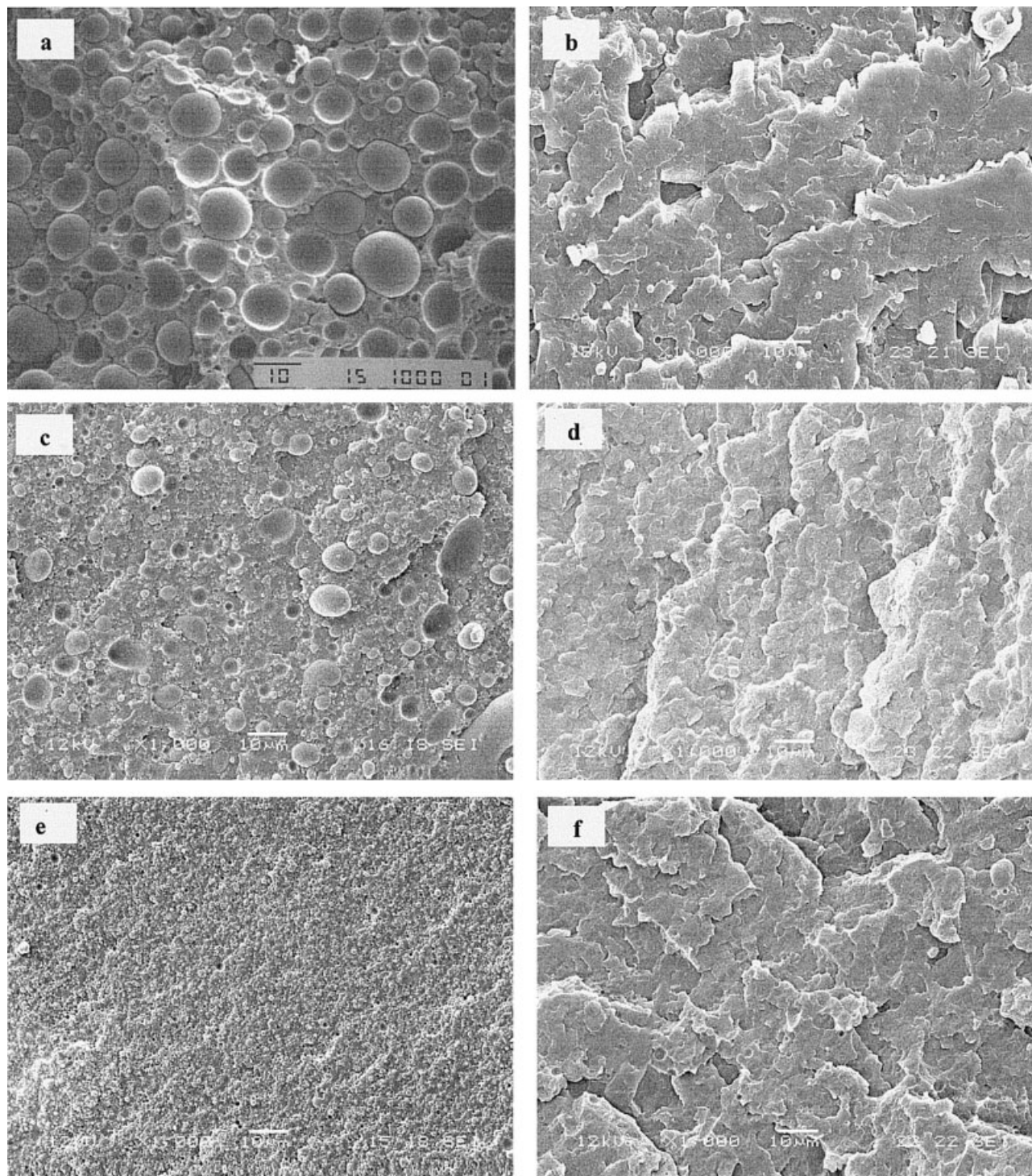


Figure 6 SEM micrographs (block copolymer content expressed in phr) of: (a) PET/PP (75:25), (b) PET/PP/SEP01-g-GMA (75 : 25 : 10), (c) PET/PP/SEBS (75 : 25 : 10), (d) PET/PP/SEBS-g-GMA (75 : 25 : 10), (e) PET/PP/SEPSEP (75 : 25 : 10), and (f) PET/PP/SEPSEP-g-GMA (75 : 25 : 10).

PET/PP blends compatibilized with block copolymers

Morphology

PET/PP blends with a composition ratio of 75 : 25 (w/w) were compatibilized by the addition of non-

modified and GMA-modified elastomers at concentrations of 2.5–10 phr. The effect of the type of compatibilizer on the phase morphology of the blends is shown in the SEM micrographs of Figure 6. The non-compatibilized 75 : 25 PET/PP blend [Fig. 6(a)] shows a neat phase separation of the components with PP

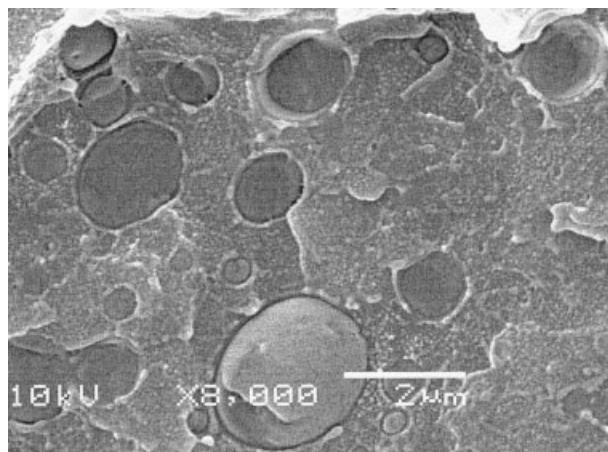


Figure 7 SEM micrograph of fracture surface of PET/PP (75 : 25) blend compatibilized with 10 phr of SEPSEP-g-GMA.

particles of an average size of about 6 μm . In ternary blends, the morphology and degree of dispersion of the PP phase are significantly affected by the structure and concentration of the copolymer. For blends with nonfunctionalized copolymers [Fig. 6(c–e)], the average size of the minor phase decreased to about 2 μm with the addition of 10 phr of SEBS and to about 1 μm with 10 phr of SEPSEP. Blends with SEP01 showed a cocontinuous morphology at a copolymer content of 10 phr, whereas blends with SEP02 displayed large coalescence phenomena.

All functionalized elastomers improved the phase dispersion and the interfacial adhesion between the PP and PET matrix [Fig. 6(b,d,f)]. For blends with 10 phr of SEBS-g-GMA and SEPSEP-g-GMA, a more homogeneous morphology and a marked reduction in particle size were found with particle diameters of less than 1 μm . An exemplary SEM micrograph is shown in Figure 7 for a PET/PP blend compatibilized with 10 phr of SEPSEP-g-GMA. It appears that the most dispersed particles were surrounded by a polymer layer (deformed by the fracture) that showed thin fibrils connecting the particle to the matrix. Thus, grafted GMA on the elastomer blocks contributed to an effective coupling between PP and PET despite the reaction with the carboxyl groups of PET.

AFM images (tapping mode) for a 75 : 25 : 5 PET/PP/SEBS-g-GMA blend are shown in Figure 8, which provides evidence of the different topologies of the PET and PP phases and the presence of a boundary layer between the matrix and the dispersed particles, supporting the compatibilizing effect of the copolymer in the interfacial region.²³

SEM analysis of 75 : 25 PET/PP blends compatibilized with SEBS-g-GMA, SEPSEP-g-GMA, and SEP01-g-GMA, obtained with a twin-screw extruder, showed that the morphology of these samples was similar to that observed for the same blends prepared in the

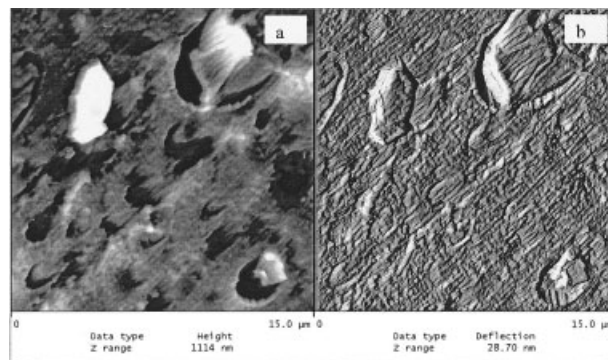


Figure 8 AFM images of PET/PP (75 : 25) blend compatibilized with 5 phr of SEBS-g-GMA: (a) height, (b) deflection.

Brabender mixer. Accordingly, in the blends with SEBS-g-GMA and SEPSEP-g-GMA the size of the dispersed particles showed a greater decrease.

Rheological behavior

The melt viscosities of PET/PP blends with 10 phr of neat and functionalized copolymers, measured at the blending temperature (260°C), are shown in Figure 9. The melt viscosity of the noncompatibilized blend (PET/PP 75 : 25) is reported for comparison; this blend had a lower viscosity than did pure PP and PET in the same shear range. The addition of the nonfunctionalized copolymers did not significantly change the viscosity behavior of the blends. In contrast, the blends with functionalized copolymers showed a large variation in viscosity with shear rate. The addition of 10 phr of SEPSEP-g-GMA, SEP01-g-GMA, and SEBS-g-GMA caused a marked increase in melt viscosity in the low shear range. Moreover, the melt viscosity of these blends decreased more rapidly with the shear

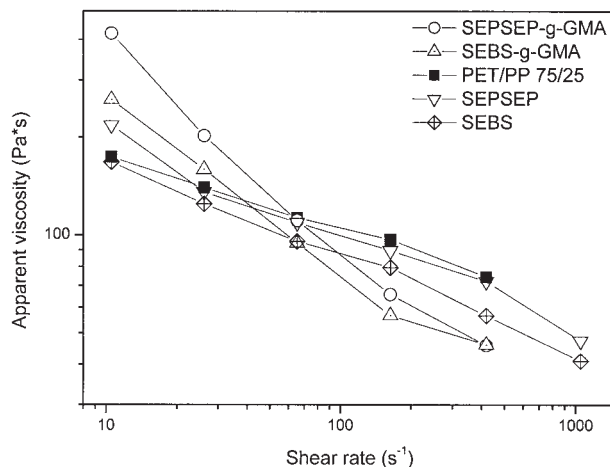


Figure 9 Apparent melt viscosity versus shear rate of PET/PP blends compatibilized with 10 phr of neat and GMA-grafted block copolymers.

TABLE II
DSC Parameters of Noncompatibilized and Compatibilized PET/PP Blends

Blend composition	Compatib. content (phr)	PP					PET				
		T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PET/PP 75/25	—	113.8	99.9	163.8	86.5	45.8	181.9	36.4	249.2	30.1	22.1
+ SEP01-g-GMA	2.5	116.8	97.0	160.1	65.8	34.8	182.5	42.6	247.1	29.7	21.8
	5	113.8	93.6	161.1	78.6	41.6	182.8	37.6	243.5	25.9	19.0
+ SEP02-g-GMA	2.5	114.1	101.6	166.0	78.2	41.4	188.4	39.3	246.1	30.9	22.7
	5	112.6	99.9	163.6	82.3	43.5	188.8	40.5	247.1	32.2	23.7
+ SEPSEP-g-GMA	2.5	113.5	105.3	165.2	81.9	43.3	186.6	40.1	246.4	25.5	18.7
	5	110.8	81.9	162.8	68.9	36.5	183.4	42.2	245.5	28.8	21.2
+ SEBS-g-GMA	2.5	111.4	98.6	165.5	78.6	41.6	187.3	37.6	245.9	28.4	20.9
	5	110.6	110.7	165.5	83.6	44.2	185.2	41.8	247.1	30.1	22.1

rate, indicating trend of the pseudo-plastic type, which was reflected by lower values of the power law index. The increased viscosity of these blends could be related to the effect of intermolecular interactions at the interface between the end groups of PET and the epoxide functionalities. A similar increase in melt viscosity at low shear rate has been reported for various systems with reactive compatibilizers.^{17,24,25}

The torque values, measured at the end of the blending process, also were affected by the copolymer concentration and functionalization. The addition of neat copolymers to PET/PP blends did not affect the torque in a visible way: the values recorded for blends with SEBS, SEPSEP, and SEPs were in the range of 8–10 Nm and were similar that of the noncompatibilized blend (10.2 Nm). In contrast, a significant increase in torque was found for blends compatibilized with SEBS-g-GMA, SEP-g-GMA, and SEPSEP-g-GMA, with values in the range of 15–18 Nm.

Thermal properties

The thermal properties of blends with functionalized copolymers are summarized in Table II. In all cases the cooling and heating thermograms displayed separate crystallization and melting peaks of the two polymer components. A comparison of the crystallization behavior of the compatibilized blends with that of the noncompatibilized blend showed that the T_c of the PP phase generally decreased with increasing compatibilizer content, whereas the T_c of the PET phase shifted to higher values. The melting behavior of the compatibilized blends was not significantly affected by the amount of compatibilizer. The melting endotherm of PET showed a main peak near 247°C and a shoulder at lower temperatures (235°C–238°C). The melting enthalpies and degree of crystallinity of the PP and PET phases in the compatibilized blends generally were lower than those of the uncompatibilized blend, with the largest effect observed for the dispersed PP phase.

Mechanical properties

The compatibilizing efficiency of the functionalized block copolymers was tested by analyzing the tensile and impact behavior of blends of various compositions. Specimens for the tensile tests were obtained from the extruded blends both by injection and compression molding.

Exemplary stress–strain plots of PET/PP blends compatibilized with 10 phr of grafted copolymers are shown in Figure 10. Mean values of the tensile and impact properties of the examined blends are summarized in Table III. The E-modulus of all blends, obtained by both procedures, was found to decrease with an increasing amount of compatibilizer, which was expected because of the elastomeric character of the compatibilizer. Moreover, an increase in elongation at break was observed in the compatibilized blends. The highest elongation at break (about 6%) was found in the blend with 10 phr of SEBS-g-GMA.

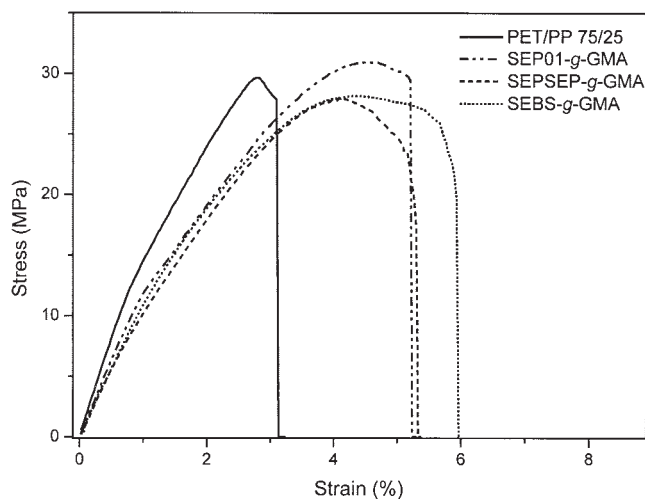


Figure 10 Exemplary stress–strain plots for PET/PP (75 : 25) blends compatibilized with 10 phr of grafted copolymers (samples prepared by injection molding).

TABLE III
Young Modulus (E), Stress (σ_y), and Strain (ϵ_y) at Yield, Stress (σ_b), and Strain (ϵ_b) at Break and Impact Energy (R) Measured for PET/PP Blends Compatibilized with Functionalized Copolymers

Blend composition	Compatib. content (phr)	E (GPa)		σ_y (MPa)		ϵ_y (%)		σ_b (MPa)		ϵ_b (%)		R (kJ/m ²)
		CM	IM	CM	IM	CM	IM	CM	IM	CM	IM	
PET/PP 75/25	—	0.70	1.45	25.1	29.1	4.8	3.1	23.7	27.8	6.7	3.2	1.9
+ SEP01-g-GMA	5	0.53	1.42	26.8	32.6	6.8	4.4	21.4	32.6	7.8	4.9	3.3
	10	0.44	1.27	18.9	32.1	5.6	4.4	16.7	31.4	6.3	4.9	4.5
+ SEPSEP-g-GMA	5	0.48	1.42	19.1	32.5	6.2	4.1	18.8	32.4	8.1	4.3	3.1
	10	0.45	1.10	18.6	28.1	6.0	4.2	14.2	26.4	8.1	4.6	4.3
+ SEBS-g-GMA	5	0.48	1.18	25.8	32.3	7.6	4.5	21.6	30.4	9.2	6.2	4.0
	10	0.46	1.11	17.4	28.2	5.3	4.4	16.4	26.1	5.6	5.9	4.1

CM, compression-molded samples.

IM, injection-molded samples.

The stress at break of the compatibilized blends was higher than that of the uncompatibilized blend but decreased with increasing compatibilizer content. It was observed that samples obtained by compression molding had better tensile behavior with higher elongation at break than those obtained by injection molding. Such an effect was attributed to the different degree of crystallinity of PET in these samples. In fact, the PET phase of the compression-molded samples displayed a lower degree of crystallinity ($X_c = 12\%$) than did that of the injection-molded samples ($X_c = 17\%$).

The notched Izod impact test was used to study the impact behavior of the injection-molded blend samples (Table III). The noncompatibilized blend showed intermediate values, between those of the neat PP and the PET. A significant improvement of the impact resistance was observed upon the addition of grafted copolymers with any of the examined compositions.²⁶ In particular, the presence of a small amount (5 phr) of SEBS-g-GMA was found to increase the impact resistance of the blend up to 4 kJ/m², twice the value of the noncompatibilized blend (1.9 kJ/m²), whereas values close to 4.5 kJ/m² were reached with the addition of 10 phr of SEP01-g-GMA and SEPSEP-g-GMA.

Heino et al.¹² analyzed the properties of the PET/PP (80 : 20) blends compatibilized with both MAH- and GMA-grafted SEBS and reported a large improvement in impact strength using SEBS-g-GMA (5 wt %). To gain further insight into the effect of the functional groups, we also tested the properties of PET/PP (75 : 25) blends compatibilized with various amounts (2.5–10 phr) of a commercially available SEBS-g-MAH copolymer. The results of rheological and thermal analyses for blends with MAH-grafted copolymer were similar to those obtained employing SEBS-g-GMA, whereas a significant difference was found in the tensile properties of these blends. In fact, blends compatibilized with SEBS-g-GMA displayed enhanced ductility and elongation at break when compared to the blends compatibilized with SEBS-g-MAH.

This behavior could be accounted for by the different reactivity ratios of MAH and GMA functionalities to the PET end groups. Experimental results have provided evidence that the reaction of MAH with a hydroxyl end group of PET is thermoreversible and that the equilibrium shifts toward the reactants with an increasing reaction temperature.⁴ The blend preparation involved a blending step at 260°C, which appears to be detrimental for the efficiency of the MAH compatibilization reaction. In contrast, the reaction between the epoxide of GMA and the carboxyl end groups also is an equilibrium reaction but is shifted toward the final products with increasing temperature. Thus, a high processing temperature is more favorable for the epoxide compatibilization reaction.

The ability of the GMA functional groups to react with the carboxyl and/or hydroxyl end groups of PET was studied using selective extraction tests carried out on ternary blends containing 5–10 phr of functionalized SEBS and SEPSEP. The etched surfaces were examined by SEM, and the solution was analyzed by FTIR in order to characterize the soluble species. SEM pictures showed the appearance of empty zones at the interface between the dispersed phase and the matrix, indicating that the block copolymer was at least partially dissolved by the solvent. The FTIR spectrum of the acetone-extracted fraction showed peaks characteristic of the polystyrene block (in the range of 1350–1600 cm⁻¹) and only a very weak absorbance at 1736 cm⁻¹, corresponding to the carbonyl stretching of grafted GMA, when compared to those of pure grafted copolymer.¹⁷ These findings support the contention that most of the GMA groups had chemically reacted with PET, so that the grafted copolymer was mainly linked to the matrix phase, whereas a small fraction of it (likely with very low degree of grafting) could be solubilized. To clarify such aspects, a more detailed and complete analysis of the reactive processes in these systems is presently being conducted using FTIR and NMR spectroscopy.

CONCLUSIONS

The properties of binary blends of PET with GMA-grafted and neat SEBS, SEP, and SEPSEP block copolymers were analyzed by SEM, DSC, and rheological and tensile tests. Significant changes in the morphology were observed for the blends with functionalized copolymers, which showed enhanced phase dispersion and interfacial adhesion when compared to the nonfunctionalized systems. The marked increase in torque and melt viscosity observed for the blends with GMA-grafted copolymers was accounted for by the occurrence of chemical reactions between the epoxide groups and the end groups of PET. The results of thermal analysis indicated that both the crystallization and reorganization processes of PET during melting were significantly influenced by the compatibilization (and crosslinking) reactions with the functionalized polyolefins.

The pure and grafted copolymers were then evaluated as compatibilizers for PET/PP blends with a PET matrix. Generally, the addition of any of these copolymers was found to improve the morphology, resulting in increased phase dispersion and reduced coalescence. However, the emulsifying effect was far more pronounced in the presence of SEPSEP-*g*-GMA and SEBS-*g*-GMA. The effectiveness of the functionalized copolymers can be related both to good mixing of the elastomer blocks with the PP phase and to strong interfacial interactions between the GMA groups and the end groups of PET. The increased melt viscosity in the functionalized systems, the changes in the crystallization behavior, and the improved impact resistance, as a result of stronger adhesion at the interface, are indications that interactions occurred in the presence of grafted copolymers, as shown by the results of the selective extraction tests.

The compatibilizing effectiveness of the various copolymers was related to several aspects of the copolymers, such as copolymer structure, number of grafted groups on the copolymer chain, molecular weight, concentration, and location at the interface. We observed that the emulsifying effect was higher for SEPSEP and SEBS, which have lower molecular weights than SEP copolymers and shorter polystyrene sequences. The observations presented in the previous section indicated that the tetrablock copolymer generally was more effective than the triblock and diblock copolymers, likely because of the effect of both molecular weight and degree of grafting. The importance of molecular weight and copolymer structure on the compatibilizing efficiency of the block copolymers has been pointed out in various studies.^{7,27,28} Diblock copolymers are believed to be more effective because the elastomer blocks can easily mix with the polyolefin phase, providing strong entanglements, whereas triblock copolymers are less interacting because of conformational restraints. From this point of view, the effect of a tetrablock copolymer is expected to be more

similar to that of a diblock copolymer (assuming comparable molecular weights of the elastomer sequences). Further, it must be taken into account that the emulsifying activity is controlled by the content of functional groups on the copolymer chain at the interface. Because the degree of grafting is related to elastomer content,¹⁴ the tetrablock copolymer that has the highest concentration of GMA results in a more effective interaction with the polymer components, as shown by the morphological characteristics of the compatibilized blends. Finally, a comparison of blends compatibilized with GMA- and MAH-grafted SEBS indicated that the compatibilizing effect was greater in the presence of GMA groups.

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