Phase Morphology Development During Processing of Compatibilized and Uncompatibilized PBT/ABS Blends

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ABSTRACT: The development of the multiphase morphology of uncompatibilized blends of poly(butylene terephthalate) (PBT) and acrylonitrile–butadiene–styrene terpolymer (ABS) and PBT/ABS blends compatibilized with methyl-methacrylate glycidyl-methacrylate (MMA-GMA) reactive copolymers during compounding in a twin-screw extruder and subsequent injection molding was investigated. Uncompatibilized PBT/ABS 60/40 (wt %) and compatibilized PBT/ABS/MMA-GMA with 2 and 5 wt % of MMA-GMA showed refined cocontinuous morphologies at the front end of the extruder, which coarsened towards the extruder outlet. Coarsening in uncompatibilized PBT/ABS blends is much more pronounced than in the compatibilized PBT/ABS/MMA-GMA equivalents and decreases with increasing amounts of the MMA-GMA. For both systems, significant refinement on the phase morphology was found to occur after the blends pass through the extruder die. This phenomenon was correlated to the capacity of the die in promoting particles break-up due to the extra elongational stresses developed at the matrix entrance. Injection molding induces coarsening of the ABS domains in the case of uncompatibilized PBT/ABS blends, while the reactive blend kept its refined phase morphology. Therefore, the compatibilization process of PBT/ABS/ MMA-GMA blends take place progressively leading to a further refinement of the phase morphology in the latter steps, owing to the slow reaction rate relative to epoxide functions and the carboxyl/hydroxyl groups. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 102–110, 2007

Key words: blends; reactive compatibilization; phase morphology; PBT/ABS; MMA-GMA

INTRODUCTION

Polymer blending represents one of the most attractive methods to develop new polymeric materials with advanced properties.[1–4] However, since the blend components are usually immiscible, mixing two polymers yields multiphase systems. The corresponding performance is strongly determined by the phase morphology, which depends on composition, rheological and physical characteristics of the components, relative compatibility, and nature and intensity of mixing. Hence, control of phase morphology, i.e., of the blend performance, can be achieved by controlling the mixing parameters and/or by compatibilization. The latter, using *in situ* reactive copolymers, has been used for this purpose.[5] Compatibilizer molecules located at the blend components interface reduce the interfacial tension[6–8] and suppress coalescence of the disperse phase.[9,10] Consequently, compatibilization results in a fine and more stable dispersion of a minor and/or high viscous blend component in the matrix. Compatibilizers also promote interfacial adhesion, which improves stress transfer between the blend phases.[11–14]

Several poly(butylene terephthalate)/acrylonitrile–butadiene–styrene terpolymer (BT/ABS) blends are available commercially.[15] The selection of appropriate ABS grades without the addition of a compatibilizer can produce PBT/ABS blends with excellent properties, but these are strongly dependent on the processing conditions,[16] which results from the fact that PBT/ABS blends have unstable phase morphology; the ABS domains coarsen upon processing under some conditions. A strategy for compatibilizing this system consists of the addition of an *in situ* compatibilizer copolymer, which is miscible with the ABS phase, particularly with its SAN phase, and can react with PBT end groups. The effectiveness of methyl-methacrylate glycidyl-methacrylate copolymers (MMA-GMA) for controlling the morphology of PBT/ABS blends has been pointed out before.[17–20]

Several types of reactions may occur when the PBT/ABS/MMA-GMA system is processed at high temperatures. Figure 1 identifies the reactions that can
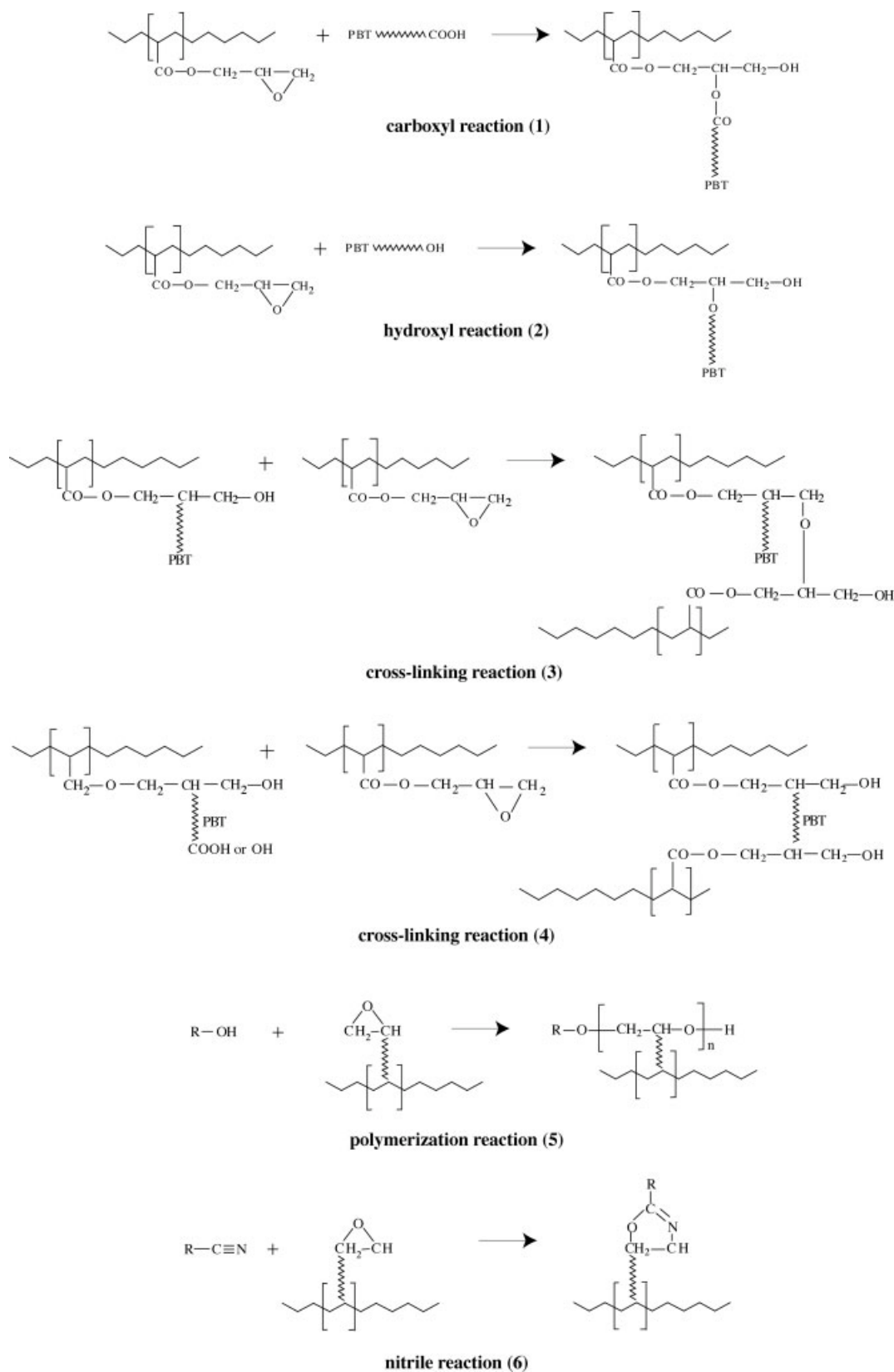
Figure 1 Possible reactions between epoxide units and PBT and ABS functionalities.

occur between the epoxide functions contained in GMA and the PBT end groups, and also between epoxide groups and ABS groups. Hale et al.[17] sug- gested that three types of reactions might occur between PBT and MMA-GMA in the melt state: inter- facial reactions, crosslinking, and polymerization.

Both —COOH and —OH end groups of PBT molecules can act as nucleophiles that react with epoxides via nucleophilic substitution (reactions 1 and 2, respectively). According to Sun et al.,[21] the reaction rate between PBT carboxylic acid end groups and MMA-GMA epoxide group is higher by a factor of 10–20 than that between the PBT hydroxyl end group and the epoxide group. These reactions are related to the interfacial reactions between MMA-GMA and the PBT that produce the *graft* compatibilizer copolymer and are considered the main reactions that can occur between PBT and MMA-GMA at the conditions of interest here. In addition, competitive reactions can also take place during melt processing of PBT/ABS/MMA-GMA blends. The interfacial reactions generate hydroxyl groups, which can potentially react with another epoxide groups to cause crosslinking (reaction 3). Crosslinking can also occur because of to the difunctionality of the PBT (reaction 4). Although Hale et al.[17] reported that the former crosslinking reaction is more difficult to occur under the conditions of interest here, Martin et al.[22] obtained experimental evidence that both crosslinking reactions (reactions 3 and 4) can take place. Epoxides can also polymerize via ring-opening reactions (reaction 5). Other reactions are possible. For example, nitrile groups contained in the SAN phase of ABS can react with epoxides in the presence of acid catalysts to form oxazoline linkages (reaction 6). Nitriles can also undergo hydrolysis to carboxyl groups, which in turn can react with the epoxide groups. MMA-GMA can react with functionalities contained in emulsion-made ABS, such as surfactants, coagulants, residual initiators, and postpolymerization additives. Finally, trace metals from polyester polymerization catalysis, e.g., antimony, titanium, etc., have been shown to have a large effect on the extent of reaction between PBT and GMA-contained copolymers.[19]

Despite the relative good understanding of the reactions taking place during the preparation of PBT/ABS/MMA-GMA systems, there is much less information on the resulting phase morphology evolution during processing, which will dictate its final performance. Therefore, the aim of this study was to investigate the development of the phase morphology of uncompatibilized PBT/ABS and reactive compatibilized PBT/ABS/MMA-GMA blends during compounding in a corotating twin-screw extruder and subsequent processing by injection molding. In the case of extrusion, samples were collected at various locations along the barrel by means of special devices that were able to remove ∼ 1–2 g of material.

EXPERIMENTAL

Materials

The characteristics of the materials used in this work are summarized in Table I.

Methods

The copolymers MMA-GMA were synthesized by mass polymerization following standard procedures.[23] A third monomer, ethyl-acrylate, was also used during MMA-GMA polymerization to prevent unzipping. The GMA content (10 wt %) of the MMA-GMA copolymer was determined by FTIR spectroscopy and the molecular weight by gel permeation chromatography (GPC).

The rheological behavior of each material and of its mixtures with MMA-GMA copolymer was characterized by torque rheometry (using a HAAKE Rheomix 600p), at 220°C and 50 rpm, with a 70% partially filled chamber.

The blends were prepared in a modular Leistritz LSM 30.34 ($L/D = 29$) intermeshing corotating twin-screw extruder, equipped with series of sampling devices, whose location is shown in Figure 2. Generally, these correspond to zones of the screw working with high filling ratios and inducing intensive shear, with the corresponding generation of interfacial area, i.e., where the most important changes in chemistry and phase morphology are likely to occur. The screw configuration is also illustrated in Figure 2. It comprises of two staggered kneading blocks separated by a conventional conveying section. The set upstream contains twelve elements at −60°, while the set down-

**TABLE I**
Characteristics of the Materials Used in This Work

Designation used here	Supplier designation	Haake Torque[a] (N m)	Source	Molecular weight[b] (g mol^{-1})
PBT	Valox 325F	2.5	GE Plastics	–
MMA-GMA[c]	–	0.4	Our Labs	$M_n = 60,000$; $M_w = 115,000$
ABS[d]	Cycolac GPM 5500S	3.7	GE Plastics	–

[a] 220°C and 50 rpm after 10 min.
[b] Determined by GPC through a calibration curve based on mono-dispersed polystyrene standards.
[c] Acrylic copolymer containing 10 wt % of GMA.
[d] Terpolymer containing 16 wt % of rubber as determined by FTIR.
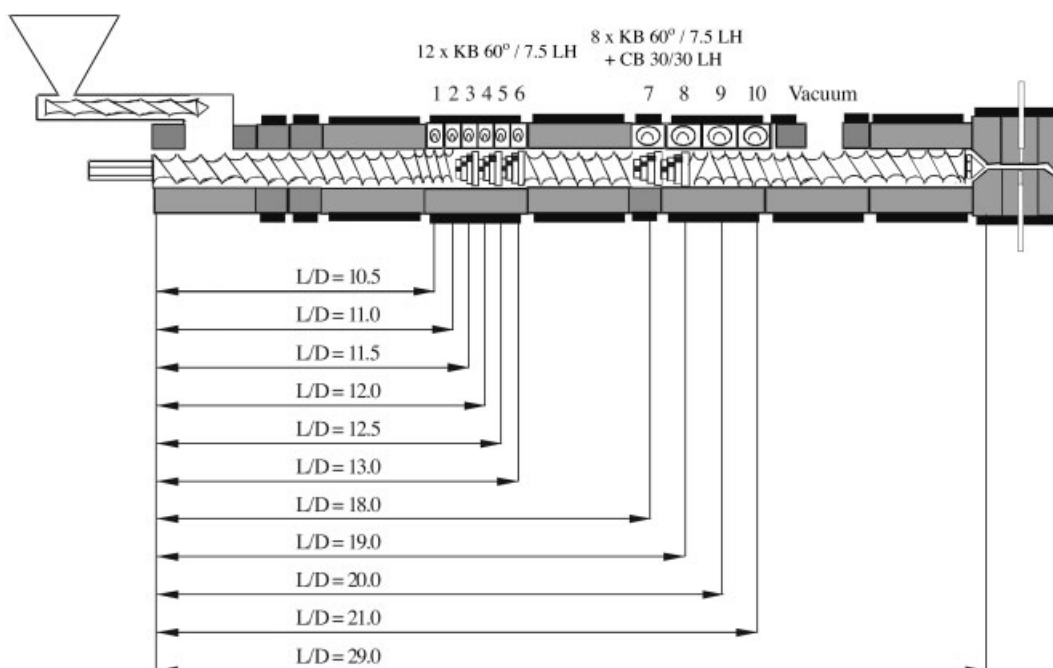
**Figure 2** Twin-screw configuration employed and sampling devices.

stream involves eight disks followed by a left hand element. The barrel temperature was set at 220°C and the screws rotated at a frequency of 170 rpm. The premixed blend components were incorporated in the machine by a gravimetric feeder set at 4.0 kg h^{-1}.

Injection-molded Izod bars were prepared in an injection molding machine ARBURG 270V at 240°C with a mold temperature of 50°C.

To investigate the effect of MMA-GMA on the evolution of PBT/ABS phase morphology during processing, three compositions were prepared with a fixed amount of 40 wt % of ABS, and changing the amount of MMA-GMA in the blends: (i) uncompatibilized PBT/ABS/MMA-GMA 60/40/0 (wt %); (ii) compatibilized PBT/ABS/MMA-GMA 58/40/2 (wt %); and (iii) compatibilized PBT/ABS/MMA-GMA 55/40/5 (wt %).

The samples for phase morphology investigations were obtained from the extruder operating at steady state condition with the sampling device at the indicated barrel locations by collecting material and quenching it immediately in liquid nitrogen, which is in a temperature well below the glass transition temperature (T_g) of the blend components, avoiding then any further morphological or chemical changes. Samples were obtained along the extruder from valves V3, V4, V5, V6, V7, and V8 as indicated in Figure 2. It was not possible to obtain samples from locations V1, V2, V9, and V10 shown in Figure 2, because the internal pressure at these valves were not high enough to promote melt flow through the sampling device. The phase morphologies of the blends after passing through the extruder matrix and also after injection molding were also analyzed.

The phase morphologies of the blends were examined using a PHILIPS CM 120 transmission electron microscope (TEM) at an accelerating voltage of 120 kV. Ultra-thin sections were obtained by cryo-microtoming the samples using a REICHERT ULTRACUT FC S microtome at −50°C. In the case of the extrudates and injection-molded Izod bars, sections were made perpendicular to the flow direction, whereas in the samples taken from valves V3, V4, V5, V6, V7, and V8, sections were made in a random direction. Sections 50-nm thick were stained with OsO$_4$ vapor for 15 h prior to their examination. The rubbery phase of ABS
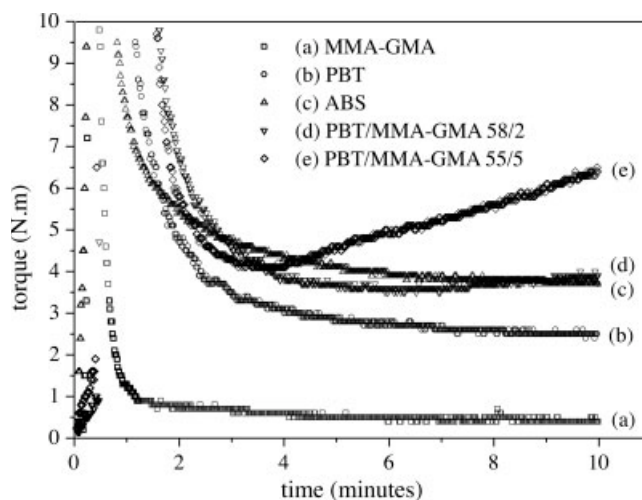
Figure 3 Torque rheometry curves for MMA-GMA, PBT, ABS, and PBT/MMA-GMA mixtures.
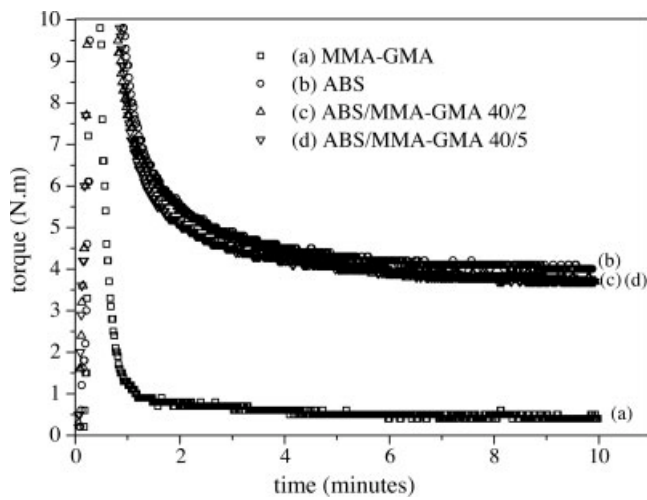
Figure 4 Torque rheometry curves for MMA-GMA, ABS, and ABS/MMA-GMA mixtures.

appears as dark areas, whereas the SAN phase of ABS appears as gray features in the TEM images.

RESULTS AND DISCUSSION

Rheological measurements

Torque rheometry tests were performed to obtain evidences of reaction between the components PBT, ABS, and MMA-GMA and also to estimate the viscosity ratio between the blends neat components. The PBT/MMA-GMA and ABS/MMA-GMA ratios employed in torque rheometry tests are the same as in the PBT/ABS/MMA-GMA blends under study.

Figure 3 shows torque versus time curves for MMA-GMA, PBT, ABS neat components, and PBT/MMA-GMA mixtures. From this figure it can be observed that the addition of MMA-GMA to PBT increases the level of torque to process the mixture compared to neat PBT and MMA-GMA. This effect was attributed to the possible formation of more viscous PBT-*graft*-MMA compatibilizer through the reaction between the carboxylic acid end groups of PBT and epoxide groups of MMA-GMA. It can also be noticed in Figure 3 that the level of torque at 10 min of mixing for PBT/MMA-GMA 55/5 is higher than for PBT/MMA-GMA 58/2, and for both mixtures the torque curves grow continuously with the mixing time. These torque rheometry observations suggest that the formation of PBT-*graft*-MMA molecules proceeds with the mixing time probably due to the fact that the reactivity of COOH and GMA groups of PBT/MMA-GMA systems is expected to be quite slow.[24] Also, the ratio between the concentration of the acid end groups of PBT molecules and the epoxide groups of MMA-GMA is higher than the unity for the PBT/MMA-GMA com-
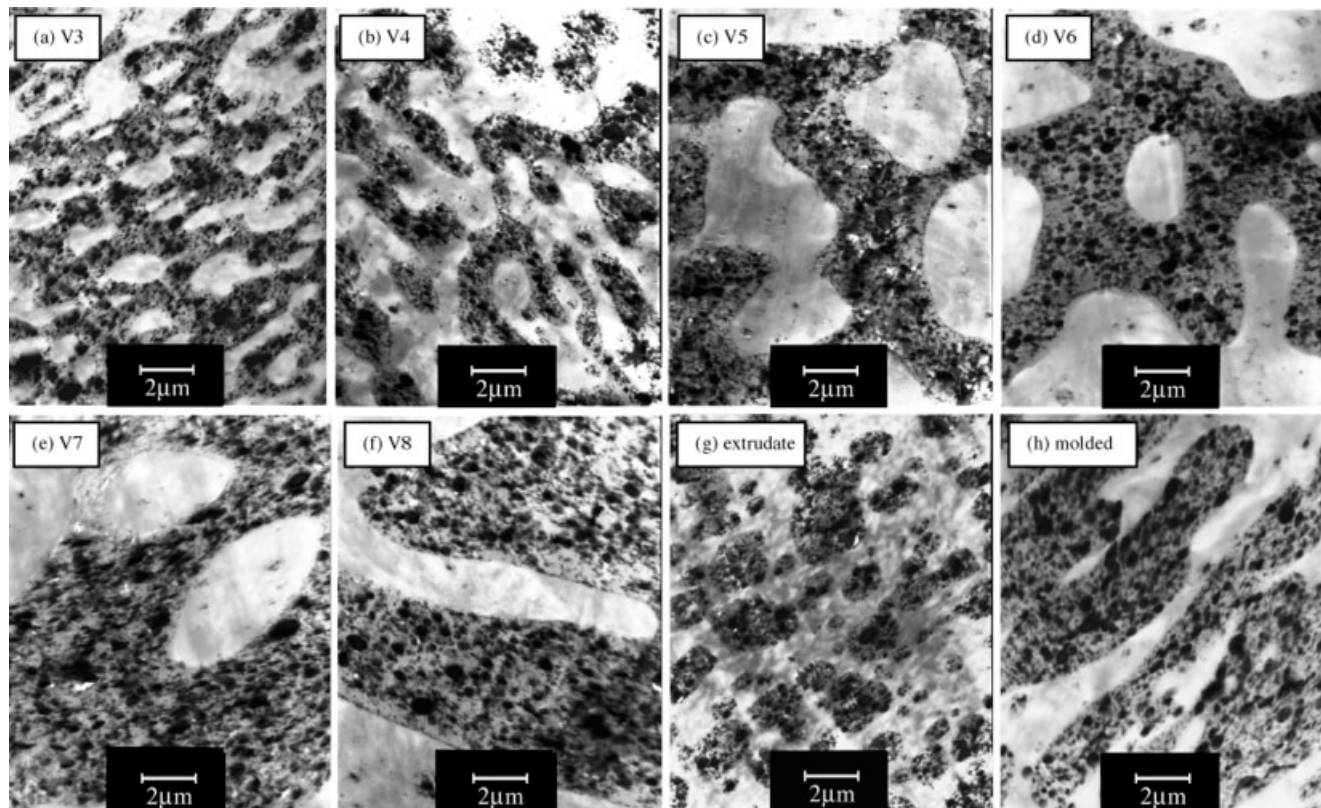
Figure 5 Phase morphology evolution during processing of uncompatibilized PBT/ABS 60/40 blend.

positions studied. Interfacial reactions were considered the main reactions between PBT and MMA-GMA; however, the experiments performed do not allow us to discard the occurrence of crosslinking reactions (see reactions 3 and 4 in Fig. 1), which can be related to the torque increase with time of PBT/MMA-GMA as well.

It can also be observed in Figure 3 that the level of torque to process the neat ABS is higher than the PBT by a factor of nearly 1.5; however, PBT/MMA-GMA 58/2 mixture requires higher torque to process compared to the neat PBT, approximately matching the torque required to process the neat ABS. The PBT/MMA-GMA 55/5 mixture shows a torque response beyond that for neat ABS. The torque (viscosity) ratio between the major phases is an important parameter that controls the phase morphology of an immiscible polymer blend and, therefore, it must also be taken into account on PBT/ABS phase morphology discussion.

Figure 4 shows torque versus time curves for MMA-GMA, ABS, and ABS/MMA-GMA mixtures. On a distinct behavior compared to the PBT/MMA-GMA mixtures, ABS/MMA-GMA mixtures showed slight lower levels of torque as that of neat ABS and this indicates, to some extent, that no reaction has occurred between MMA-GMA and the grade of ABS used.

Phase morphology investigations

The evolution of phase morphologies during processing of PBT/ABS 60/40 blend, PBT/ABS/MMA-GMA 58/40/2 blend, and PBT/ABS/MMA-GMA 55/40/5 blend are shown in Figures 5–7, respectively. TEM photomicrographs shown in these figures provide information about the phase morphology of these various blends at different preparation stages. Rubber particles in the ABS appear dark, whereas the SAN phase appears gray due to the selectiveness of the OsO_4 staining. The latter allows the outline of the entire ABS domains to be distinguished from PBT.

For both uncompatibilized PBT/ABS 60/40 blend, compatibilized PBT/ABS/MMA-GMA 58/40/2 blend, and compatibilized PBT/ABS/MMA-GMA 55/40/5 blend, refined cocontinuous morphologies at the front end of the extruder just after the melting of the pellets at the first kneading discs zone were observed [Figs. 5(a), 6(a), and 7(a), respectively]. This is in a good agreement with experiments performed by Potschke and Paul[25] who observed stable cocontinuous structures during the initial stage of morphology development in polymer blends. Subsequently, the refined cocontinuous morphology goes through coarsening phenomena towards the exit of the extruder. The coarsening phenomena during extrusion of PBT/ABS/MMA-GMA blend compatibilized with 2 wt %
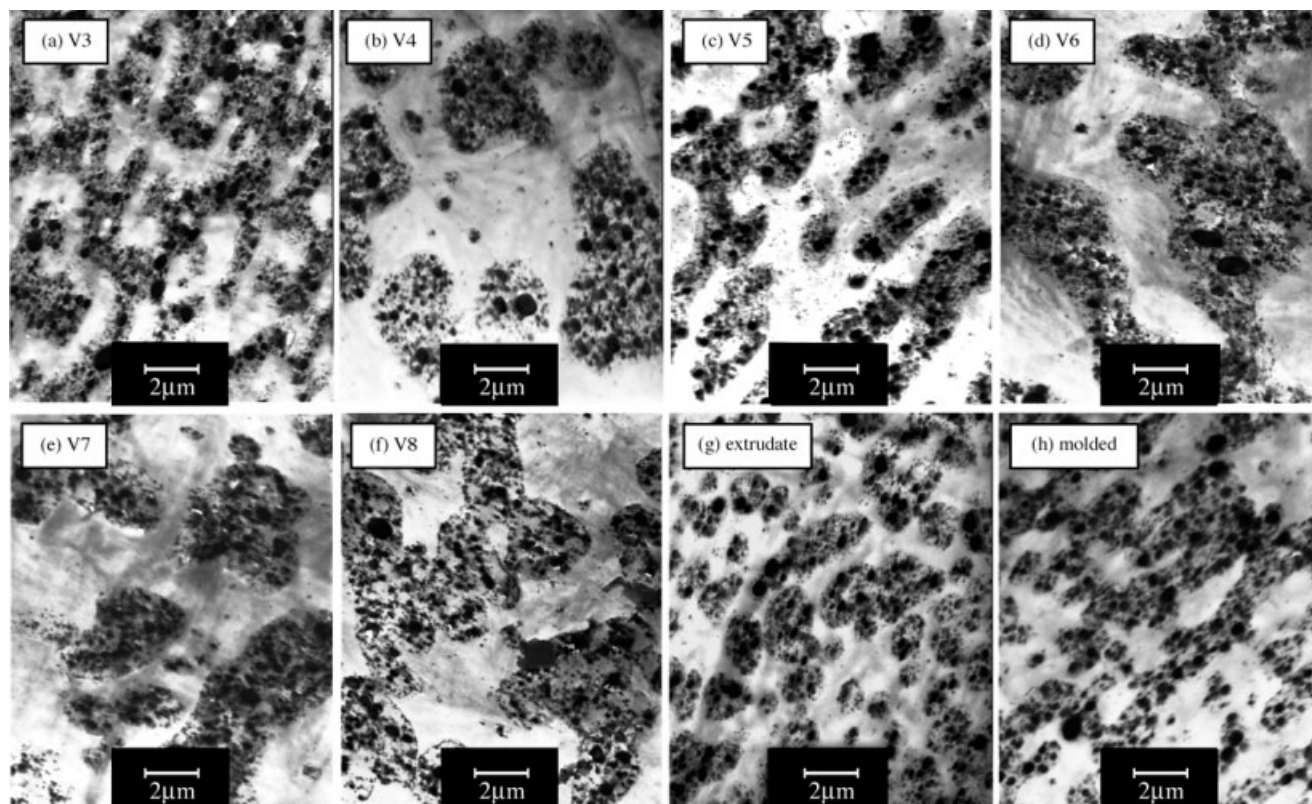
Figure 6 Phase morphology evolution during processing of compatibilized PBT/ABS/MMA-GMA 58/40/2 blend.
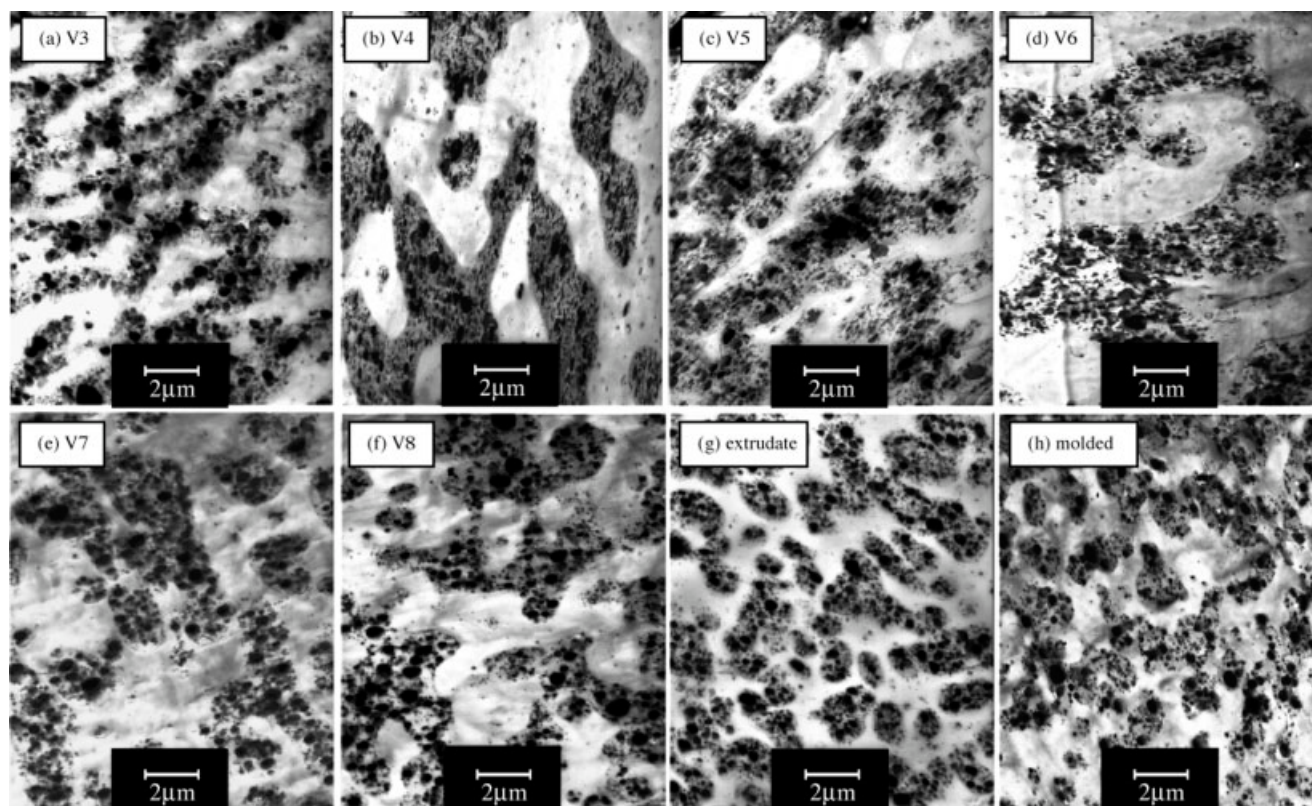
Figure 7 Phase morphology evolution during processing of compatibilized PBT/ABS/MMA-GMA 55/40/5 blend.

of MMA-GMA Figure 6(a–f) are slightly less pronounced compared to that of uncompatibilized PBT/ABS blend [Fig. 5(a–f)]. The coarsening process seems to be further minimized by the addition of the largest amount (5 wt %) of MMA-GMA copolymer to PBT/ABS blend [Fig. 7(a–f)], resulting in more refined morphologies.

Our observations suggest that the process of coalescence along the screw length for both uncompatibilized PBT/ABS and compatibilized PBT/ABS/MMA-GMA blends is very intense and predominantly over break-up. This process seems to be intensified by the presence of kneading blocks along the extruder screws and the high volume fraction of ABS in these blends (40 wt %). Some experiments reported in literature[26,27] have shown that flow induced coalescence rates in polymer blends are intensified by the increase of shear stresses and the volume fraction of minor blend component.

After the uncompatibilized PBT/ABS 60/40 blend, compatibilized PBT/ABS/MMA-GMA 58/40/2 blend and compatibilized PBT/ABS/MMA-GMA 55/40/5 blend pass through the extruder die, the coarsened phase morphologies towards the last few stages of the extruder observed for these systems [Figs. 5(f), 6(f), and 7(f), respectively] are replaced by ABS finely disperse phase morphologies [Figs. 5(g), 6(g) and 7(g), respectively]. The phenomenon observed on morphol-

ogy when the blends pass through the extruder die can be correlated to some extent to the capacity of the die in intensifying particles break-up due to the extra elongational stresses developed in the converging flow at the matrix entrance, once particles are more efficiently broken in elongational than in shear flow.[26,27] It is reasonable to expect that in the blends that were studied, the ABS form, the discrete phase, and the PBT forms the continuous one, once ABS is the minor and most viscous blend component (Fig. 3). Also, the extrudate of the PBT/ABS/MMA-GMA blends showed phase morphologies slightly more refined than that of the uncompatibilized PBT/ABS blend, suggesting some compatibilization.

Injection molding causes a significantly coarsening effect on the refined phase morphology of the extrudate for uncompatibilized PBT/ABS 60/40 blend, changing significantly its morphology and resulting in larger ABS phase sizes [Fig. 5(h)]. Therefore, in the uncompatibilized PBT/ABS system studied, it seems that coalescence plays an important role on the morphology development during extrusion and on injection molding process as well. On the other hand, after injection molding, compatibilized PBT/ABS/MMA-GMA blends basically kept their fine phase morphology that was observed prior to the injection molding process [Figs. 6(h) and 7(h), respectively]. Hence, the coalescence process is suppressed on injection mold-

ing process by the addition of MMA-GMA. We suppose that the addition of the MMA-GMA to the PBT/ABS blends promoted stabilization of ABS domains against coalescence caused by steric hindrance due to the preferential location of the compatibilizer molecules at the interface between PBT and ABS phases. In addition, the effect of increasing PBT viscosity by the formation of PBT-*graft*-MMA copolymer could also favor a dispersive mixture of the ABS domains in PBT matrix.

The observations made through this work and discussion above show that compatibilization process of PBT/ABS/MMA-GMA blends take place progressively leading to a further refinement of the phase morphology on injection molding process. These observations agree with the work of Martin et al.,[28] who studied the morphology development of blends of PBT and ethylene-methyl acrylate-glycidyl methacrylate (E-MA-GMA) copolymers processed in a batch mixer. The authors concluded that for PBT/E-MMA-GMA systems, in the earlier stages of mixing, the evolution of the compatibilized blend morphology should be similar to that of the PBT/E-EA uncompatibilized blends and it is essentially governed by physical factors such as viscosity ratio, composition, shear rate, and interfacial tension. As the mixing time increases, however, the chemical reactions (compatibilization) take place progressively leading to a further refinement of the morphology and subsequent stabilization. Analogous, for PBT/ABS/MMA-GMA blends compounded at twin-screw extruder and on injection molding machine, phase morphology refinement and stabilization were attained only at the latter process, where a sufficient amount of PBT-*graft*-MMA molecules for effective compatibilization was formed.

Also, the evolution of the phase morphology of PBT/ABS/MMA-GMA blends is quite different if compared to the behavior of polyamide/maleic anhydride-containing polymers. For the latter, the ultimate blend phase morphology is practically developed in the first stages of mixing, just after the melting.[29,30] The difference between the morphology developments of these two systems arises from the reactivity of COOH and GMA groups of PBT/MMA-GMA system that is expected to be quite slow compared to that one between amine and maleic anhydride functions[24] contained in blends of polyamide/anhydride-functionalized polymers.

CONCLUSIONS

The development of the phase morphology in uncompatibilized PBT/ABS and in compatibilized PBT/ABS/MMA-GMA blends during compounding in a twin-screw extruder and subsequent injection molding has been investigated and reveals the importance of studying the dynamics of formation of phase morphology in immiscible polymer blends concerning their compatibilization aspects. For PBT/ABS and PBT/ABS/MMA-GMA blends, coarsening was found to take place along the screw length of the twin-screw extruder, however, this process was observed to be more pronounced in uncompatibilized PBT/ABS blends than in the compatibilized PBT/ABS/MMA-GMA equivalents and decreases with increasing amounts of MMA-GMA compatibilizer. For both systems, significant refinement on the phase morphology was found to occur after the blends pass through the extruder die (extrudate) and this phenomenon was correlated to the capacity of the die in promoting particles break-up due to the extra elongational stresses developed at the matrix entrance. After injection molding process, compatibilized PBT/ABS/MMA-GMA blends basically kept their fine phase morphology that was observed prior to the injection molding process, whereas uncompatibilized PBT/ABS blends undergo significant coarsening. Therefore, the compatibilization process of PBT/ABS/MMA-GMA blends takes place progressively leading to a further refinement of the phase morphology in the latter steps, owing to the slow reaction rate relative to epoxide functions and the carboxyl/hydroxyl groups. This is quite different compared to well-known highly reactive blends of polyamide and maleic anhydride-functionalize polymers, where the ultimate blend phase morphology is practically developed in the first stages of mixing, just after the melting.

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