Thermoplastic Elastomers Based on Compatibilized Poly(butylene terephthalate) Blends: Effect of Functional Groups and Dynamic Curing

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ABSTRACT: Two sets of graft copolymers were prepared by grafting glycidyl methacrylate (GMA) or allyl (3-isocyanate-4-tolyl) carbamate (TAI) onto ethylene/propylene/diene terpolymer (EPDM) in an internal mixer. These graft copolymers were used as the compatibilizer to prepare the thermoplastic elastomers (TPEs) containing 50 wt % of poly(butylene terephthalate), PBT, 30 wt % of compatibilizer, and 20 wt % of nitrile-butadiene rubber, NBR. The indirect, two-step mixer process was chosen for dynamic curing. The TPEs were characterized by differential scanning calorimetry, scanning electron microscopy, transmission electron microscopy, tensile testing, and dynamic mechanical thermal analysis. It was found that this kind of TPEs possess enhanced toughness and stiffness when compared with the mechanical properties of binary blend EPDM/PBT; the compatibility between EPDM and PBT was improved when grafted EPDMs were used; EPDM-g-GMA and EPDM-g-TAI showed similar effects on the morphology and ultimate mechanical properties of TPEs. The indirect dynamic vulcanization has negative effect on the reactive compatibilization. Both indirect dynamic vulcanization and reactive compatibilization were crucial to obtain droplets of dispersed rubber phase in a continuous thermoplastic matrix. The above results are important for academic knowledge and industry applications. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3963–3972, 2008

Key words: poly(butylene terephthalate); thermoplastic elastomer; grafted EPDM; curing of polymers

INTRODUCTION

Thermoplastic elastomers (TPEs) have been widely used as materials for automobile, industrial, electrical products, etc. for their unique mechanical behavior. In fact, TPEs behave as rubbers around room temperature and as thermoplastic resins in the higher temperature range. Conventional TPEs are block copolymers made by copolymerization of two or more monomers by using block or graft polymerization techniques.[1] Blends of poly(butylene terephthalate), PBT, and rubbers offer alternatives to conventional TPEs.[2] However, the customary applied elastomers such as styrene/butadiene rubber, SBR, ethylene/propylene copolymer, EPR, ethylene/propylene/diene terpolymer, EPDM are highly immiscible with PBT and thus the related blends show unfavorable mechanical properties.[3] To improve the compatibility of polymer blends and increase the interfacial adhesion, the "in situ" formation of compatibilizer through the blending of the components can be adopted. This method is based on the formation of a block or grafted copolymer A-B at the interface between the different phases during melt-mixing.[3–5] Because most polymers do not have the appropriate functional groups, functionalization of the components is generally required.[6–13]

The nature of the reactive species is the key factor that determines the efficiency of the reactive compatibilization.[12–16] Lee studied the compatibilization of blends of PBT with oxazoline-grafted polyolefins and reported that the presence of oxazoline reduces the particle size of the dispersed phase and improves adhesion between the two phases.[6] Kim et al. found that blends composed of PBT and ethylene-vinyl acetate copolymer (EVA) grafted with maleic anhydride, MAH, presented a morphology with finely dispersed domains, showing that the functionalized EVA was able to compatibilize the blends through reactions occurring during the melt-mixing.[7] Suh and coworkers[8,9] and Ding[10] have introduced

the isocyanate groups to toughen PBT and PA6, respectively. Their studies showed that the isocyanate group has a good reactivity towards hydroxyl, carboxyl, and amine groups, and the morphologies of the resultant blends were notably improved. About the reactive blending involving glycidyl methacrylate (GMA) or other molecules bearing the epoxide groups, there are papers on PBT/epoxidized EPDM,[11] PBT/ethylene-methacrylate-glycidyl-methacrylate terpolymer (E-MA-GMA),[12] and PBT/acrylonitrile-butadiene-styrene (ABS)/methyl methacrylate-glycidyl methacrylate-ethyl acrylate terpolymer (MGE).[13] Actually, the epoxy and isocyanate functional groups appear to be more effective in PBT blend modification than the anhydride functional group.[17] However, the effect of these two species on the compatibility of PBT-based blends has not been compared.

Dynamic curing is another method to improve the rubber performance and stabilize the morphology of blends of thermoplastics with elastomers.[2,3,18] This process consists in vulcanizing the elastomer during the melt-mixing with a noncurable thermoplastic. In most cases, small ideally fully crosslinked droplets of 0.1–2.0 μm diameter are dispersed in the thermoplastic matrix, which favors the elastic recovery after a mechanical deformation.[2]

In the present study, TPEs containing PBT, EPDM, and NBR were prepared in different reaction conditions, for example, by introducing isocyanate and epoxy groups to EPDM and indirect vulcanizing or not. The NBR rubber was used because, in a previous study, the best mechanical performances were observed for PET-based blends containing NBR.[3] The novelty of this work arises from two aspects: firstly, this kind of TPE (ternary blends) possesses enhanced toughness and stiffness when compared with the mechanical properties of binary blend EPDM/PBT; secondly, the conjugated effect of reactive compatibilization and dynamic vulcanization on the morphology and ultimate mechanical properties of the PBT-based blends are deeply studied.

EXPERIMENTAL

Materials

Poly(butylene terephthalate), PBT, was provided by DSM (Emmen, The Netherlands). Its trade grade was Arnite thermoplastic polyester (T04 200). Its [η] value (in m-cresol) was about 1.85 dL/g, and the contents of the carboxylic and hydroxyl end groups were 45 and 66 μmol/g, respectively. Ethylene–propylene–diene terpolymer (EPDM) was provided by Mitsui Chemical. Ethylene and diene contents were 56 and 11 mol %, respectively. The Mooney viscosity ML (1 + 4) at 100°C was 59. Nitrile-butadiene rubber
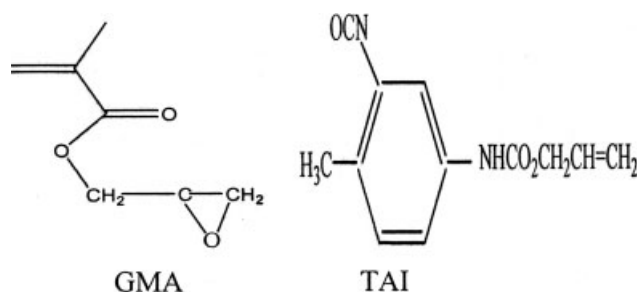

Figure 1 Chemical structures of GMA and TAI.

(NBR) with 33 wt % acrylonitrile content was purchased from JSR Industries (Japan). Its Mooney viscosity ML (1 + 4) at 100°C was 30.

Allyl(3-isocyanate-4-tolyl) carbamate (TAI) was synthesized according to the method reported by Ding et al.[10]; the small amount of the isomer byproduct, that is, allyl (5-isocyanate-2-tolyl) carbamate, was not removed. GMA was purchased from Suzhou-Anli Chemical, (China). The chemical structures of GMA (a) and TAI (b) are shown in Figure 1.

The peroxide Trigonox 1010 was provided by Akzo Nobel Company, Deventer, (Netherlands). Dicumyl peroxide (DCP) was kindly offered by Taichang Special Agent Factory (China). Trifluoroacetic acid (TFA), AR, was provided by National Chemical Reagent (China).
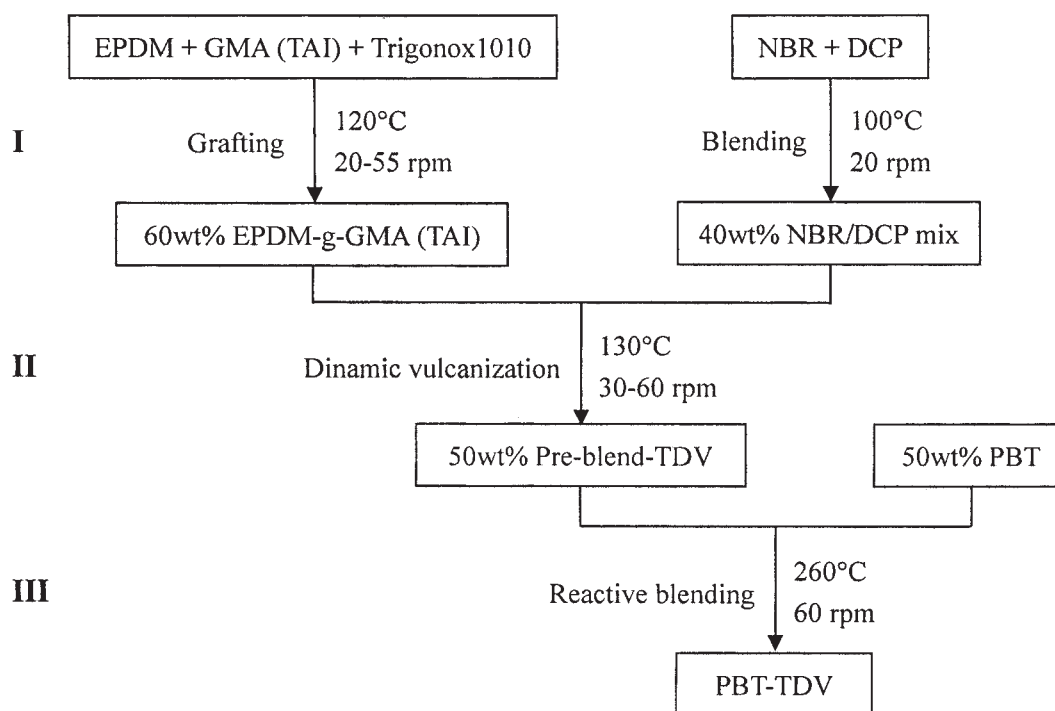
Preparation of the PBT-based thermoplastic elastomers

The various steps followed for the preparation of the PBT-based TPEs are sketched in Figure 2.

Step I

In the first step, EPDM functionalization and the peroxide addition to NBR were performed separately.

Epdm functionalization. The liquid GMA or TAI premixed with the liquid peroxide (Trigonox 1010, 0.6 phr) were introduced into the mixing chamber of an internal batch mixer (Thermo Haake) after 2 min mastication of the required amount of EPDM at about 120°C and 20 rpm. The mixing chamber was kept closed by a ram and its temperature was increased, to initiate the free radical grafting reaction, by increasing the mixing speed up to 55 rpm. After the reaction ended, the samples were discharged from the mixing chamber and cooled to room temperature. The samples were purified following the method described by Papke[19] and Ding;[10] the grafting degree (GD) was determined by titration in non aqueous media following the procedures adopted by Yang et al.[20] and Ding et al.[10]

Figure 2 Step-production of PBT-based thermoplastic elastomers.

Addition of peroxide to NBR. NBR and DCP were pre-mixed (3.75 phr peroxide, 100°C, 20 rpm) at a temperature lower than the decomposition temperature of the peroxide.

Step II

In this step, the blend labeled Pre-blend-thermoplastic dynamic vulcanizate (TDV), constituted by 60 wt % functionalized EPDM rubber and 40 wt % NBR/DCP mixture, was prepared at 130°C and 30 rpm and dynamically cured by increasing the mixing speed up to 60 rpm for 5 min to allow the peroxide decomposition.

Step III

The final TDV was prepared by blending equal amounts of the Pre-blend-TDV with PBT at 260°C and 60 rpm for 6 min.

The PBT-TDVs were cryogenically crushed into small pellets and dried at 120°C for 12 h before any further characterization.

To study the effect of dynamic curing on the morphology and ultimate properties of PBT-based blends, some samples no dynamically cured were prepared by blending 60 wt % functionalized EPDM rubber with 40 wt % NBR as described earlier, but without adding the peroxide. Some samples were prepared by direct dynamical vulcanization, as well. The direct dynamical vulcanization means that we

skipped the step II and prepared the samples by adding DCP to the blend of graft EPDM, NBR, and PBT directly in step III.

FTIR spectroscopy

The IR spectra were performed on a Bruker IFS 28 spectrometer, time constant 4, 50 kHz; scan time 32. The samples were made by compression molding or solution casting.

Differential scanning calorimetry (DSC) measurement

Differential scanning calorimetry (DSC) performed on a Perkin–Elmer DSC-7 thermal analysis system was used to provide the direct evidence on the interface reactions between grafted EPDM and terminal groups of PBT. For this purpose, PBT-based thermoplastics (100–150 mg) were packed in a preweighed nickel net and put in a Soxhlet extractor, extracted with trifluoroacetic acid (TFA) for 24 h, then dried in a vacuum oven at 60°C until its weight was constant. The neat PBT and extracted samples were first melted at 250°C for 5 min to erase any previous thermal history, and then cooled to room temperature with the cooling rate of 2°C/min. All data acquisitions and analyses were performed using the Pyris software package.
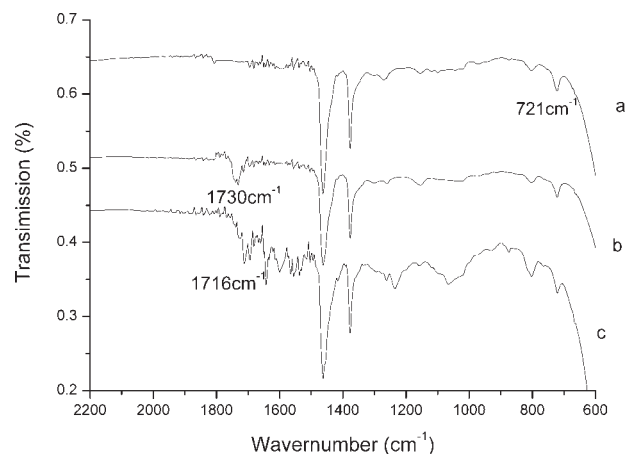
Figure 3 FTIR spectra for EPDM (a); EPDM-*g*-GMA (2.57 wt %) (b); EPDM-*g*-TAI (2.65 wt %) (c).

Morphological observations

The blend morphology was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM analysis was performed on fracture surfaces with a Hitachi S570 Microscope. Samples were fractured at liquid nitrogen temperature and coated with a 20 nm Au/Pd layer before examination. The experiment was performed at 20 kV accelerating voltage. TEM analysis was performed with a Philips EM 301 microscope operating at 100 kV. For this purpose, samples were cryoultramicrotomed into thin slices of ∼ 50 nm by keeping the sample temperature at −90°C to avoid deformation of the specimens. The sections were then stained by exposition (10 min) to aqueous vapors of RuO_4 (2 wt % aqueous solution) before examination.

Tensile testing

The specimens (plates of 2 mm thickness) were prepared by compression molding at 300°C for 3 min.

Tensile tests were carried out on an Instron Universal Testing Machine (Model 1121) at ambient conditions according to the ASTM D638 method for tensile tests. Crosshead speed was set at 10 mm/min. All results are averages of at least 10 measurements.

Thermomechanical evaluation

The viscoelastic response of the PBT-TDV blends was studied by dynamic mechanical thermoanalysis (DMTA) using a Metravib MAK-04 (Netzsch, Germany). Rectangular specimens of $37 \times 14 \times 1$ mm^3 (L $\times$ W $\times$ T) were subjected to oscillating tensile loading. The selected static preload was $3 \pm 0.5N$ on which an oscillating load of $1.5 \pm 0.3N$ at 10 Hz frequency was superimposed. The heating was performed at a rate of 5°C/min in a temperature range between −100 and 250°C.

RESULTS

Grafting reactions

The typical FTIR spectra of neat EPDM (a), purified EPDM-*g*-GMA (b), and purified EPDM-*g*-TAI (c) are shown in Figure 3. In the spectrum of neat EPDM, the two peaks at 1375 and 1470 cm^{-1} are attributed to the bending vibration of —CH$_3$ and —CH$_2$ group, respectively.[10] In the spectra of grafted EPDM, the new strong peaks at 1730 and 1716 cm^{-1} belong to the carboxyl group of grafted GMA[20] and grafted TAI,[10] respectively. The FTIR spectra indicate clearly the diagnostic absorbances of GMA and TAI and suggest the occurring of grafting reactions. The grafting conditions and GD are listed in Table I. At high monomer loading, similar GD of EPDM-*g*-GMA and EPDM-*g*-TAI are obtained at the same feed ratio of monomer, indicating a similar reactivity of GMA and TAI towards free radicals on the backbone of EPDM.[21]

TABLE I
Grafting Degree of EPDM Functionalized with GMA or TAI

Monomer		Composition (phr)			
GMA	Samples	EPDM	GMA	Trigono 1010	GD (%)[a]
	EPDM-g-GMA$_1$	100	2	0.6	1.68
	EPDM-g-GMA$_2$	100	4	0.6	2.09
	EPDM-g-GMA$_3$	100	6	0.6	2.47
	EPDM-g-GMA$_4$	100	8	0.6	2.57
	EPDM-g-GMA$_5$	100	10	0.6	2.78
TAI		EPDM	TAI	Trigono 1010	
	EPDM-g-TAI$_1$	100	2	0.6	0.68
	EPDM-g-TAI$_2$	100	4	0.6	1.32
	EPDM-g-TAI$_3$	100	6	0.6	1.81
	EPDM-g-TAI$_4$	100	8	0.6	2.65
	EPDM-g-TAI$_5$	100	10	0.6	2.95

[a] Presetting temperature: 120°C; mixing speed: 20–55 rpm.
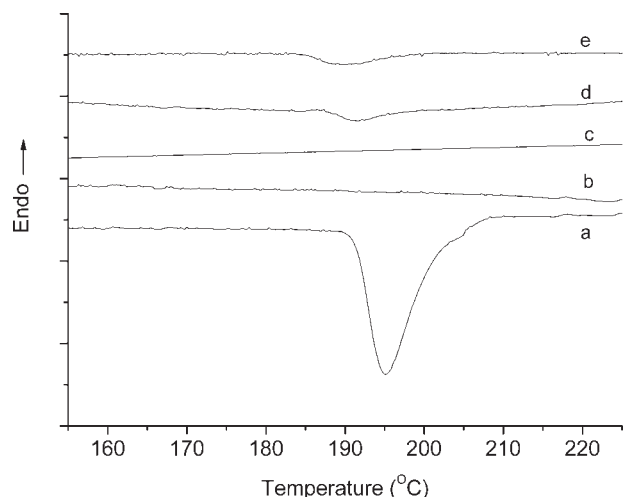
Figure 4 DSC cooling thermograms of PBT and PBT-based thermoplastics extracted by trifluoroacetic acid (TFA): neat PBT (a); PBT/EPDM (50/50 wt %) (b); PBT/EPDM/NBR (50/30/20 wt %) (c); PBT/EPDM-g-GMA$_5$/NBR (50/30/20 wt %) (d); PBT/EPDM-g-TAI$_5$/NBR (50/30/20 wt %) (e).

Interface reactions

Figure 4 displays DSC cooling thermograms of neat PBT and PBT-based thermoplastics extracted by TFA. The neat PBT crystallizes at about 195°C (a); no crystallization peaks are detectable in the DSC traces of the extracted samples for PBT/EPDM (50/50 wt %) blends (b) and PBT/EPDM/NBR (50/30/20 wt %) blends (c), indicating that no interface reactions have occurred; for the extracted samples of PBT/EPDM-g-GMA$_5$/NBR (50/30/20 wt %) blends (d) and PBT/EPDM-g-TAI$_5$/NBR (50/30/20 wt %) blends (e), the crystallization peaks in the DSC thermograms are observable, this provides the evidence of interaction between grafted EPDM and terminal groups of PBT. Because of the confined PBT chains in the rubber phase, the crystallization temperatures of PBT of the extracted samples are lower than that of neat PBT.

Morphology of blends

Figure 5 displays SEM micrographs of cryofractured and etched PBT/EPDM (50/50 wt %) (a) and PBT/EPDM/NBR (50/30/20 wt %) (b) blends. These two samples are not dynamically vulcanized, and the rubber phase was extracted by boiling xylene using a Soxhlet apparatus. The holes in the micrographs are due to the rubber phase that has been preferentially extracted by the solvent. The features of the PBT/EPDM (50/50 wt %) blend [Fig. 5(a)] are typical of an incompatible system, where both the components exist as continuous phases; this is in agreement with the findings of Martin et al.[22] In Figure 5(b), reduced domain dimensions are observed, but with broad distribution of domain sizes. The comparison between Figure 5(a,b) shows that the presence of NBR improves the compatibility of EPDM and PBT.

Figure 6 presents the TEM morphology of PBT/EPDM-g-GMA/NBR (50/30/20 wt %) and PBT/EPDM-g-TAI/NBR (50/30/20 wt %) blends. Figure 6(a,b) shows the morphology of blends containing GMA as functional group with GD of 1.68 and 2.78 wt %, respectively. It can be seen that the domain size decreases with increasing content of GMA grafted. A similar behavior is observed for PBT/EPDM-g-TAI/NBR (50/30/20 wt %) blends [Fig. 6(c,d)] with GD of 1.32 and 2.95 wt %, respectively. The reduction in domain size with the addition of functionalized EPDM is due to the higher compatibility between PBT and EPDM caused by the presence of graft copolymer at the blend interface that broadens the interfacial region through the penetration of the copolymer chain segments into the corresponding adjacent phases.[2,3,11–13]

Figure 7 shows TEM micrographs of PBT/EPDM-g-GMA$_5$/NBR obtained without dynamic curing (a), with direct dynamic curing (b), and with indirect dynamic curing (c). The large domain size of rubber
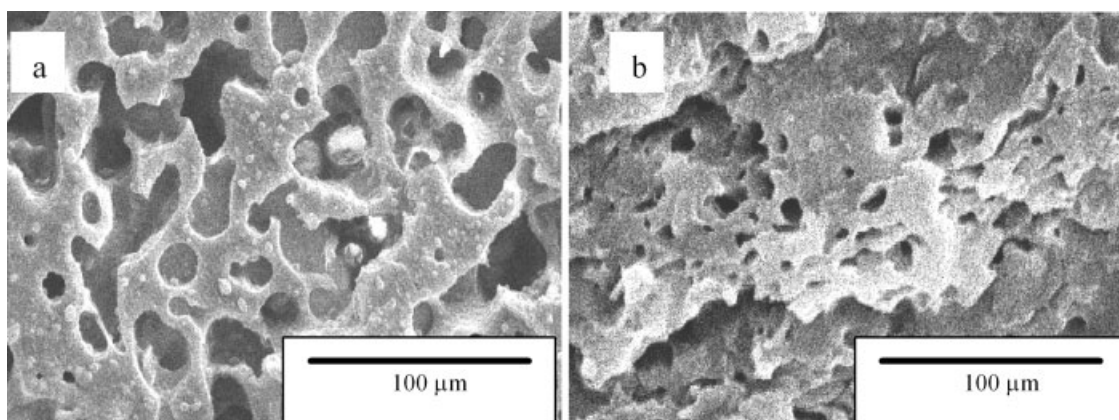
Figure 5 SEM pictures of cryofractured and etched PBT/EPDM (50/50 wt %) (a) and PBT/EPDM/NBR (50/30/20 wt %) (b) blends. These two samples are not dynamically vulcanized.
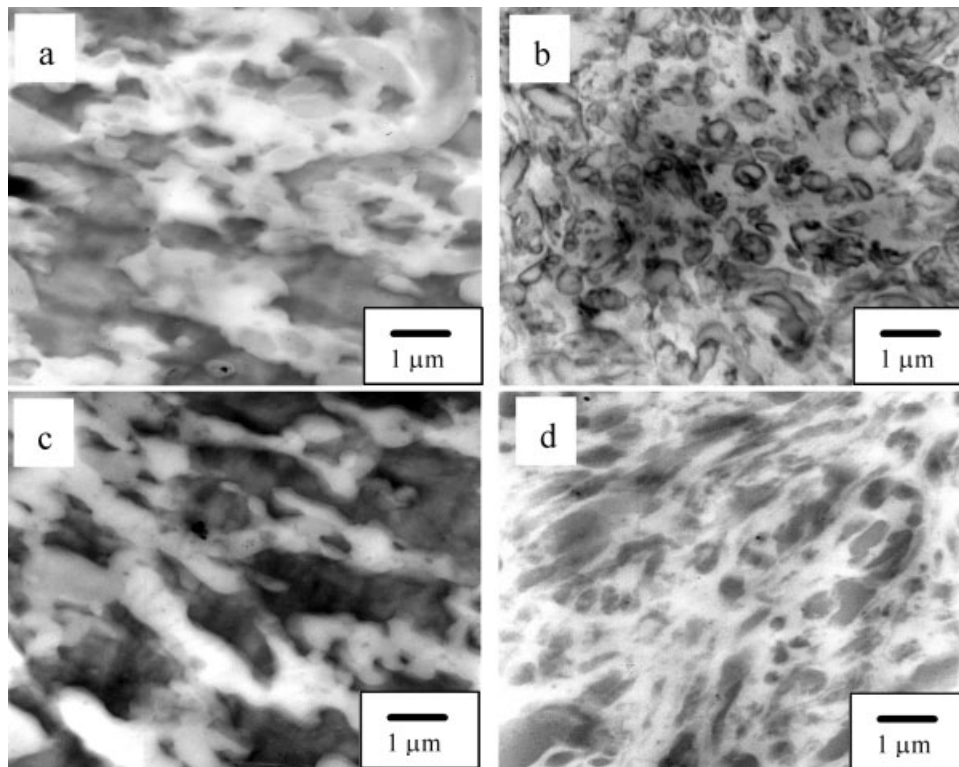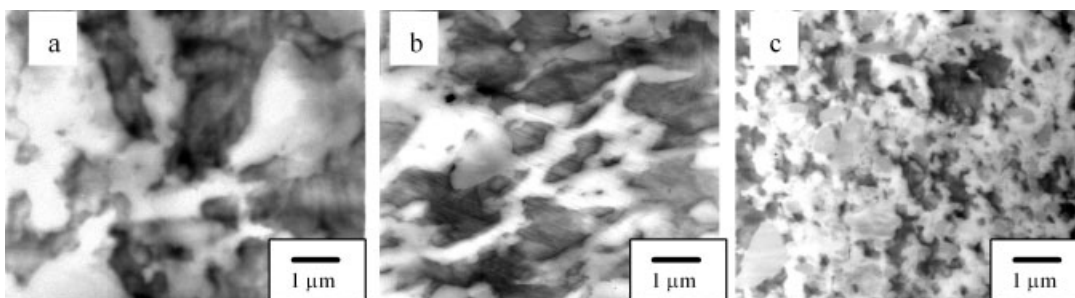
Figure 6 TEM pictures of: PBT/EPDM-g-GMA$_1$/NBR (50/30/20 wt %) (a); PBT/EPDM-g-GMA$_5$/NBR (50/30/20 wt %) (b); PBT/EPDM-g-TAI$_2$/NBR (50/30/20 wt %) (c); PBT/EPDM-g-TAI$_5$/NBR (50/30/20 wt %) (d).

phase or the cocontinuous structure is observed in Figure 7(a,b), indicating that the desired structure, that is, rubber particles well dispersed in the PBT matrix [shown in Fig. 7(c)] cannot be obtained only by reactive compatibilization or direct dynamic vulcanization.

Tensile testing of blends

The results of tensile testing and their standard deviation are collected in Table II in terms of tensile modulus, E, tensile strength, σ_b, elongation at break, ε_b, and energy to tensile failure E_b; the last quantity is related to impact tensile strength. In agreement with the results obtained by Papke,[3] balanced properties, in terms of both enhanced stiffness and toughness, are obtained when the NBR is added to the PBT/EPDM blends, the optimal properties being obtained when the composition (PBT/EPDM/NBR) is 50/30/20 (wt %). Thus, this composition was used to prepare the ternary systems in the subsequent runs. Table II shows the enhanced tensile properties after the introduction of GMA and TAI onto EPDM. At the same composition, the samples obtained by the indirect dynamic vulcanization show the well-balanced mechanical properties when compared with those of the samples prepared by direct dynamic vulcanization and without dynamic vulcanization. The

Figure 7 TEM pictures of PBT/EPDM-g-GMA$_5$/NBR (50/30/20 wt %) without dynamic curing (a), with direct dynamic curing (b), and with indirect dynamic curing (c).

Blends composition (wt %)	E (MPa)	σ_b (MPa)	ε_b (%)	E_b (J cm^{-3})
PBT/EPDM/NBR				
PBT/EPDM/NBR 50/50/0	93.6 ± 5.0	3.4 ± 0.1	7.2 ± 0.4	7 ± 1
PBT/EPDM/NBR 50/40/10	115.2 ± 3.0	3.8 ± 0.1	7.6 ± 0.2	11 ± 1
PBT/EPDM/NBR 50/30/20	175 ± 10	4.4 ± 0.2	7.7 ± 0.7	12 ± 1
PBT/EPDM/NBR 50/20/30	150 ± 9	4.2 ± 0.1	7.5 ± 0.2	10 ± 1
PBT/EPDM/NBR 50/10/40	122 ± 8	4.1 ± 0.2	7.4 ± 0.3	9 ± 1
PBT/EPDM-g-GMA/NBR 50/30/20				
PBT/EPDM-g-GMA$_1$/NBR	186 ± 8	5.9 ± 0.2	9 ± 0.4	18 ± 2
PBT/EPDM-g-GMA$_1$/NBR[a]	131 ± 20	4.6 ± 0.1	10 ± 1.2	15 ± 2
PBT/EPDM-g-GMA$_5$/NBR	294 ± 10	8.1 ± 0.2	11 ± 0.1	28 ± 2
PBT/EPDM-g-GMA$_5$/NBR[a]	196 ± 1	5.8 ± 0.3	15 ± 1.5	24 ± 3
PBT/EPDM-g-GMA$_5$/NBR[b]	252 ± 10	7.2 ± 0.2	10 ± 0.1	26 ± 1
PBT/EPDM-g-TAI/NBR 50/30/20				
PBT/EPDM-g-TAI$_1$/NBR	202 ± 17	7.2 ± 0.4	9 ± 2.3	20 ± 3
PBT/EPDM-g-TAI$_5$/NBR	296 ± 5	9.8 ± 0.6	9 ± 1.9	26 ± 2
PBT/EPDM-g-TAI$_5$/NBR[a]	160 ± 18	7.8 ± 0.1	19 ± 4.2	22 ± 2
PBT/EPDM-g-GMA$_5$/NBR[b]	276 ± 5	8.1 ± 0.6	8 ± 1.9	23 ± 2

[a] Without dynamic vulcanization.
[b] Direct dynamic vulcanization.

improvement of tensile properties is due to the synergic effect of compatibilization and dynamic vulcanization.[3,22]

Thermomechanical properties of blends

The DMTA results of PBT/NBR, PBT/EPDM, and PBT/EPDM/NBR are presented in Figure 8 in terms of temperature dependence of the absolute complex modulus value, |G*|, and the loss factor tan δ, respectively. At room temperature, PBT/NBR blend shows the highest |G*|; moreover, |G*| of PBT/EPDM/NBR is higher than that of PBT/EPDM [Fig. 8(a)]. In the PBT/EPDM blend, the glass transition temperature (T_g) of PBT is about 75°C, the shift of T_g for PBT towards lower temperature is detectable in the PBT/NBR ($\sim$ 56°C) and PBT/NBR/EPDM blends ($\sim$ 58°C), indicating that NBR is more miscible than EPDM with PBT.[23] As the tensile modulus of NBR is higher than that of EPDM,[3] the addition of NBR increases the stiffness of the blend [Fig. 8(b)].

The traces of |G*| and tan δ versus T obtained for PBT/EPDM-g-GMA/NBR (50/30/20 wt %) are displayed in Figure 9(a,b), respectively. |G*| increases on increasing GD of functionalized EPDM, and the shift of T_g of PBT towards lower temperatures when compared with that of PBT/EPDM blends is observed. These findings indicate that an increasing interface adhesion between PBT phase and functionalized EPDM. Figure 10 shows the DMTA behavior of PBT/EPDM-g-TAI$_5$/NBR blends with and without dynamic vulcanization. In the temperature range between the glass transition temperature of EPDM and PBT, |G*| of PBT/EPDM-g-
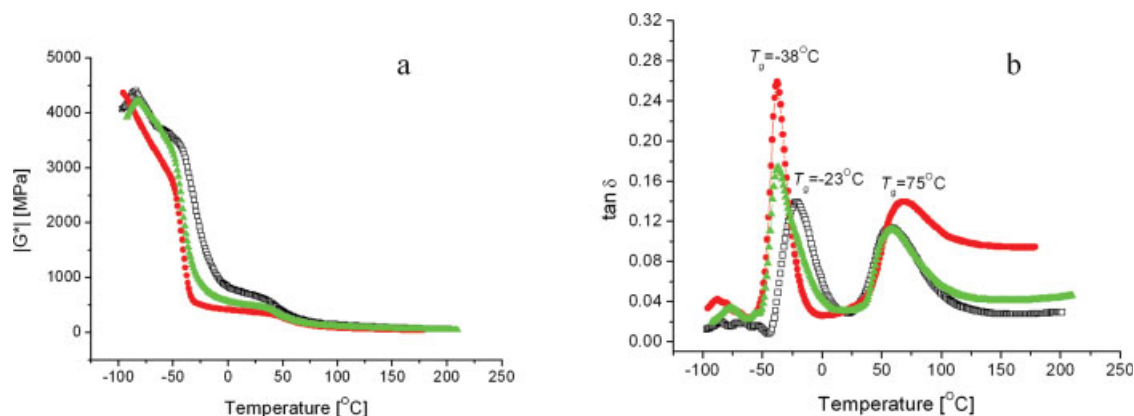
Figure 8 Complex modulus |G*| (a) and tan δ (b) versus T traces for: (□) PBT/NBR (50/50 wt %); (●) PBT/EPDM (50/50 wt %); and (▲) PBT/EPDM/NBR (50/30/20 wt %) blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
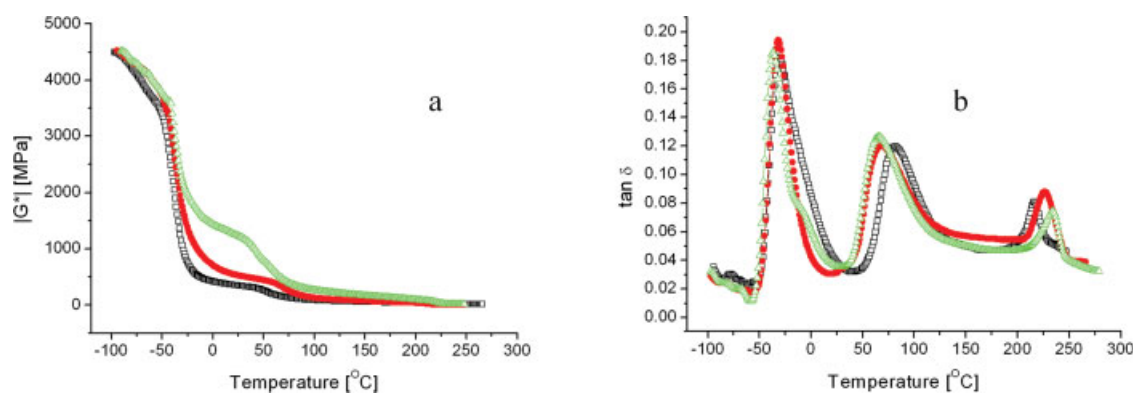
Figure 9 Complex modulus |G*| (a) and tan δ (b) versus T traces for PBT/EPDM-g-GMA/NBR (50/30/20 wt %) blends at different grafting degree: (□) GMA$_1$ (1.68 wt %); (●) GMA$_3$ (2.47 wt %); and (△) GMA$_5$ (2.78 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TAI$_5$/NBR blends dynamically vulcanized, is found to be higher when compared with the corresponding unvulcanized samples. PBT T_g of these blends is about 65°C and not affected by the dynamic vulcanization.

DISCUSSION

The main reactions between EPDM-g-GMA (TAI) and PBT terminal groups are summarized in Figure 11.[12,16,24] Reaction 1 is a compatibilization reaction that involves epoxy groups of EPDM-g-GMA and carboxyl end groups of PBT; this reaction suggests the formation of PBT-co-EPDM copolymer at the interface. The copolymer, acting as compatibilizer, decreases interfacial energy and promotes mixing. This leads to fine dispersed rubber particles and, in turn, to increased mechanical properties, with respect to those of the corresponding PBT/EPDM/NBR blends. For PBT/EPDM-g-TAI/NBR blends, isocyanate groups readily react with hydroxyl groups and the urethane formation is dominant (Reaction 2).[24] Because the reactivity of epoxy and isocyanate groups toward the terminal groups of PBT is different,[16,24] it is reasonable to conclude that the compatibilization could be different in PBT/EPDM-g-GMA/NBR and PBT/EPDM-g-TAI/NBR system.[3,12,16] However, for the PBT/EPDM-g-GMA$_5$/NBR and PBT/EPDM-g-TAI$_5$/NBR blends, no substantial difference in morphology is observed. This can be attributed to: (i) a nearly same concentration of carboxyl and hydroxyl groups on PBT; (ii) the reduction of reaction compatibility due to the indirect dynamic vulcanization and the crosslinking reactions between the functional groups and PBT.

Reactions 3 and 4 illustrate the crosslinking mechanism likely occurring in PBT-based ternary blends. Reactions 3 and 4 are based on the bi-functionality of the PBT matrix. The crosslinking in the rubber/thermoplastic interface and the indirect dynamic vulcanization increase the viscosity of the rubber phase and droplet breakup is prevented.[2,22] As a
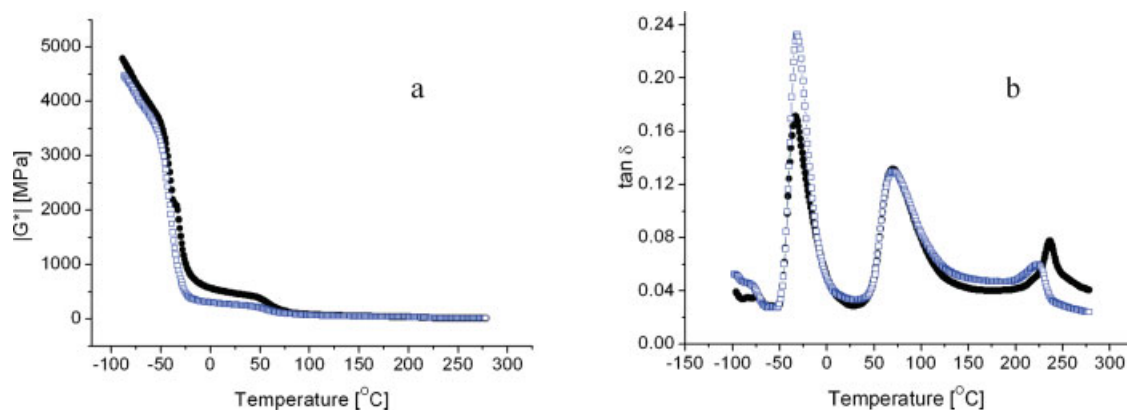
Figure 10 Complex modulus |G*| (a) and tan δ (b) versus T traces for PBT/EPDM-g-TAI$_5$/NBR (50/30/20 wt %) blends: (●) with dynamic vulcanization and (□) without dynamic vulcanization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
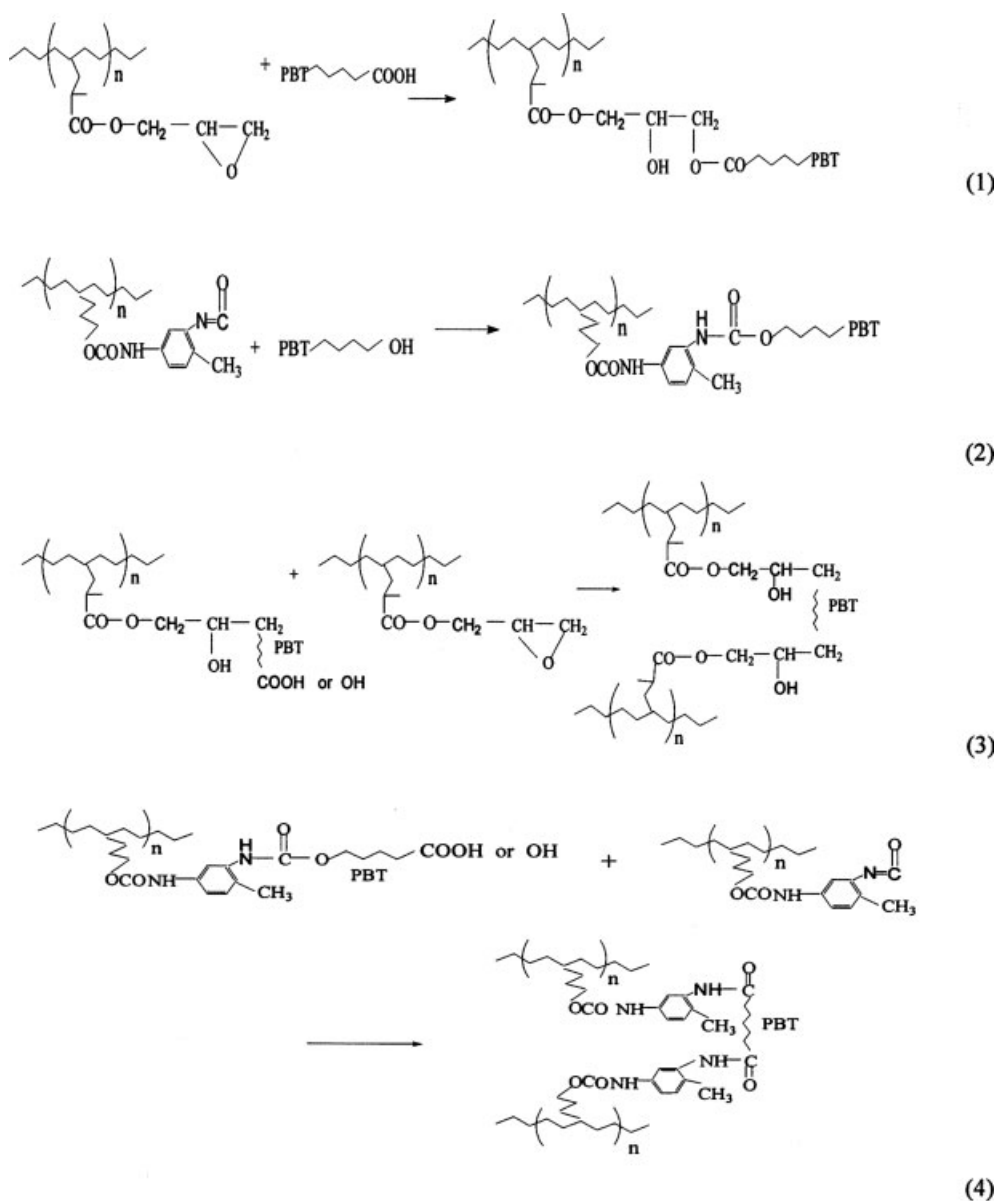
Figure 11 Main reactions between grafted EPDM and terminal groups of PBT.

consequence, morphological difference are observable due to different density and chemical nature of the functional groups.

It should be noted that although the morphology is slightly influenced by functional groups, the tensile testing and DMA show that the ultimate mechanical properties increase with increasing density of functional groups. This observation can be explained as follows: the EPDM and NBR differ in insaturation and polarity degree, and the corresponding vulcanizates normally display a heterogeneous crosslink distribution.[23] The introduction of the functional groups onto EPDM changes the polarity degree of EPDM, thus, a homogeneous-distributed network is easily formed, and a substantial increase of strain recovery of elastomer is observed.[2]

Furthermore, the dynamic vulcanization and subsequent crosslinking may favor the formation of semi-interpenetrating network. (semi-IPN),[3,18] which improves the ultimate mechanical properties.

As shown in Figure 7, the well-dispersed rubber particles in the PBT matrix cannot be obtained by direct dynamic curing, thus, the indirect dynamic curing is used in this work. The major advantage of indirect dynamic vulcanization is that it decreases the initial plastic/rubber viscosity ratio and favors the rubber dispersion. When compared with the large domain size of rubber phase in the samples obtained without dynamic vulcanization or direct dynamic curing, the desired microstructure, consisting of a continuous plastic matrix with a very high loading of small dispersed vulcanized rubber

particles, is obtained by indirect dynamic vulcanization. Because the dynamic vulcanization occurs only in the rubber phase, the peroxide does not interfere with the PBT, thus the deleterious effect on the thermoplastic phase is eliminated.[2] For these reasons, Table II shows that the blends obtained by indirect dynamic vulcanization have better balanced properties than those obtained by direct dynamic vulcanization and those without dynamic vulcanization. However, the crosslinked EPDM/NBR particles are difficult to be broken into finer particles (<0.1 µm), even though the interfacial tension is reduced by the formation of graft copolymers.[2]

CONCLUSIONS

Two sets of EPDM-*g*-GMA or EPDM-*g*-TAI copolymers containing various amounts of epoxide (GMA) or isocyanate (TAI) functions have been prepared by melt blending, then the NBR and the grafted EPDM have been used as impact modifier for PBT blends. The presence of NBR and modified EPDM influences the morphology and the related mechanical properties in elastomeric blends composed of PBT (50 wt %), functionalized EPDM (30 wt %), and NBR elastomer (20 wt %). The mechanical properties of TPEs increase with increasing density of functional groups, and because of dynamic vulcanization and crosslinking in the interface, the different reactivity of GMA and TAI with PBT terminal groups results in slight difference in morphology and corresponding ultimate mechanical properties of ternary blends.

Because the dynamic vulcanization occurs only in the rubber phase, the peroxide does not interfere with the PBT, thus the deleterious effect on the thermoplastic phase is eliminated. With the indirect dynamic curing, the desired microstructure consisting of a continuous plastic matrix with a very high loading of small dispersed vulcanized rubber particles is obtained.

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