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Polymer 42 (2001) 2463–2478

polymer

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Competitive reactions during compatibilization of blends of polybutyleneterephthalate with epoxide-containing rubber

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Received 28 March 2000; received in revised form 14 June 2000; accepted 25 June 2000

Abstract

Blends of polybutyleneterephthalate (PBT) with ethene–ethyl acrylate copolymer (E–EA) and ethene–methyl acrylate–glycidyl methacrylate terpolymer (E–MA–GMA) were investigated. E–MA–GMA terpolymers containing various concentrations of epoxide functions were synthesized in a preliminary step by melt modification of commercial E–MA–GMA with benzoic acid molecules. The blends were analyzed by several techniques including electron microscopy and separation experiments. PBT/E–EA (80/20 w/w) blends presented the general features of uncompatibilized polymer blends, such as a lack of interfacial adhesion and a relatively coarse unstabilized morphology. No evidence of transesterification reaction was found to occur according to the used blending conditions. In contrast, blends containing both virgin and modified E–MA–GMA terpolymers exhibited a very complex behavior. Fractionation experiments demonstrated that two competitive reactions take place during the melt blending viz. (1) compatibilization due to interfacial reactions between PBT chains end and terpolymer epoxide groups, resulting in the formation of E–MA–GMA/PBT graft copolymer and (2) rapid crosslinking of the rubber phase due to the simultaneous presence of hydroxyl and epoxide groups on E–MA–GMA chains. This competition between compatibilization and crosslinking is clearly dependent on the type of the terpolymer, since the modified E–MA–GMA already contains hydroxyl groups before mixing but for the pure E–MA–GMA hydroxyl groups are formed as a result of the in situ compatibilization reaction with PBT. Rubber phase crosslinking through double reaction with PBT chain can not be excluded but is expected to occur only to a smaller extent. All these phenomena result in a very complex processing/morphology interrelationships and probably also affects the final blend properties.

Keywords: PBT/Rubber polymer blends; Epoxide functions; Crosslinking

1. Introduction

Blending polymers represents one of the most attractive techniques to generate new polymeric materials [1,2]. It provides an economic and rapid alternative to synthesizing new monomers and polymers and is an interesting route for polymers recycling.

Polymer blends can be miscible or not, depending on the specific interactions occurring between the polymer chains. Polymers usually exhibit weak interactions, so immiscible systems are formed. Such blends are multiphasic and very promising, since each constitutive polymer keeps its intrinsic properties. A broad range of blend properties can be obtained by an adequate choice of the initial blend components and of the blend composition. However, simple blends of immiscible polymers usually have poor mechanical properties. This is a direct consequence of polymer incompatibility, which promotes a coarse and unstable morphology, coalescence and a weak interface between the two phases.

Polymer/polymer compatibility can be enhanced by the addition of appropriate pre-synthesized copolymers to the blends [1–5]. This process is known as compatibilization. Typically, compatibilizers consist of block or graft copolymers with different segments having affinity for either of the two blend components. Such copolymers can also be formed “in situ” during the blending process, i.e. reactive compatibilization. It is now clearly established that incorporation of block or graft copolymers in polymer blends induces a large decrease in interfacial tension between the blend components and a decrease in dispersed phase coalescence due to steric stabilization [4–10]. This results in a fine and stable dispersion of the minor and/or high viscous component in the matrix. Compatibilizers also promote interfacial adhesion, which enables stress transfer. All these effects ensure improved mechanical properties.

The use of premade graft or block copolymers with

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PII: S0032-3861(00)00496-1

well-controlled structures is usually too expensive for industrial applications. Reactive compatibilization often is the most attractive way to achieve high performance polymer blends and is nowadays extensively used [11–13]. The method consists in blending two immiscible polymers bearing suitable reactive functions. These functions react with each other during the blending. As a result, block or graft copolymers are directly formed at the interface ensuring blend compatibilization. Functionalized polymer can be obtained directly during the synthesis process, for example by polycondensation, or by chemical modification of inert polymers. Interfacial reaction between the two functionalized polymers must be completed within a few minutes, which is the typical processing time in industrial blending devices. In this context, reactive functions such as anhydride, amine, carboxyl, hydroxyl, oxazoline, nitrile and epoxide are the most commonly used.

Blends of polyesters and polyolefins have attracted much attention over the last decade [14–34]. Polyesters, such as polybutyleneterephthalate (PBT) and polyethylene terephthalate (PET), generally have good thermal resistance, dimensional stability and water absorption. These polymers provide very useful materials for automotive and electronic applications. Unfortunately, polyesters are also notch sensitive, brittle at low temperatures and sensitive to hydrolysis. Thus, there is an interest in developing compatible polyester/polyolefin blends. Compatibilization of polyester/polyolefin blends can be achieved by several approaches, using acrylate based copolymers [14–16], maleic-anhydride-containing elastomers [17–19], epoxidized polyolefins [20–30], ethylene–vinyl acetate copolymer [31], oxazoline-modified polymer [32] or core–shell impact modifiers [33,34]. Transesterification between ester groups and hydroxyl or carboxyl species has been extensively studied over the last decade. The occurrence of such reactions in blends containing acrylate-based copolymers has been reported. Gravalos et al. [14] have shown that a grafted copolymer can be formed in the melt when E–EA copolymer is blended with predominantly hydroxyl terminated PET. The grafting efficiency is directly related to the ratio of the hydroxyl and ester concentrations and is maximal when this ratio is close to one. On the other hand, epoxide-containing elastomers are known to be very effective to toughen PBT or PET [26–30]. It is suggested that this is due to reaction between epoxide functions and both hydroxyl and carboxyl polyesters chain ends during processing. As reported in several studies, reaction with carboxyl groups proceeds more rapidly. Hydroxyl functions are expected to be less reactive by a factor ten or twenty [20]. In order to obtain more insight in the reactivity and the reaction kinetics of both hydroxyl and carboxyl chain ends with epoxide functions, we have performed several experiments using low molecular model compounds. The results of this study will be presented in another paper.

Copolymer of ethylene (E) and glycidyl methacrylate (GMA) or terpolymers of E, GMA and methylacrylate (MA) have been extensively used as compatibilizers or as dispersed phase component. In most studies, emphasis was on morphology, rheology and mechanical properties. In all cases, the improved compatibility was attributed to the formation of graft copolymers at the interface by reactions between epoxide groups and the polyesters hydroxyl or carboxyl groups. However, as reported by van Duin and Neilen [25], no extensive study has been performed on the actual interfacial chemistry nor have the compatibilizers formed at the interface been characterized in detail. Such studies are nevertheless of prime importance for understanding structure–properties relationships as has been shown for instance polyamide blends [11–13].

The aim of this study was to elucidate the compatibilization chemistry occurring during reactive processing of PBT with epoxide functionalized rubber blends. The rubber phase consisted of E–MA–GMA. E–EA was used as an inert reference. An efficient separation procedure was developed allowing the characterization of the species formed during the reactive blending. It will be demonstrated that two reactions take place simultaneously in the melt during the mixing, resulting in very complex processing/morphology/properties interrelationships. The proposed reaction scheme is expected to occur in any polymer blend compatibilized by epoxide-containing polymers.

2. Experimental

2.1. Materials

PBT was supplied by DSM. Acid and hydroxyl chain end concentrations were 49 and 35 μeq/g, respectively. Lotader AX8900 (E–MA–GMA) was purchased from Elf-Atochem Co. The composition is 68 wt% E, 24 wt% MA and 8 wt% GMA. The melt flow index is 6 g/10 min at 190°C under 325 g. Lotril 28MA07 (E–EA) was also purchased from Elf-Atochem Co. and is rather similar to Lotader AX8900, viz. a composition of 30 wt% EA content and MFI = 6 g/10 min at 190°C under 325 g. Despite some differences in the chemical structure, preliminary experiments have demonstrated that E–MA–GMA and E–EA are fully miscible.

In order to analyze the effect of E–MA–GMA epoxide concentration on the blend properties, various grades of modified E–MA–GMA were synthesized in the melt by mixing E–MA–GMA with different amounts of *para-t*-butylbenzoic acid (see below). *Para-t*-butylbenzoic acid and solvents were purchased from ACROS Chemical Co. and were used as received.

2.2. Processing

Prior to processing, all materials were dried for one night at 25°C under vacuum. Common PBT drying conditions are indeed 125°C under vacuum. However, preliminary experiments comparing both drying conditions have not shown

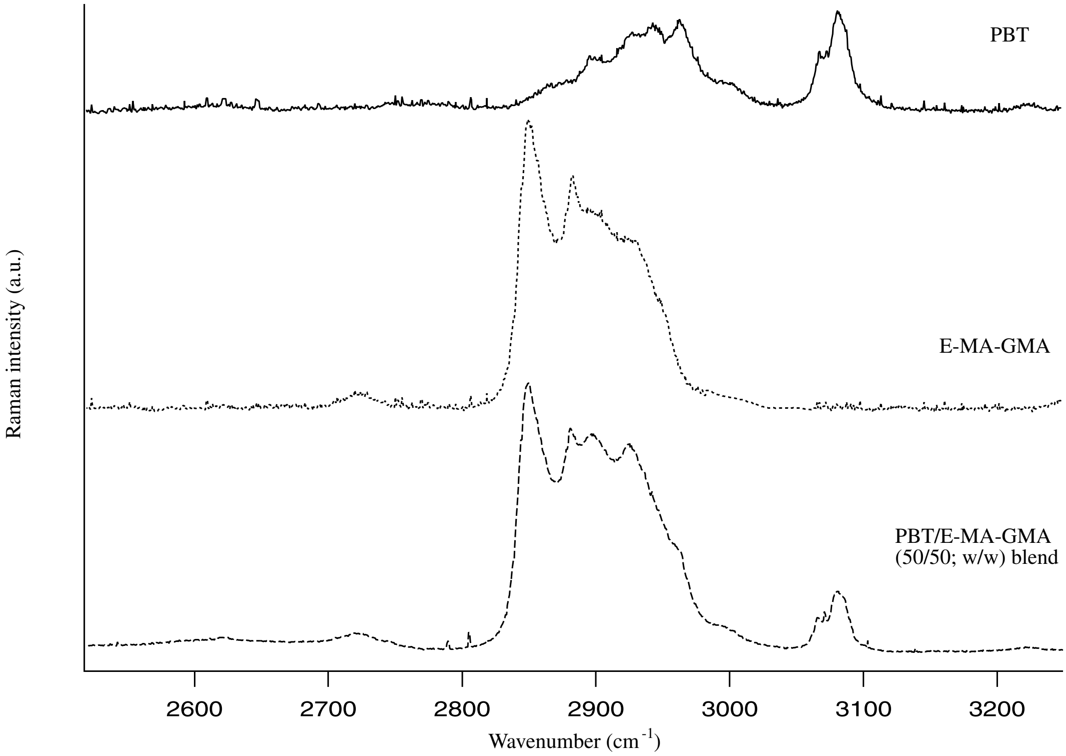


Fig. 1. FT-Raman spectra of virgin PBT, pure E–MA–GMA and PBT/E–MA–GMA (60/40; w/w) blend in 2500–3250 cm^{-1} region.

any effect on PBT degradation and on the other results presented in this study such as morphology and separation observations.

Modification of E–MA–GMA was carried out in the melt in a Brabender WE 50H internal mixer. 50 g of virgin E–MA–GMA was mixed at 200°C for 15 min with precisely calculated amounts of *para*-*t*-butylbenzoic acid in order to achieve different neutralization level of the rubber. Quantitative addition of the acid molecules in the mixing chamber was assumed because of its very high boiling point (>300°C). In order to remove unreacted residual acid, modified E–MA–GMA was purified by two successive cycles of dissolution in hot chloroform and precipitation in methanol. The products were finally dried at 25°C under vacuum for three days to remove solvent traces. In order to assure similar dispersion of the different elastomers during the blending process, the commercial E–EA and E–MA–GMA polymers were also dissolved, precipitated and dried prior to blending with PBT.

PBT/rubber blends were prepared at 250°C using the same internal mixer. The atmosphere in the mixer was controlled by purging with nitrogen gas. Blends compositions were 80/20 (w/w) PBT/rubber, except when specified differently. The PBT pellets were molten for 1 min at 30 rpm prior to addition of rubber powder. Immediately after introduction of the rubber powder, the rotation speed was increased to 90 rpm. The zero time was taken when all the rubber was introduced and the total mixing time was fixed at 18 min. At different times after rubber addition, samples were rapidly withdrawn from the mixing cavity and quenched in liquid nitrogen in order to stop the interfacial reactions and freeze in the morphology. Both mixing torque and temperature were recorded along the blending process. Torque values were corrected for the actual amount of material in the mixing chamber.

2.3. Spectroscopy

The modified E–MA–GMA was characterized by ^{1}H NMR using a Brüker 500 MHz FT-NMR spectrometer at room temperature. The samples were dissolved in 1 ml of hot deuterated chloroform and sealed in dry NMR tubes. All spectra were recorded at room temperature at 500 MHz.

Infrared spectroscopy was performed with a Perkin–Elmer PE 1760 Fourier Transform Infrared Spectrometer. All spectra were recorded with a resolution of 1 cm^{-1} and 10 accumulations. PBT films of approximately 20 μm thick were prepared by compression molding at 260°C. For virgin as well as modified E–MA–GMA, thin films were obtained by evaporation of rubber/chloroform solutions on NaCl pellets.

Raman spectra were recorded at 25°C on a Labram confocal laser Raman spectrometer from Dilor S.A. in the spectroscopic mode. The excitation wavelength was 632.8 cm^{-1} from a He–Ne laser source. The pinhole aperture and the entrance slit were both fixed to 1000 μm, which resulted in a large analyzed volume of samples. A grating of 1800 grooves/mm was used and the spectra were recorded on a CCD detector. Spectra were centered on

2900 cm^{-1}. Spectrum was the average of five accumulations of 60 s.

The presence of PBT and E–MA–GMA can be detected and quantified using the region of 2500–3250 cm^{-1} (Fig. 1). In contrast with E–MA–GMA and E–EA, PBT exhibits a clear peak at 3080 cm^{-1}, corresponding to the aromatic –CH– stretching vibration. E–MA–GMA and E–EA polymers present a strong peak at 2848 cm^{-1}, which is a $-CH_2-$ stretching vibration of $-CH_2-$ aliphatic link. As in Raman spectroscopy, the signal intensity is directly proportional to the species concentration [35]. These two peaks were used to determine the composition of the different recovered fractions (Section 2.5). A calibration was performed by analyzing eight PBT/E–MA–GMA blends of various compositions between pure PBT and pure E–MA–GMA. The relation between the composition of the analyzed samples and the ratio of the Raman intensities at 3080 and 2848 cm^{-1} appears to be linear with a correlation coefficient of 0.999. This is due to the fact that both PBT and E–MA–GMA exhibit no significant signal at 2848 and 3080 cm^{-1}, respectively (Fig. 1). In fact, PBT presents a very low diffusion at 2848 cm^{-1}, which can interfere with the E–MA–GMA or E–EA peak. However, it is clear that such contribution could be neglected according to the relatively higher intensity of the rubber at this wavenumber (Fig. 1).

Further analysis has shown that peak intensities at 3080 and 2848 cm^{-1} were not influenced by solvent molecules such as trifluoroacetic acid or *m*-cresol as well as by *para-t*-butylbenzoic acid molecules. This is probably due to the relatively small concentrations of these species. In the same way, the position and the intensity of the peak at 3080 cm^{-1} is not influenced by PBT crystallinity.

2.4. Microscopy

The blend morphology was examined by electron microscopy. Scanning electron microscopy (SEM) analysis was performed on fracture surfaces with a Hitachi S570 Scanning Electron Microscope. Samples were fractured at liquid nitrogen temperature and coated with a 20 nm Au/Pd layer prior to examination. For Transmission Electron Microscopy (TEM) observations, samples were ultramicrotomed in thin films of approximately 90 nm at −80°C in order to avoid deformation of the dispersed phase particles. The microtomed cuts were stained with RuO_4 for one hour before examination with a Philips EM 301 microscope.

After examination, the morphology was quantified by image analysis. For each sample, at least 200 particles were measured and both the volume and the number average diameters were estimated on a Macintosh computer using the public domain NIH Image program (developed at the US National Institute of Health).

2.5. Fractionation

A procedure was developed for removing free PBT chains from the PBT/rubber blends. Approximately 1 g blend was introduced in 30 ml of pure trifluoroacetic acid (TFA), a good selective solvent for PBT and stirred at room temperature for 1 h in order to solubilize the PBT phase. A milky emulsion was obtained and ultracentrifugated at 14°C and 25,000 rpm using a Beckman L7-65 ultracentrifuge. After 1 h 45 min, clear separation was achieved. The grafted rubber particles were concentrated in a white skin layer at the top of the centrifugation tube. The clear TFA solution was carefully removed and the dissolved PBT was precipitated in methanol, filtrated over a 0.5 μm PTFE filter, washed with methanol and dried at 30°C under vacuum for 24 h to yielding fraction *P1*. The rubber phase was dispersed again in 30 ml TFA and stirred for 45 min at room temperature. A second ultracentrifugation was performed for 1 h 45 min at 8°C and 28,000 rpm. Once again, trifluoroacetic acid solution containing free PBT was carefully separated from the rubber phase, precipitated and worked up to form fraction *P2*. This fraction represents only approximately 3 wt% of the total amount of material. Complete recovery of non-grafted PBT was achieved after the second washing step, since no additional free PBT was obtained when a third separation was carried out. Total amount of free PBT was equal to the sum of fraction *P1* and *P2* and was noted *P*.

After separation, the rubber phase was stirred in chloroform at 50°C for 1 h and filtered. Hot chloroform is a selective solvent for both E–EA and E–MA–GMA. An insoluble fraction, called *C*, was recovered. The free rubber was precipitated from the $CHCl_3$ solution in methanol, filtrated and dried for 24 h at 30°C under vacuum to form fraction *R*.

The weights of the initial sample and of the different fractions were precisely measured. Due to the large number of tricky experimental steps, some material was lost. Still, the mass balance was always above 90%. The amount of grafted PBT was estimated by comparison between the initial PBT content which was equal to 80 wt% for all blends and the PBT amount recovered in fraction *P1* and *P2*.

Each separation was performed on at least two blend samples. Different batches of modified E–MA–GMA were produced and used successively for blending with PBT leading to truly duplicate polymer blends. The reported results correspond to mean values of all these separations. The standard deviation for each blend fraction *P1, P2, R* and *C* was in all cases below 15%.

Besides the weight of each fraction also its composition was quantitatively determined with Raman spectroscopy. Solubility tests were performed in *m*-cresol at 130°C. This solvent is known to dissolve rapidly both PBT and E–MA–GMA. The solubility of the different *C* fractions was checked by stirring approximately 0.5 g of sample in 50 ml of *m*-cresol at 130°C for 1 h. Subsequently, the solution was filtered, precipitated in methanol, intensively washed and dried at 40°C for two nights under vacuum to remove solvent traces.

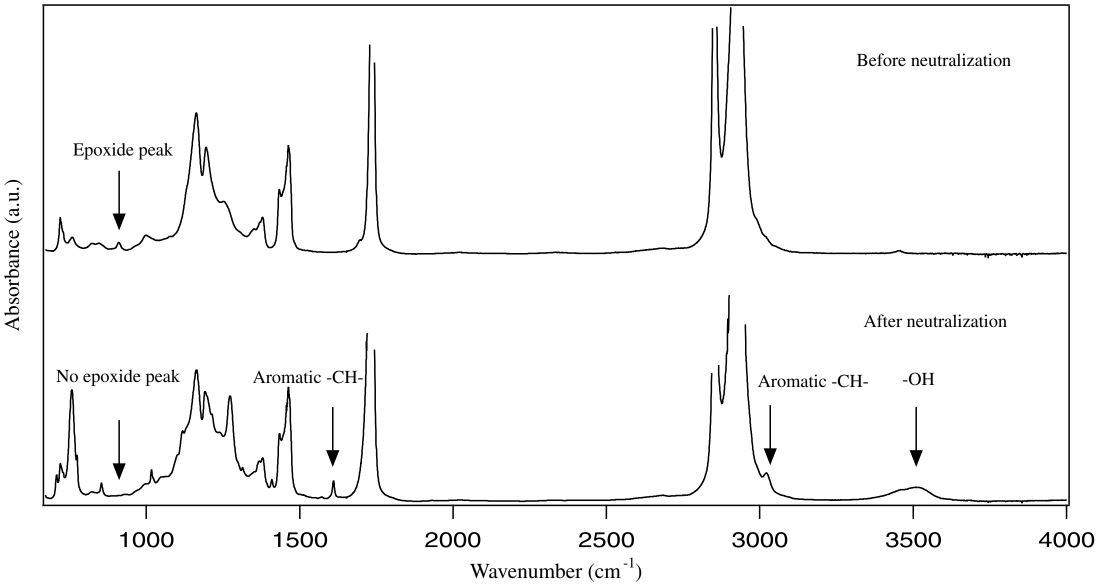


Fig. 2. FT-IR spectra of E–MA–GMA before and after modification of the epoxide groups with *para*-*t*-butylbenzoic acid (93% modification at 200°C in the Brabender plastograph).

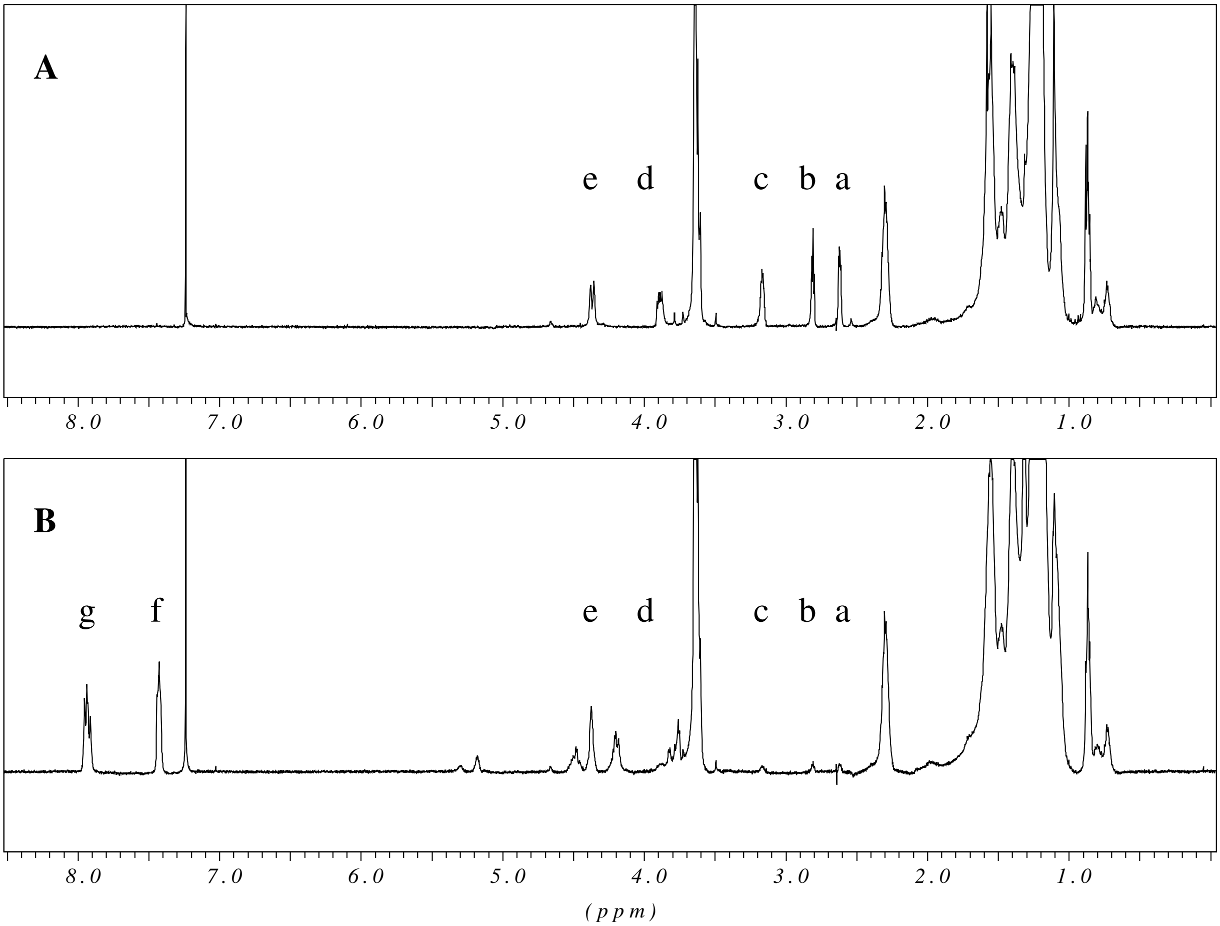
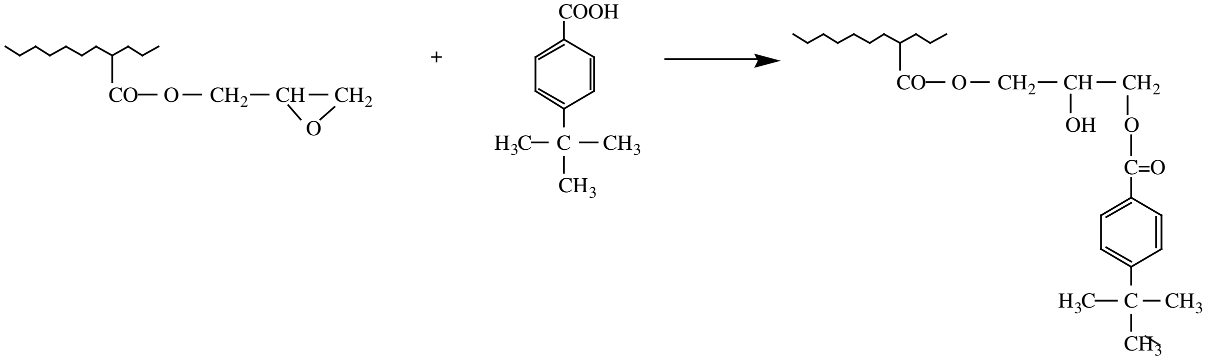


Fig. 3. ^{1}H NMR spectra of E–MA–GMA before (A) and after (B) modification of the epoxide groups with *para*-*t*-butylbenzoic acid (93% modification).



Scheme 1.

2.6. Hydrolysis

Hydrolysis of both free and grafted PBT was performed by stirring approximately 3 g of samples in a 0.05 M solution of tetrabutylammonium hydroxide in toluene/methanol (80/20; v/v) at 110°C under reflux for one night. The solution was then filtrated. The residues from hydrolysis were characterized by SEC measurements.

2.7. Rheology

The thermal stability of molten E–EA and E–MA–GMA polymers was measured using a Rheometrics ARES strain controlled rheometer equipped with a parallel plate geometry with a diameter of 25 mm and a gap of about 1.5 mm. Time sweep experiments were performed at 250°C under nitrogen atmosphere. The total test time was fixed for 30 min and the frequency was set at 1 rad/s. Care was taken to keep the experiment within the linear viscoelastic domain and the strain response was maintained below 5%.

3. Results

3.1. Partial neutralization of E–MA–GMA chains

Evidence the reaction between E–MA–GMA epoxide functions and benzoic acid molecules was obtained from IR spectroscopy and ^{1}H NMR spectroscopy. Fig. 2 shows the IR spectrum of E–MA–GMA after modification in comparison with the spectrum of the original terpolymer. A decrease in the epoxide absorbances at 911 and 844 cm^{-1} is clearly visible. In the same time, new absorption bands at 3550, 1600, 1070 and 1030 cm^{-1} are observed. The large peak at 3550 cm^{-1} is assigned to the presence of secondary hydroxyl groups on the terpolymer chains, while the other bands are assigned to *para*-*t*-butyl benzoic ester species.

Fig. 3 presents the ^{1}H NMR spectra of E–MA–GMA before and after modification. The spectra are normalized using the peak at 3.64 ppm, which corresponds to the CH_3 hydrogen of the MA unit. Virgin E–MA–GMA exhibits a very complex ^{1}H NMR spectrum due to the overlapping signals of the three constitutive monomers. The present analysis will focus only on the GMA hydrogens next to the oxirane group. The ^{1}H NMR signals are assigned as follows:

a, b, c peaks at 2.63, 2.82 and 3.18 ppm correspond to the epoxide-ring hydrogens;
d, e set of peaks between 3.7–3.8 and 4.3–4.4 ppm correspond to the methylene hydrogens next to the ester function.

Addition of *para*-*t*-butyl benzoic acid to E–MA–GMA leads to a large decrease in the intensity of the peaks a–e. New peaks are observed between 3.5 and 5 ppm and are assigned to a shift of the peaks a–e due to opening of the epoxide ring. Two distinct sets of peaks (noted f and g in Fig. 3B) appear around 7.55 and 7.9 ppm, which are assigned to benzoic acid aromatic hydrogens. These peaks were used for determining the amount of benzoic acid grafted on the E–MA–GMA. Peak at 3.64 ppm, which corresponds to the CH_3 hydrogen of the MA unit, was used as reference peak for calculation.

It is concluded that the neutralization reaction proceeds by opening of the epoxide ring and by the formation of a new ester linkage and a secondary hydroxyl groups Reaction between E–MA–GMA and *para*-*t*-butylbenzoic acid is shown in Scheme 1. The reaction appears to be fast and well controlled. We defined the modification level as the molar ratio between reacted and initial epoxide functions present in the rubber chains. As shown in Table 1, an excellent

Table 1
Efficiency of the modification procedure: comparison between calculated and experimental modification level of E–MA–GMA after reaction with *para*-*t*-butylbenzoic acid at 200°C

Calculated level (%)	Experimental level[a] (%)
20	23
40	38
50	48
60	55
80	73
100	93

[a] Determined by ^{1}H NMR.

Table 2
Composition of the insoluble fraction in the different PBT/rubber (80/20; w/w) blends (250°C and 90 rpm). Effect of solubilization in *m*-cresol at 130°C and PBT hydrolysis

Blend	% of E–MA–GMA		
	Initial	After solubilization in *m*-cresol at 130°C	After PBT hydrolysis
PBT/E–EA	100% of E–EA	–	–
PBT/93% modified E–MA–GMA	89.5	87	100
PBT/48% modified E–MA–GMA	84	86	100
PBT/E–MA–GMA	67	65	100

agreement is indeed found between the NMR modification level and the calculated value based on the amount of added acid molecules. However, complete conversion of all GMA groups was not achieved under the used conditions. For the blend study, two modified E–MA–GMA with modification level of 48 and 93% were used.

3.2. PBT/rubber (80/20) blends

3.2.1. Torque and morphology evolution

The four PBT/rubber blends investigated in this study are given in Table 2. For each blend, the evolution of the mixing torque was recorded during the blending process. As shown in Fig. 4, two different types of behavior were observed. For PBT/E–EA blends, the torque decreased monotonously after complete melting of the blend components and finally reached a plateau at long mixing times. For PBT blends with E–MA–GMA, the melting process was directly followed by a mixing torque increase, which was correlated to the epoxide content of the terpolymer, viz. the higher the epoxide content, the larger the torque increase. Finally, constant melt viscosity was reached at long mixing times.

Fig. 5 presents SEM fracture surface micrographs of the PBT/rubber blends after 8 min of mixing. For PBT/E–EA blends, rubber particles of 1–2 μm are visible. It is clear that some of the particles have been removed from the matrix by the fracture process, due to lack of interfacial adhesion. For the blends containing E–MA–GMA, smooth fracture surfaces are observed (Fig. 5b–d), indicating that interfacial adhesion was improved to a large extent.

Fig. 6a–d displays TEM micrographs of the four PBT/Rubber (80/20; w/w) blends after 8 min of mixing. The PBT/E–EA blend exhibits the coarsest morphology. The dispersed phase particles are almost spherical and the blend interface is relatively smooth. The PBT/E–MA–GMA blends exhibit a finer morphology and submicron dimensions are observed. No PBT inclusions are observed in the rubber particles. The size of the dispersed phase particles decreases as the reactivity of the E–MA–GMA increases and the finest morphology was obtained with unmodified E–MA–GMA. It is worth noting that in this case the rubber particles do not remain spherical. Indeed already after already 8 min of mixing one can see in Fig. 6b and c that some particles are of irregular shape. This effect is even more noticeable for longer mixing time. Fig. 7 presents the evolution of the number average diameter d_n of the rubber particles versus the mixing time. As a rule, the blend morphology becomes finer and more homogeneous as the mixing time increases. In contrast with the PBT/E–EA blends, morphology development is rapid in

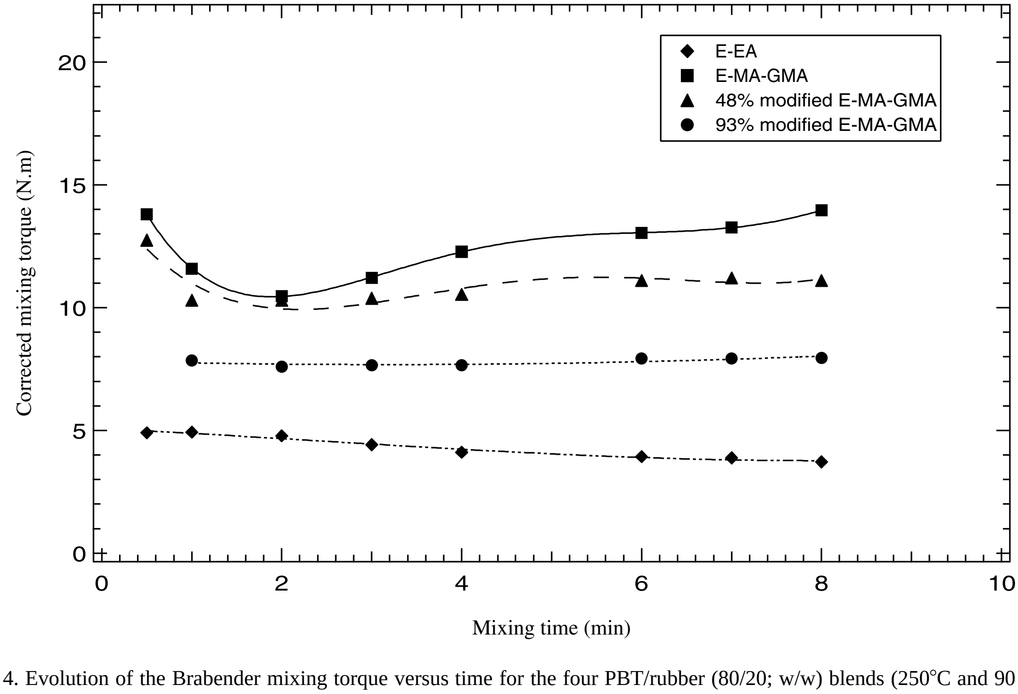


Fig. 4. Evolution of the Brabender mixing torque versus time for the four PBT/rubber (80/20; w/w) blends (250°C and 90 rpm).

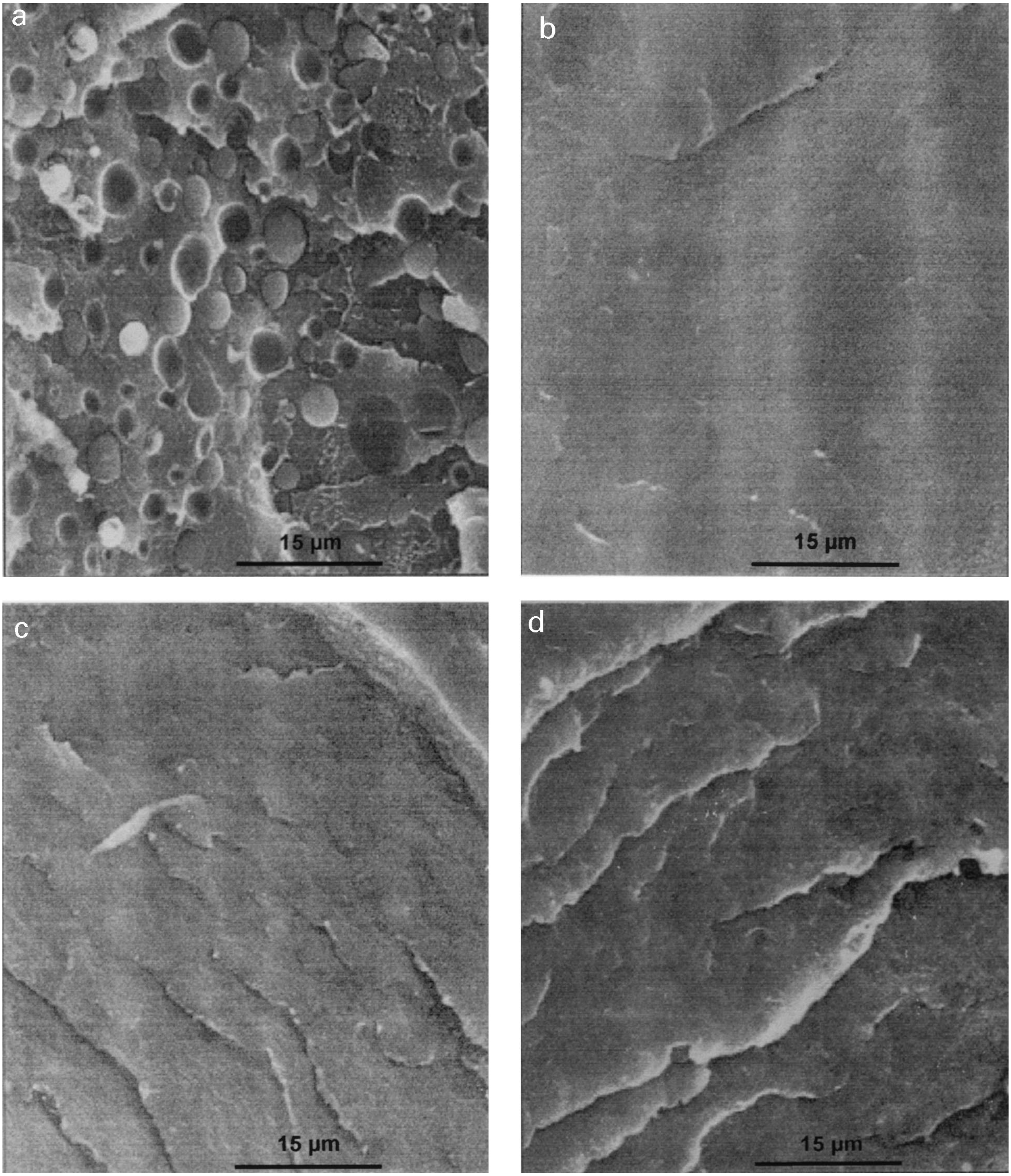


Fig. 5. SEM micrographs of fracture surfaces of PBT/rubber (80/20; w/w) blends (8 min mixing time, 250°C, 90 rpm): (a) E–EA; (b) E–MA–GMA; (c) 48% modified E–MA–GMA; and (d) 93% modified E–MA–GMA.

the case of the PBT/E–MA–GMA blends. Independently of the used E–MA–GMA, the morphology does not change anymore after 5 min of mixing. The finest morphology was obtained for the blend containing unmodified E–MA–GMA.

The electron microscopy results are in agreement with the torque measurements and suggest that interfacial reactions occur in the melt between PBT and E–MA–GMA chains leading to the blend compatibilization.

3.2.2. Fractionation

Fractionation experiments give more direct evidence for interfacial reaction. Preliminary experiments were performed in order to analyze the influence of the separation procedure on the blend components. Pure PBT, E–EA and E–MA–GMA were separately stirred for 6 h in TFA and worked up. IR and SEC analysis of the recovered PBT showed no changes, indicating that the polyester chains remain mostly unchanged by the fractionation process. According to Kenwright et al. [36], a reaction between carboxyl and hydroxyl chain ends of PBT with the solvent can not be ruled out. However, this reaction is very slow and takes only place to a small extent under the current experimental conditions.

On the other hand, IR analysis of E–MA–GMA treated with TFA revealed that, although the procedure was carried out at room temperature, trifluoroacetic acid molecules react with the epoxide groups. This is not surprising in regard with the known epoxide-carboxyl reactivity. As expected, the inert E–EA did not exhibit any reaction with the acid and therefore remained unchanged.

To check the possibility of reaction between the two polymers during the fractionation procedure, the same procedure was also applied to a physical PBT/E–MA–GMA (80/20; w/w) mixture. No insoluble fraction *C* was detected after work up and pure PBT and E–MA–GMA were recovered with an experimental error of 10%. No reaction between PBT and E–MA–GMA occurs at the fractionation temperature (25°C). However, a fast conversion of the epoxide groups of the E–MA–GMA is noticed as a result of the side reaction with the solvent.

The separation procedure was also applied to the PBT/E–EA blend. No insoluble fraction was recovered. Moreover, amount of free PBT that measured after separation was larger than 79 wt%, which is very close to the PBT concentration introduced in the mixture (80 wt%). In the same way, amount of free E–EA recovered at the end of the separation procedure was close to 20 wt% (experimentally 18.5 wt% after 18 min of mixing).

Evolution of the concentrations of the fractions *P*, *R* and *C* for PBT/E–MA–GMA blends as a function of the mixing time is presented in Fig. 8a, b and c, respectively. In Fig. 8a, the amount of free PBT decreases rapidly. In all cases, a plateau seems to be reach at long mixing time. The decrease is more noticeable for higher rubber epoxy contents. Fig. 8b shows that the concentration of free E–MA–GMA decreases also rapidly with increasing mixing time and falls rapidly to zero for blends containing modified E–EA–GMA. In Fig. 8c, two distinct behaviors are clearly visible. For blends containing modified E–MA–GMA, the amount of fraction C increases very rapidly and reaches a plateau after 8 min of mixing. The equilibrium concentration is more important with the 48% modified E–MA–GMA than with the 93% modified E–MA–GMA. A slower evolution is observed when pure E–MA–GMA was used as rubber phase.

The chemical composition of the different fractions was established by Raman spectroscopy. Fractions *P1* and *P2* appeared to be pure PBT. Fraction *R* was identified to be pure E–MA–GMA. No traces of PBT were detected in this

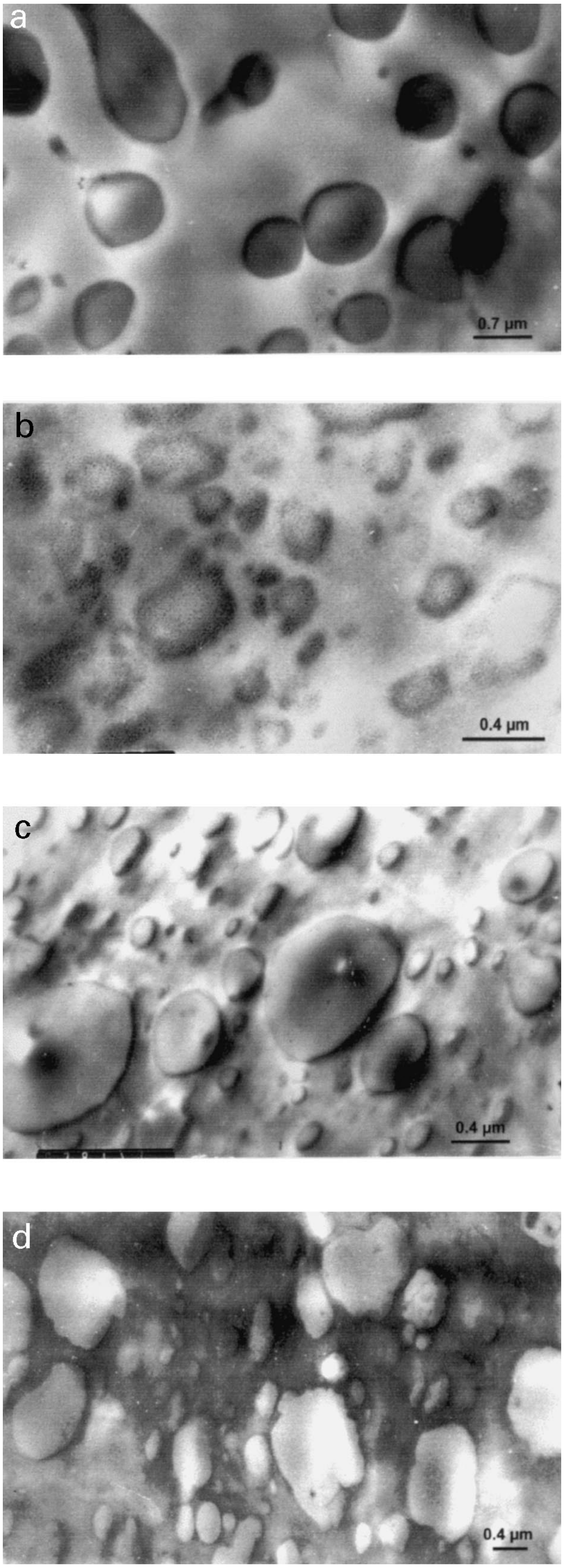


Fig. 6. TEM micrographs of PBT/rubber (80/20; w/w) blends (8 min mixing time, 250°C, 90 rpm): (a) E–EA; (b) E–MA–GMA; (c) 48% modified E–MA–GMA; and (d) 93% modified E–MA–GMA.

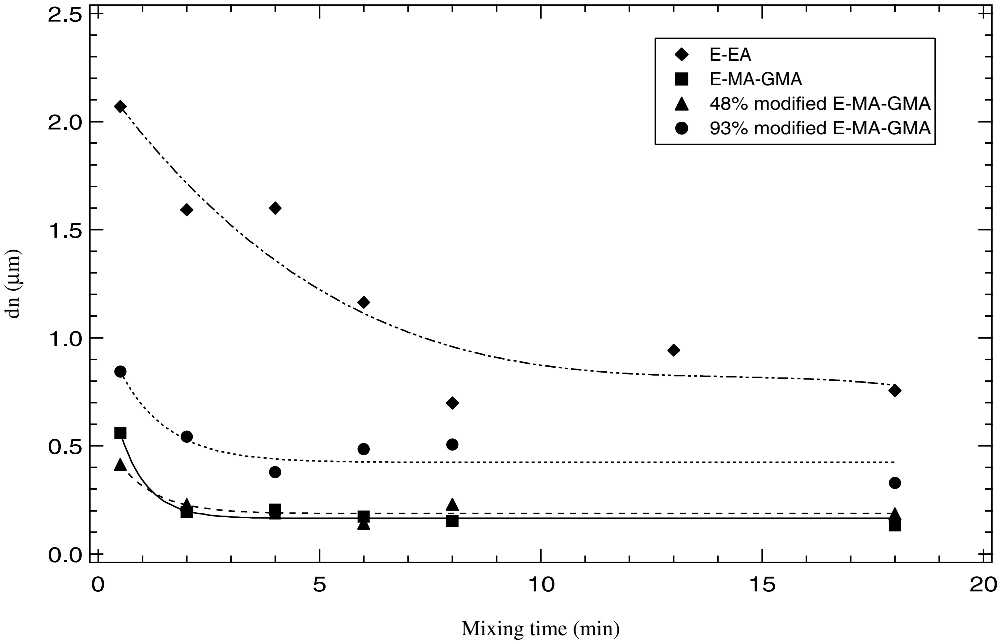


Fig. 7. Evolution of dispersed phase domain size as a function of mixing time for PBT/rubber (80/20; w/w) blends (250°C, 90 rpm, Brabender plastograph).

fraction. In contrast, fraction *C* contains both PBT and E–MA–GMA (Fig. 9). The PBT content of fraction *C* increases when the mixing time and/or the rubber epoxide groups concentration increases.

It is also worth to compare the time scale of the different observations. Image analysis showed that for compatibilized blends morphology does not change after 6 min of mixing whatever the rubber phase (Fig. 7). As we can see in Fig. 8, evolution of the different fractions is rather different. For blends containing modified E–MA–GMA, amount of free PBT reaches a plateau after approximately 8 min and amount of free rubber decreases up to 0 wt% after 10 min. Meanwhile amount and composition of *C* fraction reach a constant value after 8 min. These trends are especially obvious for the 48% modified rubber. Blends containing unmodified E–MA–GMA exhibit a different behavior. The free PBT concentration decreases continuously and tends to a plateau at long mixing times while the concentration of free E–MA–GMA (fraction *R*) decreases more slowly than for modified rubbers. Meanwhile, insoluble fraction *C* increases continuously and becomes richer and richer in PBT.

For all blends processed for 8 min, fractions *C* were submitted to solubility and hydrolysis tests. First the solubility in *m*-cresol, a common solvent of both PBT and E–MA–GMA at 130°C, was investigated. Care was taken to avoid any additional reaction in solution between the two polymers. Pure E–MA–GMA was dissolved in *m*-cresol, precipitated and washed. IR analysis revealed that solvent molecules react with the epoxide functions grafted on the rubber chains during the solubilization. We assume therefore that further reaction between PBT and E–MA–GMA during the solubility tests can be excluded as a result of the high concentration and the high diffusivity of *m*-cresol. This was confirmed by dissolving a PBT/E–MA–GMA (80/20; w/w) physical mixture under the same conditions. No trace of reaction between PBT and the rubber was observed by both IR and Raman spectroscopies.

Independently on the type of the PBT/rubber blends, all the *C* fractions are insoluble after one hour in *m*-cresol. The various fractions were recovered after stirring by filtration, washing and drying. The composition was analyzed by Raman spectroscopy (Table 2) and compared to the initial composition before solubilization. It is clear that stirring in *m*-cresol did not modify the composition of the fraction. These observations confirm that the *C* fractions only contain crosslinked material.

In a second step hydrolysis of the PBT present in the *C* fractions was carried out. Table 2 compares the initial compositions of the three different fractions *C* with those measured after hydrolysis. Obviously, all PBT was completely removed and only rubber remained. The hydrolyzed residues were also submitted to a solubility test in hot chloroform. Once again, the fractions remained insoluble independently of the rubber used.

3.2.3. Rheological measurements

The thermal stability of the different rubbers used in this study was studied by rheological measurements. At this stage, it is important to note that these measurements were performed on each different rubber phases and not on the PBT/rubber blends. Fig. 10 shows the evolution of the dynamic shear viscosity as a function of time at 250°C for E–EA copolymers and for (modified) E–MA–GMA terpolymers. Two types of behaviors can be observed. E–EA and E–MA–GMA have a low melt viscosity, which

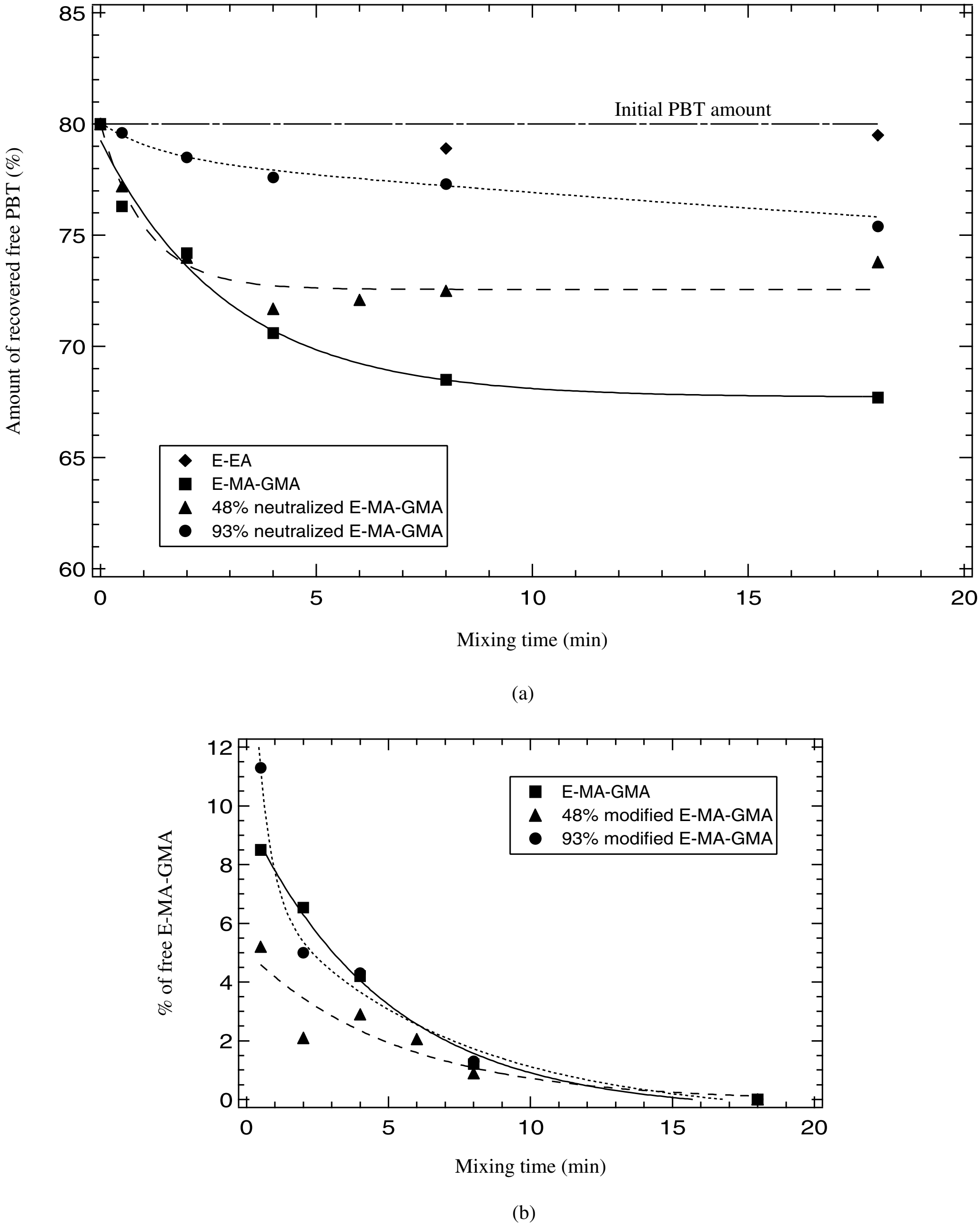
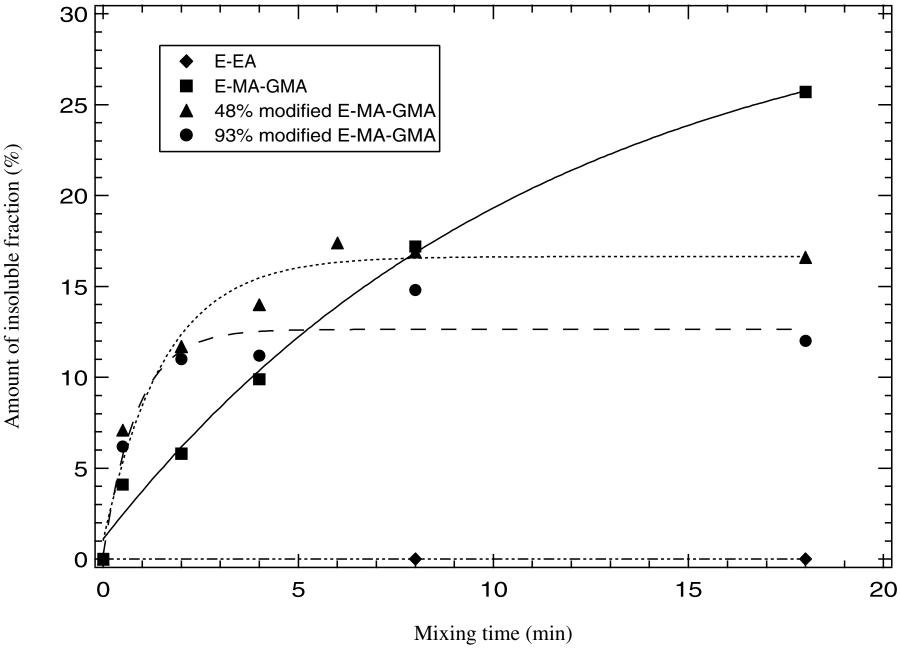


Fig. 8. (a) Free PBT concentration after separation for PBT/E–MA–GMA (80/20; w/w) blends as a function of the mixing time. (b) Free E–MA–GMA concentration after separation for PBT/E–MA–GMA (80/20; w/w) blends as a function of the mixing time. (c) Insoluble fraction concentration after separation for PBT/E–MA–GMA (80/20; w/w) blends as a function of the mixing time.

stays constant for 30 min at 250°C. We also observed that both storage and loss moduli, G' and G'' remain more or less constant although a small increase with time is observed (Fig. 11). It is worth noting that G' remains lower than G'' along all the experiment. For the modified E–MA–GMA, the starting materials already exhibit higher viscosities than the parent polymer. Moreover, a large viscosity increase is observed throughout the experiment. Increase is more noticeable for the 48% modified E–MA–GMA. More interesting is the evolution of G' and G'' as a function of the curing time (Fig. 11). Pronounced increase in G' and G'' are observed with modified E–MA–GMA. In these cases, G' is larger than G'' and the difference between the two quantities increases continuously. In other words, the melt becomes more and more elastic as the time increases.

4. Discussion

PBT/E–EA (80/20; w/w) blends exhibit general features of uncompatibilized blends. After 18 min mixing, no evidence of transesterification reaction between PBT and



(c)

Fig. 8. (*continued*)

E–EA was found. A cohesive fracture (Fig. 5a) and a coarse unstabilized morphology (Fig. 7) were both observed. Moreover, no grafted copolymer was recovered after blend fractionation. Such results can be explained by the used blending conditions, which are less severe than those of the Gravalos's study [14]. Moreover, the ratio of PBT hydroxyl and E–EA ester concentrations used in this study is much smaller than that used in the Gravalos's study. However, the occurrence of reactions between PBT and E–EA can not be excluded for longer mixing times, indeed the morphology becomes finer as the mixing time increases.

In contrast with PBT/E–EA blends, it is clear that blend compatibilization is observed for PBT/E–MA–GMA blends. This conclusion is supported by the mixing torque increase (Fig. 4), the adhesive fracture (Fig. 5b–d) and the fine and stabilized morphology (Fig. 7). These results suggest that a (E–MA–GMA)–PBT graft copolymer was formed in situ due to reaction of carboxyl and/or hydroxyl

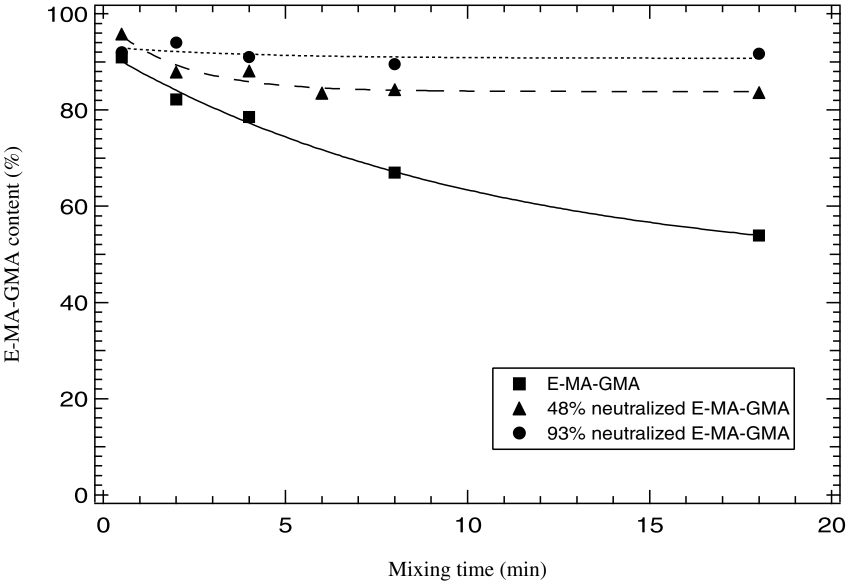


Fig. 9. Composition of insoluble fraction *C* after separation for PBT/E–MA–GMA (80/20; w/w) blends as a function of mixing time.

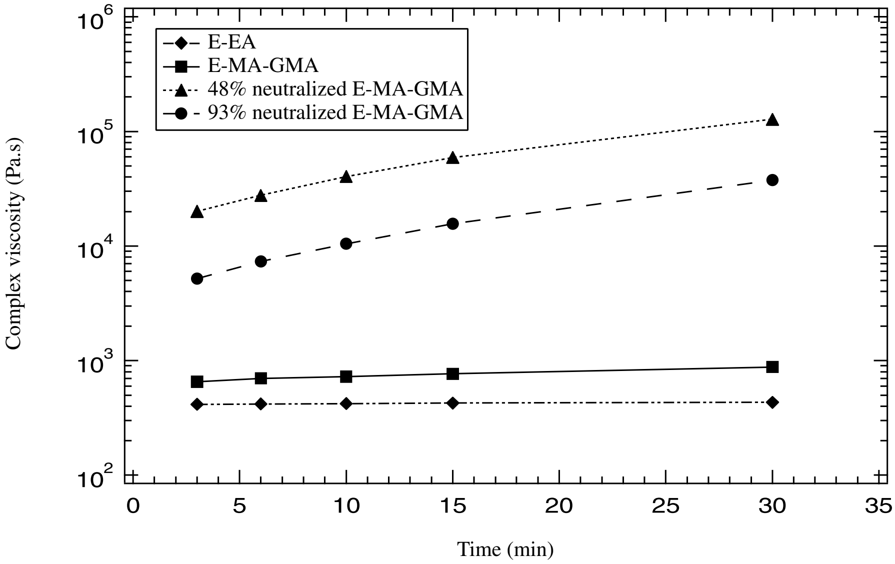


Fig. 10. Thermal stability of acrylate rubbers as studied by evolution of complex viscosity as a function of time at 250°C.

PBT end groups with the E–MA–GMA epoxide functions. These reactions have already been postulated by several authors [20–30], however, few studies provide conclusive experimental evidences for such reactions. The results obtained from the fractionation procedure clearly prove that indeed such interfacial reactions take place during the blending process.

To explain our results we assume, as summarized in Scheme 2 (description of the reactions occurring during processing of PBT/E–MA–GMA (80/20; w/w) blends at 250°C.), that four reactions can take place simultaneously in the melt. Reactions 1 and 2 represent interfacial reactions between the epoxide groups of the rubber chains and the PBT carboxyl and hydroxyl end groups, respectively. These reactions have already been reported by several authors [20–30] and proceed by epoxide ring opening. As a consequence, a new bond and a secondary hydroxyl group are formed. According to some studies [20,26] reaction 1 proceeds slower than reaction 2. The extent of both reactions depends on the concentrations of reactive species and is, therefore, influenced by the concentration of epoxide groups of E–MA–GMA. However, such interfacial

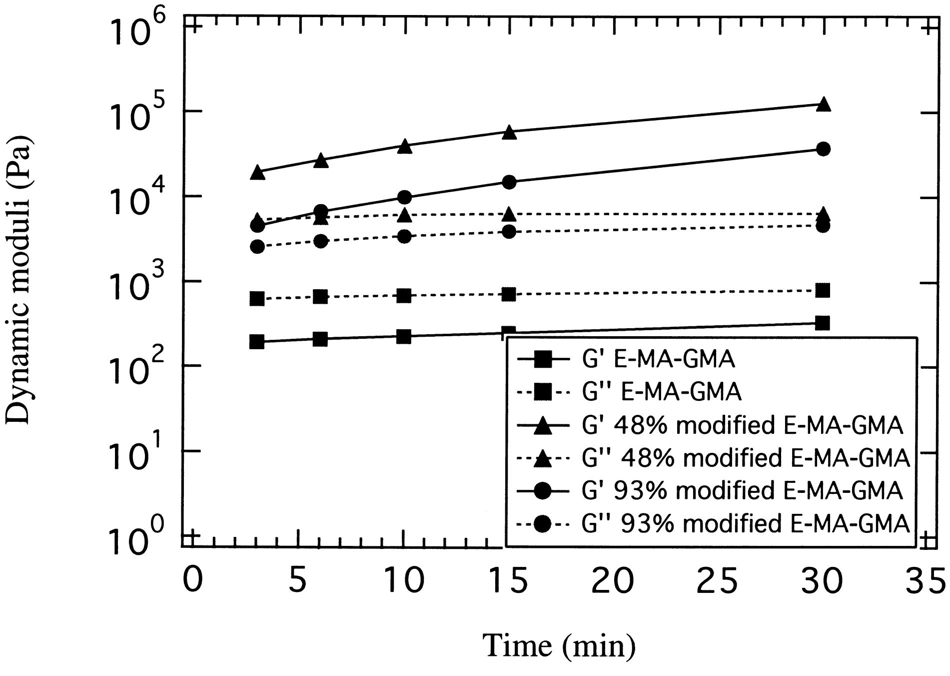
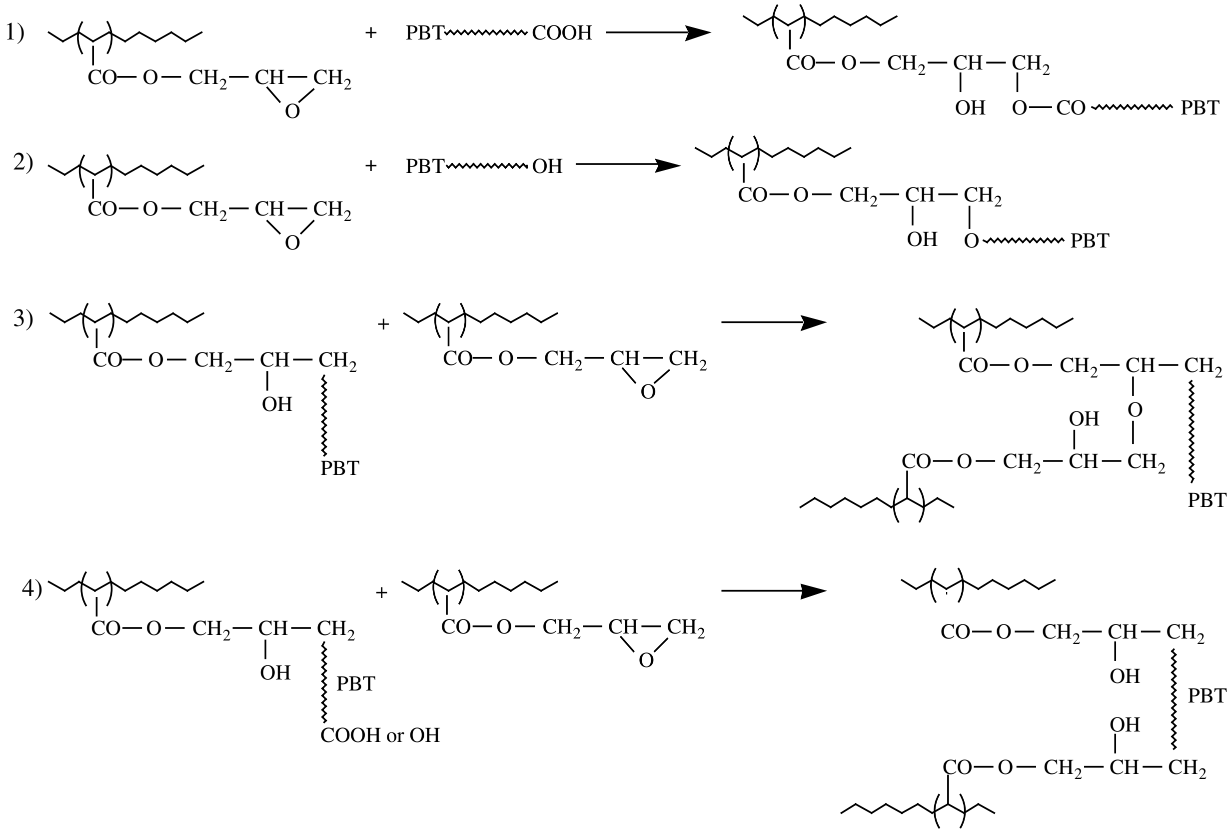


Fig. 11. Evolution of storage and loss moduli as a function of time for acrylate rubbers at 250°C.



Scheme 2.

reactions do not explain the insolubility of the recovered fractions *C*. Reaction 3 involves a crosslinking reaction between the rubber chains. Indeed due to the formation of secondary alcohol functionalities, E–MA–GMA chains can react together and form a network structure. In contrast with reactions 1 and 2, which occur at the blend interface, reaction 3 takes place in the rubber phase itself. This kind of reaction is well known for the curing of epoxy resins [37,38], but has received few attention in the case of toughened thermoplastics containing epoxide-functionalized impact modifiers. Reaction 4 suggests that PBT chains may act as crosslinking agents between E–MA–GMA terpolymer chains. This is a direct consequence of the PBT difunctionality. Both carboxyl and hydroxyl groups are known react with an epoxide groups. In contrast with reaction 3, this second crosslinking reaction has already been reported by several authors [20,24,39]. Since it will occur mainly at the interface, it probably proceeds slower than reaction 3.

Scheme 2 is very useful to explain the observed results for PBT/E–MA–GMA (80/20; w/w) blends. Reactions 1 and 2 postulate for the formation of (E–MA–GMA)–PBT graft copolymers at the blend interface. This can explain the observed torque evolution as well as the microscopy observations and the fractionation results. (E–MA–GMA)–PBT graft copolymers act indeed as compatibilizers promoting blend viscosity increase (Fig. 4), interfacial adhesion (Fig. 5b–d) and fine stable dispersion of the rubber phase in PBT (Fig. 7). Both reaction rates (1 and 2) are proportional to the reactive group concentrations present at the interface. It is therefore obvious that, as observed in Figs. 8a and 9, amount of grafted PBT increases with time and with the rubber epoxide content. Although reaction 2 is slower than reaction 1 [20,26], the performed experiments do not allow to discard one reaction from the other. E–MA–GMA reactivity towards carboxyl and hydroxyl groups has been studied by using model compound and the results will be presented in another paper.

The rheological behavior of the modified E–MA–GMA (Figs. 10 and 11) is a direct consequence of reaction 3. In contrast with pure E–MA–GMA, modified E–MA–GMA contains a large amount of secondary hydroxyl groups as a result of the reaction between epoxide functions and *para-t*-butylbenzoic acid. The –OH concentration is equivalent to the amount of added acid. At sufficiently high temperatures, reaction 3 will occur for both modified E–MA–GMA resulting in a large increase of the melt viscosity and elasticity (Figs. 10 and 11). As the reaction rate is proportional to the concentrations of both epoxide and hydroxyl groups, it is not surprising to observe the larger viscosity drop for the 48% modified E–MA–GMA. In pure E–MA–GMA, absence of hydroxyl groups inhibits such crosslinking reaction.

Crosslinking of the rubber chains during melt blending also explain the insolubility of the different *C* fractions. The *C* fractions consist of rubber–PBT graft. In previous studies [20,24,39], reaction 4 was considered to be the only possible crosslinking reaction. Reaction 3 was either not considered or neglected. However, such assumptions have not been confirmed by experimental evidences. According to the rheological experiments performed on the modified rubber phase (and hence in absence of PBT), crosslinking between E–MA–GMA chains via reaction 3 is important. Moreover, since the *C* fractions remain crosslinked after hydrolysis of PBT, we must assume that reaction 4 is not predominant. In this latter case, network structure should have been destroyed by the hydrolysis procedure resulting in free soluble E–MA–GMA chains. However, presence of such reaction can not be excluded.

This reaction scheme (Scheme 2) explains the fractionation results in detail. On the one hand, the amount of free PBT chains decreases due to interfacial reactions 1 and 2. The rate of the two reactions is proportional to the concentration of reactive groups at the interface. These concentrations are obviously greater for pure E–MA–GMA than for the modified rubbers. This explains why amount of free PBT decreases continuously and in a greater extent in blends containing unmodified E–MA–GMA (Fig. 8a). On the other hand, the crosslinking reaction leads to a decrease of free rubber and an increase of the insoluble fraction. As modified E–MA–GMA already contain secondary hydroxyl groups, the crosslinking reaction will occur immediately during the first minutes of mixing, especially for the 48% modified E–MA–GMA, which exhibits high concentrations of both hydroxyl and epoxide groups. As a result, amount of free rubber will disappear rapidly and amount of fraction *C* will increase drastically (Fig. 8b and c). In the meantime, the concentration of epoxide groups at the interface also decreases rapidly. This could explain why the amount of free PBT and the composition of fraction *C* reach a plateau in case of PBT/modified E–MA–GMA blends (Fig. 8a and 9). For unmodified terpolymer, the network formation is directly correlated to the reactions 1 and 2, which generate the necessary secondary hydroxyl groups. As a result, amount of free rubber decreases more slowly up to 0 wt% (Fig. 8b) and amount of fraction *C* increases more progressively (Fig. 8c). Absence of plateau for the evolution of the amount of free PBT and for the composition of fraction *C* could be due to the higher epoxide initial concentration at the interface and to the fact that reaction 3 is delayed of some minutes.

Finally, it is worth noting that two different blending mechanisms should be distinguished depending on whether pure or modified E–MA–GMA was used. For PBT blends with the modified terpolymers, the competition between compatibilization of the blend and crosslinking of the dispersed phase will take place in the melt immediately. Interfacial reactions 1 and 2 lead to formation of graft copolymer molecules at the interface, which promotes fine dispersion of the rubber and inhibits coalescence. In the meantime, reaction 3 proceeds throughout the whole E–MA–GMA particles. This crosslinking reaction affects both dispersion and coalescence processes. As a result of crosslinking, the rubber particles become more viscous, more elastic and less deformable. Finally, homogeneously crosslinked E–MA–GMA particles are obtained which prevents coalescence and explains the non-spherical shape of the dispersed particles and the rough interface observed at long mixing time.

For PBT blends with unmodified terpolymer, competition between the two types of reactions will be somewhat delayed. In the first stages of mixing, compatibilization occurs through interfacial reactions 1 and 2. This generates secondary hydroxyl groups on the rubber chains close to the interface. At that time only reaction 3 starts and proceeds progressively from the interface to the core of each dispersed particle. The morphology development is thus more complex and the dispersed phase particles will probably have a large heterogeneity and may even have a core–shell type structure. The core will be formed by virgin E–MA–GMA surrounded by crosslinked E–MA–GMA. The thickness of each layer should be intimately correlated to the processing conditions.

This situation can even be more complicated if we assume that reaction 4 can also occur in some extent during the blending process. Indeed, reaction 4 could result in crosslinking not only of the interfacial region but also of the entire material.

The classical concepts of reactive blending are not sufficient for explaining the PBT/E–MA–GMA blend behavior. The final blend morphology appears to be governed by a very complex processing/composition interrelationship. Further experiments are currently performed to better understand this relationship and control the blend morphology and subsequently the blend properties.

5. Conclusions

A set of E–MA–GMA terpolymers containing various amounts of epoxide functions has been synthesized by partial modification of commercial E–MA–GMA with *para-t*-butylbenzoic acid in the melt. The modification reaction appears to be fast. However, complete modification of E–MA–GMA could not be achieved.

In a second step, the modified E–MA–GMA has been used as impact modifier for PBT-rich blends. Pure E–EA copolymer and E–MA–GMA terpolymer have also been used as dispersed phase. The different blends were analyzed and compared in terms of morphology and amount and composition of the copolymers formed at the interface as a function of time.

PBT/E–EA (80/20; w/w) blends exhibit general features of incompatible polymer blends. Low interfacial adhesion and coarse unstable morphology were observed for short mixing times. No trace of interfacial reaction between

PBT and rubber chains has been found from the separation procedure. Interface between the blend components appears to be smooth and well defined.

PBT/E–MA–GMA (80/20; w/w) blends display a fine stabilized but complex morphology, which is intimately correlated to the functionality of the rubber chains. For several blends, the dispersed phase particles are not spherical and the interface is rough. Two types of competitive reactions are identified and shown to take place simultaneously during melt blending, viz. 1) compatibilization reactions which involve reactions between E–MA–GMA epoxide functions and both hydroxyl and carboxyl PBT end groups and 2) crosslinking of the dispersed rubber phase. Previous studies [17,21,38] have considered such crosslinking to be a direct consequence of the difunctionality of PBT. The results presented in this work show that this reaction is not predominant during processing. Crosslinking mainly takes place through reaction between epoxide groups and secondary hydroxyl species present on neighboring E–MA–GMA chains either as a result of modification before blending or as a result of reaction with PBT during blending. The modification level of the rubber chains and the processing conditions governed competition between the two types of reaction. The existence of such a reaction scheme exerts a considerable effect on the morphology development and probably also on the final blend properties.

This work emphasizes the importance of the nature of the functional groups used for in situ compatibilization since the conclusions can be extended to any polymer blend containing epoxide-functionalized polymers. A thorough characterization of the interfacial reaction formed during reactive blending is therefore of prime importance for a better understanding of the product behavior of such polymer blends.

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