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Particle-in-particle morphology in reactively compatibilized poly(butylene terephthalate)/epoxide-containing rubber blends

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Abstract

The possibility to generate particle-in-particle morphology by controlling blending sequence has been investigated for reactive processing of poly(butylene terephthalate) (PBT) with ethylene-methyl acrylate-glycidyl methacrylate (E-MA-GMA) random terpolymer. Composite droplet morphology consisting of a PBT matrix, a E-MA-GMA dispersed phase and PBT sub-inclusions is spontaneously formed upon melt mixing due to the coalescence of poorly stabilized E-MA-GMA particles. The development and dimensions of this complex morphology is mainly controlled by the relative kinetics between the coalescence process and the chemical reactions occurring during the melt processing. This can be influenced by an adequate adjustment of various blending parameters such as blend composition, PBT viscosity and rubber phase reactivity. The generation of particle-in-particle morphology can also be forced by using a two-step blending sequence. In this latter case, blend morphology consisting in PBT matrix with PBT/E-MA-GMA core-shell particles can be generated.

Keywords: Polymer blends; Particle-in-particle morphology; Crosslinking

1. Introduction

During the last decades, polymer blending has been a major path to tailor properties of polymeric materials [1,2]. This strategy represents indeed a rapid and economic alternative to the synthesis of new polymers. As polymers usually exhibit weak interactions, immiscible multiphase systems are formed. The final properties of such materials are intimately related to the properties of the initial components, the blend composition and the phase morphology. The most frequent blend morphology is the classical matrix/droplet arrangement. Such dispersions are nowadays extensively used for the toughening of brittle thermoplastics by an elastomer [2].

In the recent years, there has been a growing interest for the control by melt mixing of a more complex structure, the so-called 'particle-in-particle' morphology [3–10]. This microscopic phase structure is composed of three parts: two distinct phases with inclusions of one phase within the other one, i.e. subinclusions. Depending on the concentration of the subinclusions, the blend morphology is known as composite droplet morphology or as core-shell structure (Fig. 1). Until now, the origin and the effects of particle-in-particle morphology have been only scarcely analyzed.

In case of non-compatibilized polymer blends, the development of particle-in-particle morphology has been reported by several authors [3–7]. For A/B/C ternary systems, subinclusions formation can be interpreted on the basis of the interfacial energy differences between the blend components, i.e. the spreading coefficient approach [3,4]. As a rule for a three-component system, the particle, which forms the highest interfacial tension with the matrix tends to get included the other dispersed phase in order to shield the unfavorable interactions [3]. Recently, Reignier et al. has demonstrated for HDPE/PS/PMMA blends that the encapsulation process occurs very early in the mixing process [5]. Manipulation of the dispersed phase internal structure from small PMMA subinclusions in large PS particles to a PS/PMMA core-shell structure was achieved upon decreasing the PS/PMMA ratio. In case of binary polymer blends, particle-in-particle morphology can also be spontaneously

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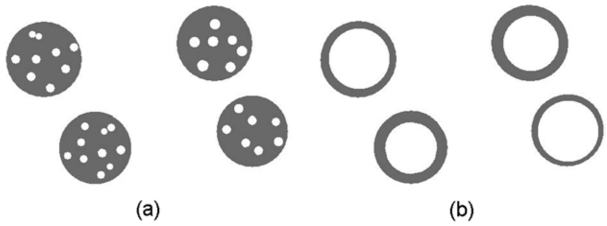


Fig. 1. Particle in-particle morphologies in immiscible polymer blends: (a) composite droplet and (b) core-shell microstructures.

generated when blending polymers near the phase inversion region [6,7] or by selectively imposing phase inversion and subsequently controlling the time of mixing [7]. In all cases, both the concentration and the stability of the subinclusions seem to increase with the melt viscosity of the dispersed phase.

The formation of particle-in-particle morphology has also been reported in compatibilized polymer blends [8,9]. In most cases, the complex microstructure is assumed to develop in the early stages of the mixing, before the phase morphology is stabilized. The melting rate of the reactive polymers has a strong effect on the development of the phase morphology. When the minor phase melts prior to the major one, very small particles of the major phase are trapped within the minor phase [9]. In a recent paper, Pagnoulle and Jérôme [10] have demonstrated that, depending on the mixing sequence and on the grafting kinetics, the particle-in-particle morphology can be forced or occurs spontaneously during the compatibilization of modified styrene-co-acrylonitrile copolymers (SAN) with modified ethylene-propylene-diene rubber (EPDM). The authors suggest that, during in situ compatibilization, subinclusions can be spontaneously generated by coalescence of poorly stabilized dispersed particles during the later stages of mixing, i.e. when coalescence dominates over the melting/softening process. The occluded particles are stabilized by interfacial reaction between the subinclusions and the dispersed phase. As a rule, higher reaction rate tends to reduce the coalescence and therefore the formation of subinclusions. According to the authors' conclusions, the kinetics of interfacial grafting is the main parameter controlling the spontaneous formation of composite droplet morphology. Moreover, particle-in-particle morphology can also be forced by first dispersing, a part of SAN in the EPDM, followed by addition of large amounts of SAN, which triggers phase inversion. In contrast to the previous approach, faster reaction is favorable to the retention of occluded SAN. In this case, to ensure good final properties, the blending sequence must be adjusted to promote interfacial reaction at the interface between the matrix and the dispersed particles [10]. From this latter study, it is clear that the kinetics of interfacial grafting have a large influence on the development of particle-in-particle morphology in compatibilized polymer blends.

In this paper, the possibility to generate particle-in-particle morphology during reactive compatibilization of poly(butylene terephthalate) (PBT) with ethylene-methyl acrylate-glycidyl methacrylate (E-MA-GMA) random terpolymer has been investigated. As previously described [11], this system exhibits a very complex reactivity since two competitive reactions take place during melt processing, viz. compatibilization and rubber phase crosslinking. In addition to the influence of the blending sequence, the effect of several blending parameters such as phase viscosity and phase reactivity has been studied using different PBT and E-MA-GMA grades. In contrast with previous studies available in the literature, the presented results demonstrated that the formation of particle-in-particle morphology does not depend strongly on the grafting kinetics but is rather intimately related to the relative kinetics between the coalescence process and the chemical reactions occurring during processing. In other words, composite droplet morphology can be generated spontaneously almost independently of the kinetics of interfacial grafting if the kinetics of coalescence process between the dispersed phase particles is fast enough.

2. Experimental

2.1. Materials

The different PBT grades were supplied by DSM. Their main characteristics such as acid and hydroxyl chain end concentrations and number-average molecular weight are given in Table 1. Each PBT grade is identified by its molecular weight and its carboxyl chain end content.

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. The number-average and weight-average molecular weight are 10 and 31 kg/mol, respectively. According to these values, the average number of epoxide functions per terpolymer chain can be calculated at around 5–6 functions per chain.

A modified E-MA-GMA grade was obtained by reacting 48% of the epoxide groups with calculated amount of *para-t*-butylbenzoic acid according to a previously described procedure [11].

2.2. Melt blending

Prior to melt blending, all materials were dried for one night at 25 °C under vacuum. Although normal PBT drying conditions are 125 °C under vacuum, preliminary experiments comparing both drying conditions have not shown any effect on PBT degradation and on the compatibilization for experiments performed in the internal mixer.

PBT/rubber blends were prepared at 250 °C using a Brabender WE 50H internal mixer. The atmosphere in the mixer was controlled by purging with nitrogen gas. The mixing process was conducted in two different ways:

1. PBT pellets were molten for 1 min at 30 rpm prior to addition of rubber pellets. Immediately after introduction

of the rubber, 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 8 min. Three PBT grades, i.e. High MW–High acid PBT, Low MW–High acid PBT and Low MW–Low acid PBT, and two E-MA-GMA grades, i.e. E-MA-GMA and 48% modified E-MA-GMA were used, respectively. The blend composition was fixed at 20, 40 and 50 wt% rubber, except for High MW–High acid PBT/E-MA-GMA blends (20, 40 and 45 wt% E-MA-GMA).

2. A two-step reactive procedure consisted in the prior melt blending of PBT with E-MA-GMA at various weight compositions, i.e. PBT/rubber 60/40, 20/80 and 10/90, w/w. The processing conditions were similar to the one used for the blending sequence 1. In a second step, the High MW–High acid PBT/E-MA-GMA pre-mixture was mixed with a calculated amount of neat High MW–High acid PBT in order to comply with the final PBT/rubber 80/20 weight composition (8 min, 90 rpm, 250 °C).

At the end of the mixing experiments, samples were rapidly withdrawn from the mixing cavity and quenched in liquid nitrogen in order to stop the chemical reactions and to freeze in the morphology.

2.3. Microscopy

The blend morphology was examined by transmission electron microscopy (TEM). Samples were ultra-microtomed in thin films of approximately 90 nm thickness at −80 °C in order to avoid deformation of the dispersed phase particles. The microtomed cuts were stained for 6 min under RuO_4 vapor before examination in a Philips EM 301 microscope.

2.4. Disintegration tests

For the disintegration test, hot chloroform ($CHCl_3$) was used as the selective solvent of the rubber phase while PBT was selectively dissolved at room temperature by trifluoroacetic acid (TFA). The PBT/rubber blends were submitted to dissolution in the two solvents under moderate stirring for 12 h. For blends consisting of a matrix with dispersed particles, selectively dissolving the matrix away causes a complete disintegration of the blend material and a milky emulsion is then obtained. On the other hand, using a selective solvent of the dispersed phase does not alter the macroscopic structure of the material. For some blends, both solvents were used without disintegration of the blend material. This can be seen as an indication of phase co-continuity.

2.5. Rheology

The rheological properties of molten PBT and E-MA-GMA polymer were 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. Frequency sweep experiments were performed at 250 °C under nitrogen atmosphere. The frequency was ranged from 0.1 to 100 rad/s. Care was taken to keep the experiment within the linear viscoelastic domain. For this purpose, the strain response was maintained below 5%.

3. Results and discussion

3.1. Rheological properties

Evolution of the shear viscosity as a function of the frequency at 250 °C is reported in Fig. 2 for the pure components. Both Low MW–High acid PBT and High MW–High acid PBT exhibit almost a Newtonian behavior. In agreement with the molecular weight data presented in Table 1, the melt viscosity of Low MW–High acid PBT is significantly lower than the viscosity of High MW–High acid PBT. The rheological behavior of Low MW–Low acid PBT was not measured but it is assumed to be very close to Low MW–High acid PBT, since both PBT grades should exhibit very close molecular weight and structure (Table 1). In contrast with the PBT's, the viscosity of E-MA-GMA terpolymer displays a Newtonian plateau at low frequencies and a power-law, i.e. shear-thinning, behavior at high frequencies.

3.2. Composite droplet morphology

The possibility to generate particle-in-particle morphology by reactive mixing of PBT with E-MA-GMA was first evaluated using the one-step melt blending procedure. As described elsewhere [11], blends of PBT with epoxide-containing rubber exhibit a very complex reactivity since two competitive reactions take place during melt processing, viz. compatibilization and rubber phase crosslinking the reactive processing. This results in a complex processing-morphology interrelationship. In order to modify both the rate of interfacial grafting and the kinetics of the rubber

Table 1
Characteristics of the PBT grades

Grade	[–COOH] (μeq/g)	[–OH] (μeq/g)	η_r in *m*-cresol	M_n (kg/mol)
Low MW–High acid PBT	45	66	1.85	16.1
Low MW–Low acid PBT	7	109	1.85	16.1
High MW–High acid PBT	49	31	1.98	19.8

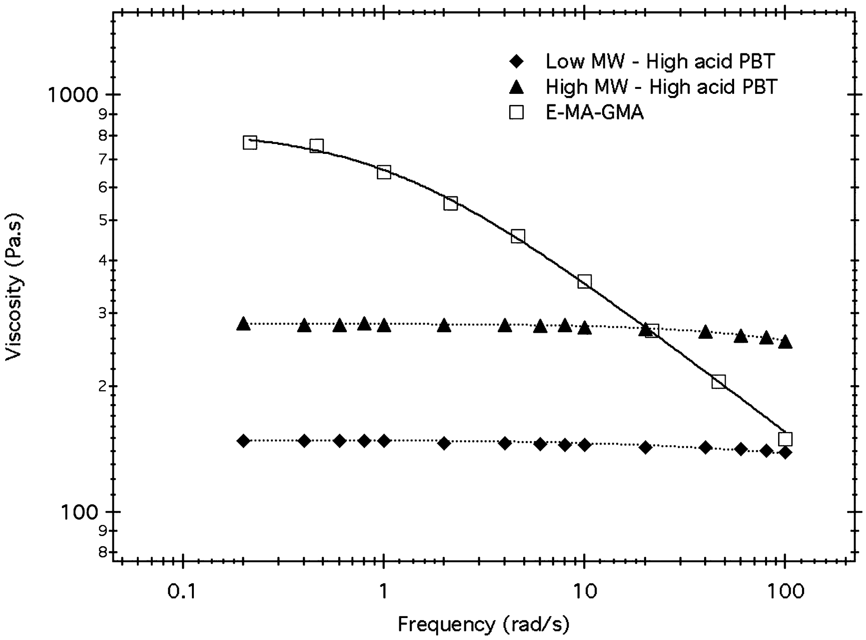


Fig. 2. Complex shear viscosity versus frequency of the blend components at 250 °C.

phase crosslinking, three PBT samples with different molecular weights and acid concentrations and two E-MA-GMA grades with different epoxy content were used, respectively. The different systems were analyzed by TEM and the results are presented in Figs. 3–6.

3.3. PBT/E-MA-GMA reactive blends

Fig. 3 displays the evolution of the blend morphology as a function of the rubber content for High MW–High acid PBT/E-MA-GMA blends. Whatever the blend composition, no evidence of particle-in-particle morphology is observed. The phase morphology evolves from dispersed E-MA-GMA particles in the High MW–High acid PBT matrix at 20 and 40 wt% E-MA-GMA (Fig. 3(a) and (b)) to a co-continuous two-phase morphology at 45 wt% rubber (Fig. 3(c)). According to a previous study [12], this latter composition corresponds to the phase inversion point.

In contrast, for blends containing Low MW–High acid PBT and Low MW–Low acid PBT, composite droplet morphology consisting in E-MA-GMA particles with PBT subinclusions is spontaneously generated (see Figs. 4 and 5, respectively). The formation of Low MW PBT sub-inclusions is related to the rubber weight fraction, since no composite E-MA-GMA particles are detected for low rubber content, i.e. 20 wt% rubber (Figs. 4(a) and 5(a)). This complex microstructure is also intimately related to the PBT reactivity. PBT sub-inclusions appear for lower rubber

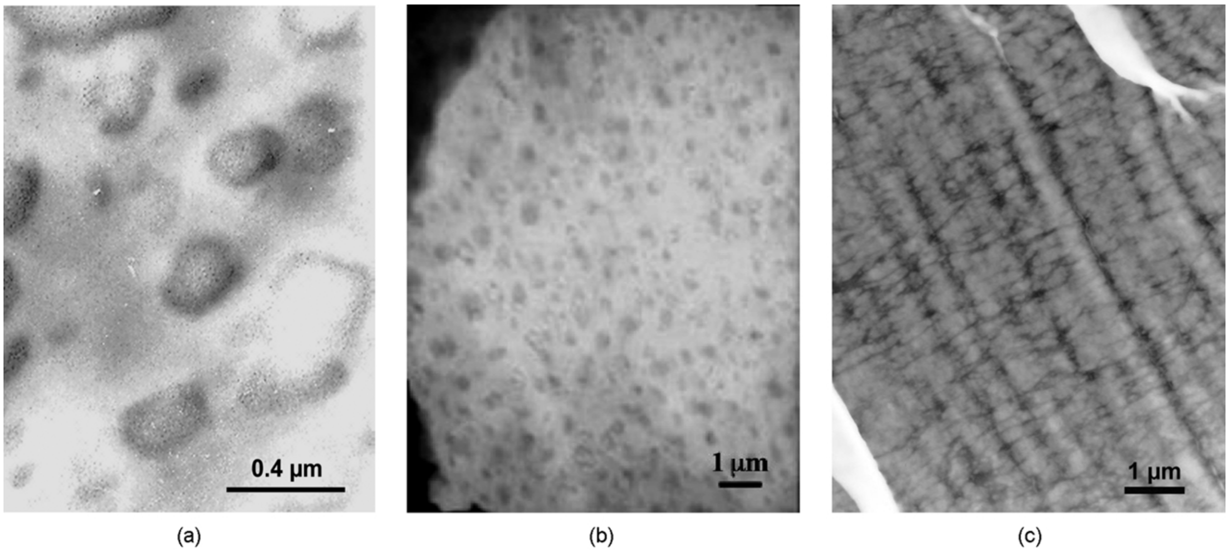


Fig. 3. TEM micrographs of High MW–High acid PBT/E-MA-GMA blends: (a) 20, (b) 40 and (c) 45 wt% rubber.

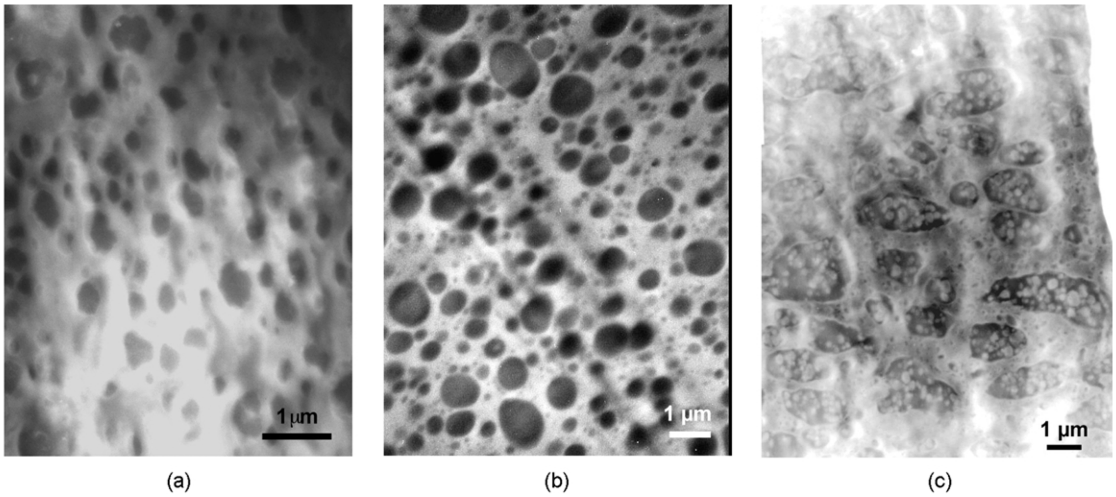


Fig. 4. TEM micrographs of Low MW–High acid PBT/E-MA-GMA blends: (a) 20, (b) 40 and (c) 50 wt% rubber.

weight fraction, in the case of Low MW–Low acid PBT blends (beyond 40 wt% rubber) compared to Low MW–High acid PBT blends (at 50 wt% rubber). In other words, the composition range, over which composite E-MA-GMA particles appear, increases as the concentration of PBT carboxyl chain ends decreases. It is interesting to note that the size of the Low MW PBT sub-inclusions seems to be smaller for blends containing Low MW–Low acid PBT.

3.4. PBT/48% modified E-MA-GMA reactive blends

Fig. 6 presents the evolution of the blend morphology as a function of the rubber content for Low MW–Low acid PBT/48% modified E-MA-GMA blends. Whatever the blend composition, no PBT sub-inclusions are observed in the rubber particles. Indeed, a classical matrix-droplet morphology is detected whatever in all cases. The spontaneous formation of composite rubber particle is therefore also related to the rate of the rubber phase crosslinking. The effect of the PBT reactivity is rather limited, since similar conclusions were also obtained for Low MW–High acid PBT/48% modified E-MA-GMA blends.

4. Discussion

The spontaneous generation of composite droplet morphology during the reactive compatibilization of immiscible polymer blends has been studied by some authors [8–10]. In the most recent study, Pagnoulle and Jérôme suggest that such particle-in-particle microstructure results from the coalescence of poorly stabilized rubber particles in the later stages of mixing and is essentially governed by the kinetics of interfacial grafting [10]. The observations reported in this study differ to some extent from this conclusion and allow for better identification of the parameters controlling the formation of particle-in-particle morphology. To explain the presented results, we assume that the determining parameter is not really the rate of compatibilization but rather the relative kinetics between

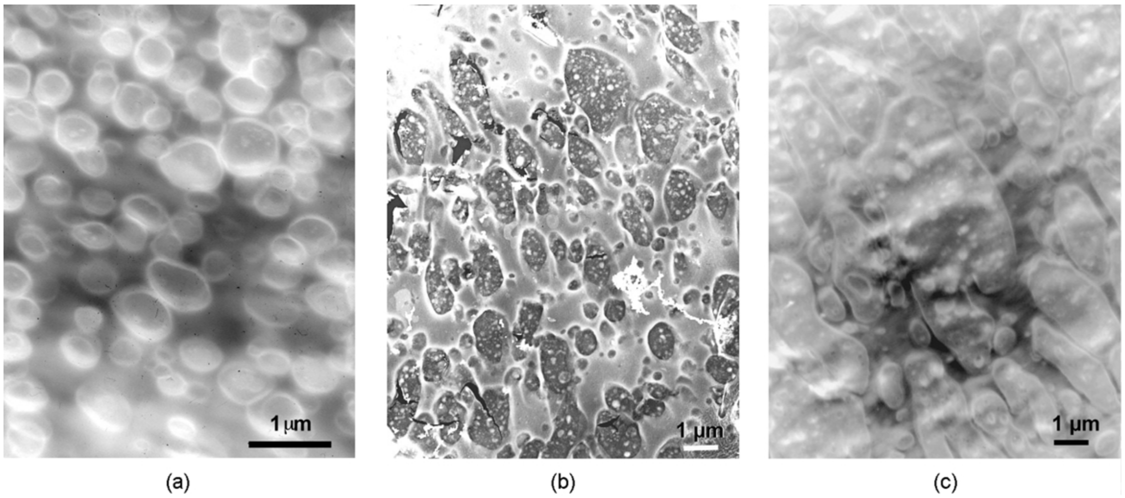
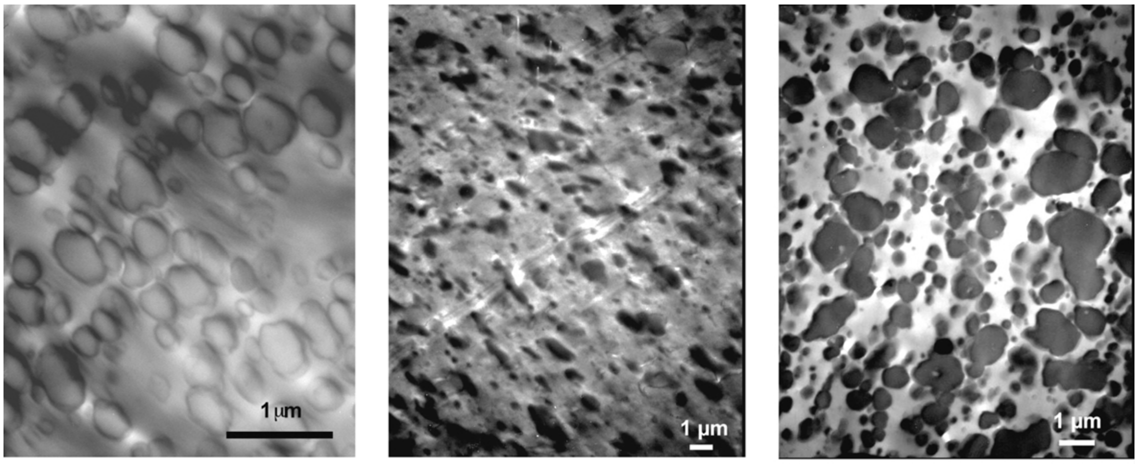


Fig. 5. TEM micrographs of Low MW–Low acid PBT/E-MA-GMA blends: (a) 20, (b) 40 and (c) 50 wt% rubber.

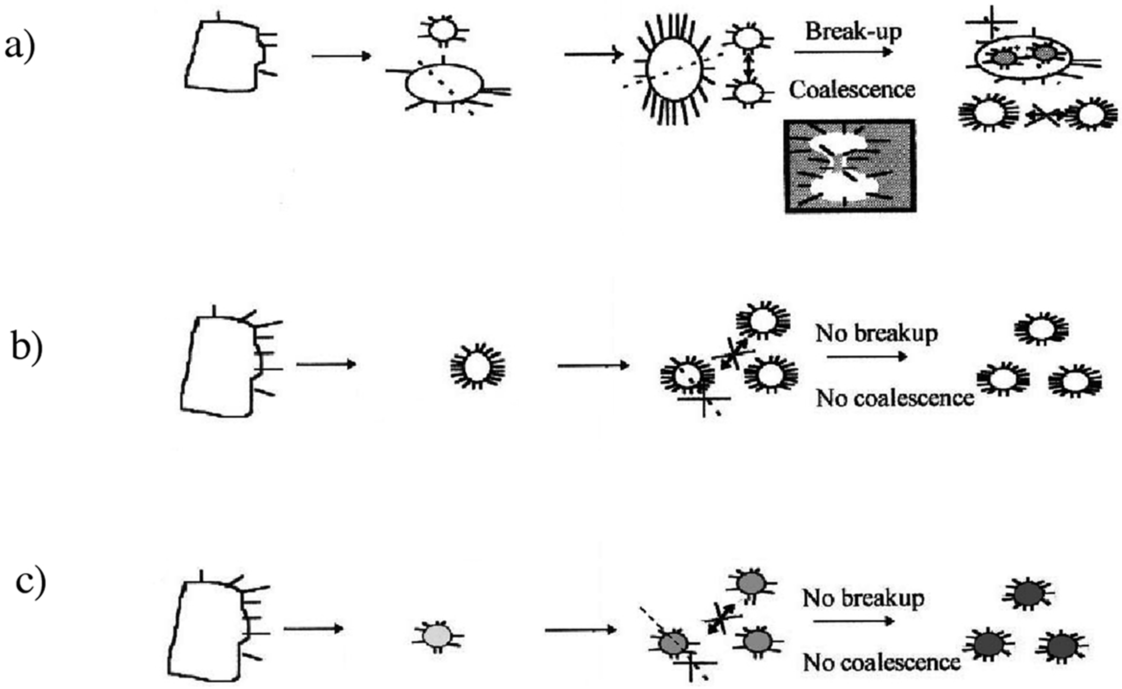


(a) (b) (c)

Fig. 6. TEM micrographs of Low MW–Low acid PBT/48% modified E-MA-GMA blends: (a) 20, (b) 40 and (c) 50 wt% rubber.

(1) the coalescence of the dispersed particles and (2) the interfacial grafting and/or the crosslinking of the dispersed phase (Scheme 1). For given processing conditions, the rate of the coalescence process is expected to increase as the rubber content increases and/or the matrix viscosity decreases. On the opposite, the rate of the chemical reactions is directly related to the concentration in reactive functions. Quantitative information about the kinetics of both rubber crosslinking and/or interfacial grafting can be found in the published studies performed on the same PBT/E-MA-GMA systems [11,13,14].

For Low MW PBT/E-MA-GMA blends, the coalescence rate is assumed to be no longer negligible with respect to the grafting rate and to the rubber crosslinking beyond a critical rubber content. According to the relatively low matrix viscosity, coalescence of poorly stabilized rubber particles is expected to occur in a large extent. As a consequence, Low MW PBT chains can be engulfed into larger rubber



Scheme 1. Composite E-MA-GMA droplet formation during reactive processing of PBT/Rubber blends. (a) Rate of coalescence ≫ rate of chemical reactions, Matrix phase can be engulfed into rubber particles together with some graft copolymer during coalescence of poorly stabilized particles, (b) Rate of interfacial reaction ≫ rate of coalescence. A large amount of graft copolymer is rapidly formed at the blend interface, which prevents coalescence of dispersed particles, and (c) Rate of rubber crosslinking ≫ rate of coalescence. Crosslinking proceeds rapidly within the rubber particles (shaded in gray), which prevents coalescence of the dispersed particles.

phases together with some graft copolymer, resulting in the formation of PBT sub-inclusions. During the early stages of the mixing, the grafting rate is expected to be higher in the case of Low MW–High acid PBT blends compared to Low MW–Low acid PBT blends, due to a higher amount of PBT carboxyl chain ends. Consequently, the amount of graft copolymer present at the interface is expected to be larger at a given mixing time. During the coalescence of the rubber particles, a larger amount of PBT should be engulfed into the E-MA-GMA phase resulting in larger PBT sub-inclusions (Scheme 1(a)). This is in agreement with the TEM observations (Figs. 4(c) and 5(c)). However, in case of Low MW–High acid PBT blends, the higher amount of graft copolymer formed at the blend interface results in more stabilized dispersed phase particles. Thus, for a given rubber content, coalescence of the rubber particles is dramatically decreased and formation of composite droplet morphology is no more possible (Scheme 1(b)). Compared to Low MW–Low acid PBT blends, composite rubber droplets can only be formed at sufficiently high coalescence rate, i.e. at higher rubber content. This explains why the composition range, over which composite E-MA-GMA particles appear, increases as the concentration of PBT carboxyl chain ends decreases (Figs. 4 and 5).

For PBT blends containing modified E-MA-GMA, it was already demonstrated that the crosslinking of the rubber phase takes place very rapidly in the melt from the beginning of the blending process [15]. This rubber crosslinking is expected to greatly limit the coalescence of the dispersed E-MA-GMA particles. As a result, the coalescence rate is decreased to a large extent and the formation of sub-inclusions is subsequently no more possible (Scheme 1(c)). In the same way, increasing the PBT molecular weight will also influence the coalescence rate. As the PBT matrix becomes more viscous, the drainage of PBT chains present between two rubber particles proceeds more slowly, so that the coalescence rate is reduced. This explains why no PBT sub-inclusions are observed for the High MW–High acid PBT/rubber blends and thus, whatever the blend composition and the nature of the rubber phase.

By modifying the kinetics of chemical reactions as well as the phases viscosities, we succeeded to modulate to some extent the coalescence rate between the rubber particles. As a consequence, we demonstrated unambiguously that the main controlling parameter for the formation of complex morphologies is not only the grafting kinetics but rather the relative kinetics between the coalescence process and the chemical reactions occurring in the blend during processing. In other words, particle-in-particle morphology can still be generated in the case of very fast compatibilization as far as the kinetics of the coalescence process is fast enough (this latter can be adjusted by changing the blend composition or/and the matrix viscosity for example). This differs largely from the conclusions reported in the literature, for which the grafting kinetics was the only determining parameter. The interest of the PBT/E-MA-GMA complex reactivity is here again clearly demonstrated. By the adequate choice of the kinetics of interfacial grafting and of rubber phase crosslinking, very different systems can be generated.

4.1. Core-shell morphology

The particle-in-particle phase morphology can also be forced when it does not occur spontaneously [7,10]. For this purpose, an efficient strategy consists in first dispersing part of polymer A within polymer B, followed by the addition of large amounts of phase A. This approach was also investigated in this work and a reactive two-step procedure was developed in case of High MW PBT/E-MA-GMA blends (see Experimental section for details). The blends obtained using this two-steps procedure were characterized by TEM and results are presented in Fig. 7 as a function of the rubber content present in the High MW–High acid PBT/E-MA-GMA pre-mixture.

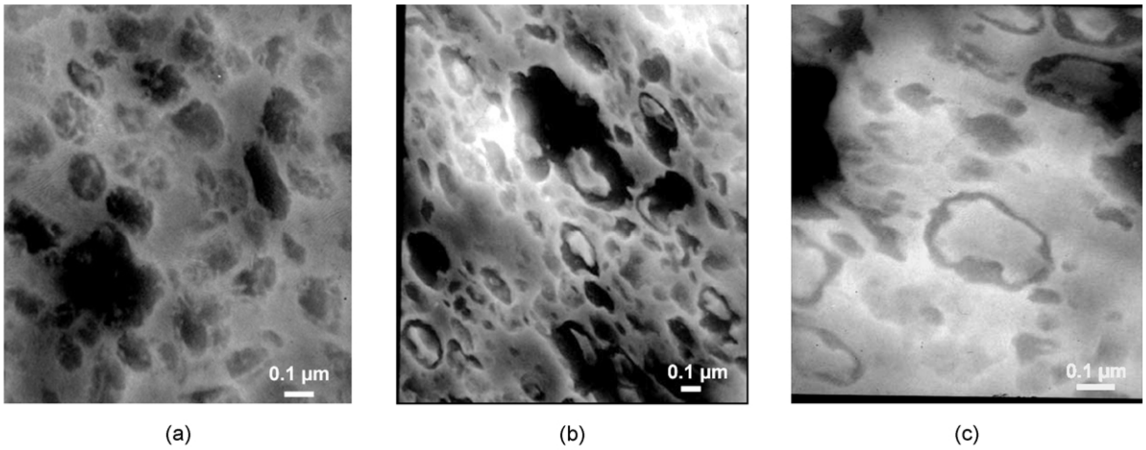


Fig. 7. TEM micrographs of High MW–High acid PBT/E-MA-GMA (80/20, w/w) blends obtained by a two-step blending procedure. Rubber content in the PBT/rubber pre-mixture: (a) 60/40, (b) 20/80 and (c) 10/90 (w/w).

Whatever the composition of the pre-mixture, the High MW–High acid PBT/E-MA-GMA (80/20, w/w) blends display a very fine morphology. For High MW–High acid PBT rich pre-mixture, the blend exhibit a classical droplet-matrix morphology (Fig. 7(a)). However, the shape of the dispersed phase particles is very irregular. In contrast, for E-MA-GMA rich pre-mixture, each dispersed phase particle presents a very complex structure consisting in a PBT core surrounded by a E-MA-GMA shell (Fig. 7(b) and (c)). This is essentially the case for the larger dispersed phase particles. No trace of composite droplet phase morphology was observed. In Fig. 7(b) and (c), the relative size of the core and the shell are directly related to the composition of the PBT/rubber pre-mixture. The higher the rubber content in the pre-dispersion, the thicker the E-MA-GMA shell in the final High MW–High acid PBT/E-MA-GMA (80/20, w/w) blend. Formation of these structures results from the interfacial reaction occurring in the melt between the carboxyl PBT chain ends and the rubber epoxide functions. In the first step, the mixing time is sufficiently long to promote the formation of E-MA-GMA/PBT graft copolymer at the blend interface and the subsequent stabilization of this interface. The morphology of the final High MW–High acid PBT/E-MA-GMA (80/20, w/w) blend will therefore be intimately related to the morphology of the pre-mixture. For High MW–High acid PBT rich pre-mixture, High MW–High acid PBT already forms the matrix [12]. Addition of further amount of neat High MW–High acid PBT does not modify the blend morphology to a large extent. For pre-mixture containing 80 or 90 wt% E-MA-GMA, the morphology consists in a rubber matrix containing dispersed High MW–High acid PBT particles. These PBT particles are stabilized by the in situ formed graft copolymer. When neat High MW–High acid PBT is added to the system in order to reach a final composition of 80/20 w/w PBT/rubber, a phase inversion has to take place in the melt. Since the PBT phases are almost fully stabilized, they remain in the rubber phase and are therefore embedded by the surrounding E-MA-GMA leading to core-shell type structure.

It is worth noting that not only the thickness but also the elastic properties of the E-MA-GMA shell are expected to vary from one blend to the other since the crosslinking extent of the rubber phase should differ for each case. This should result in large difference in the final blend performance.

5. Conclusions

The spontaneous or forced generation of particle-in-particle phase morphology during reactive processing of poly(butylene terephthalate) (PBT) with ethylene-methyl acrylate-glycidyl methacrylate (E-MA-GMA) random terpolymer has been investigated using different blending sequence.

Using a one-step compounding procedure, composite droplet morphology consisting of a PBT matrix, a E-MA-GMA dispersed phase and PBT sub-inclusions can be spontaneously obtained due to the coalescence of poorly stabilized E-MA-GMA particles during the melt processing. In contrast with published concepts, the results demonstrated unambiguously that the development and the dimensions of this complex microstructure is not only controlled by the rate of interfacial grafting but rather by the relative kinetics between (1) the coalescence of the dispersed particles and (2) the interfacial compatibilization and/or the rubber phase crosslinking. In other words, particle-in-particle morphology can still be generated in the case of very fast compatibilization as far as the kinetics of the coalescence process is fast enough (this latter can be adjusted by changing the blend composition or/and the matrix viscosity for example). This differs largely from the conclusions reported in the literature, for which the grafting kinetics was the only determining parameter. Composite droplet morphology is favored in presence of slow compatibilization, slow rubber phase crosslinking, high rubber content and low matrix viscosity.

The generation of particle-in-particle morphology can also be forced using a two-step blending sequence. In this latter case, a blend morphology consisting in a PBT matrix with PBT/E-MA-GMA core/shell particles can be obtained. The characteristic dimensions of this complex microstructure are intimately related to the composition and the morphology of the material generated at the end of the first blending step.

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