

Polyamide 6/Ethylene-Butylene Elastomer Blends Generated via Anionic Polymerization of ϵ -Caprolactam: Phase Morphology and Dynamic Mechanical Behavior

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ABSTRACT: This paper reports about the polymerization of ϵ -caprolactam monomer in the presence of low molecular weight hydroxyl or isocyanate end-capped ethylene-butylene elastomer (EB) elastomers as a new concept for the development of a submicron phase morphology in polyamide 6 (PA6)/EB blends. The phase morphology, viscoelastic behavior, and impact strength of the polymerization-designed blends are compared to those of similar blends prepared via melt-extrusion of PA6 homopolymer and EB elastomer. Polyamide 6 and EB elastomer were compatibilized using a premade triblock copolymer PA6-*b*-EB-*b*-PA6 or a pure EB-*b*-PA6 diblock reactively generated during melt-blending (extrusion-prepared blends) or built-up via anionic polymerization of ϵ -caprolactam on initiating $-NCO$ groups attached to EB chain ends (polymerization-prepared blends). Two compatibilization approaches were considered for the polymerization-prepared blends: (i) the addition of a premade PA6-*b*-EB-*b*-PA6 triblock copolymer to the ϵ -caprolactam monomer containing nonreactive EB-OH elas-

tomers and (ii) generation *in situ* of a PA6-*b*-EB diblock using EB-NCO precursor on which polyamide 6 blocks are built-up via anionic polymerization of ϵ -caprolactam. The noncompatibilized blends exhibit a coarse phase morphology, either in the extruded or the polymerization prepared blends. Addition of premade triblock copolymer (PA6-*b*-EB-*b*-PA6) to a EB-OH / ϵ -caprolactam dispersion led to a fine EB phase (0.14 μm) in the PA6 matrix after ϵ -caprolactam polymerization. The average particle size of the *in situ* reactively compatibilized polymerization-prepared blend is about 1 μm . The notched Izod impact strength of the blend compatibilized with premade triblock copolymer was much higher than that of the neat PA6, the noncompatibilized, and the *in situ* reactively compatibilized polymerization blends. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2538–2544, 2004

Key words: anionic polymerization; polyamides; blends; compatibilization; elastomer

INTRODUCTION

The concept of compounding two or more polymers to obtain new polymeric materials having high performance has received much attention from the point of view of fundamental and practical interest during the last three, up to four decades. The incompatibility of polyamides with many commercially interesting polymers such as polyolefins or olefin elastomers has already been solved by adding premade block or graft copolymers or by reactively forming them *in situ* at the interface during the compounding process.^{1–6} Recently, reactive compatibilization of immiscible blends has received more attention in terms of fine control and understanding of the phase morphology development in compatibilized blends. The reaction kinetics,

the *in situ* formed block or graft copolymer structure, and their content in the blend are the key factors that govern the properties of the resulting polymer blends. However, few studies report about the approach of *in situ* polymerization of the monomer of one of the two polymers in the presence of the other.^{7–10}

Borggreve and Gaymans⁸ have realized the above-mentioned approach for the preparation of polyamide 6/poly(butadiene-nitrile) elastomer blends by using hydrolytic polymerization of ϵ -caprolactam in the presence of butadiene-nitrile copolymer. The impact strength of polyamide 6 was significantly improved. The same authors also reported on polyamide 6/EPDM using the same approach.⁹ Comparable values of impact toughness were reported without significantly affecting the modulus of the blend; this was ascribed to the fine rubber dispersion generated (0.3 μm). By polymerizing ϵ -caprolactam via hydrolytic polymerization in the presence of functionalized ethylene-propylene elastomer could increase the impact strength of the obtained blend by a factor of 10 with

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respect to the noncompatibilized blend.¹⁰ Other reports also described a concept of *in situ* polymerization combined with *in situ* compatibilization for obtaining stabilized nanoblends based on polypropylene (PP) and PA6.¹¹ It consists of polymerizing ϵ -caprolactam in the presence of a major PP phase using a twin-screw extruder. PP bearing isocyanate groups was used as the macroactivator of ϵ -caprolactam polymerization. The size of the dispersed polyamide 6 phase in the PP matrix comprised between 20 and 100 nm. This could not be achieved otherwise by melt-blending premade PP and PA 6 components. Specimens of the reactively prepared blends of PP and PA 6 were reported to exhibit very high elongation at break.

The greatest interest of the approach of the polymerization method such as ϵ -caprolactam anionic polymerization resides in that it is a fast material generation process. It is well known that ϵ -caprolactam anionic polymerization occurs at a significantly faster rate (total conversion within only a few minutes) compared to the classical hydrolytic polymerization process, which takes about 12 to 24 h depending on the conditions used.^{12,13} This approach of polymerization can be used in flexible processes such as reaction injection molding (RIM process) for the design of blend systems based on polyamide 6.¹⁴

The purpose of the present research is to explore a new concept for the design of polyamide 6 (PA6) / EB elastomer blends having a submicron phase morphology. The approach consists of polymerizing ϵ -caprolactam, in the presence of EB elastomer bearing functional end groups such as $-OH$ or $-NCO$. For comparison purposes, extrusion melt-mixed blends of premade PA6 and EB elastomer were also prepared.

EXPERIMENTAL

Materials

All materials used in this work are commercial products. ϵ -Caprolactam ($(CH_2)_5NHCO$, having a density^{25°C} of 1.02 g/cm³, a refraction index^{25°C} of 1.4784, and a melting temperature of 69.5°C was purchased from ChPO "Electrochimprom" (Uzbekistan). ϵ -Aprolactam was purified by azeotropic vacuum distillation. Ethylene-butylene elastomer in a liquid form having one or two $-OH$ end groups (L-1203 and L-2203), respectively, were purchased from Shell. Hydrolytic polyamide 6 (Akulon, $M_n = 15,000$ g/mol, $M_w = 24,000$ g/mol) was obtained from DSM Engineering Plastics (The Netherlands). The activator used for ϵ -caprolactam polymerization was 2,4-toluene diisocyanate (TDI 102 T) having a melting temperature of 21.8°C. It was purified by vacuum distillation. Metallic sodium (Na) was used as polymerization catalyst.

Compatibilizer preparation

The triblock copolymer PA6-*b*-EB-*b*-PA6 was synthesized via anionic polymerization of ϵ -caprolactam in toluene in the presence of α,ω isocyanate end-capped EB elastomer. The latter was obtained via isocyanate substitution of the hydroxyl groups of the commercial α,ω hydroxyl end-capped EB as follows: EB elastomer was first dried at 100°C under vacuum. The temperature of the reaction vessel was kept within a 70–80°C range. An amount of 0.7 mol % of isocyanate activator was introduced into the reaction medium under nitrogen. Under these conditions the substitution reaction was completed after 6 h. At the end of the reaction the modified EB elastomer was purified from unreacted TDI. Purified EB elastomer with $-NCO$ group was dissolved in toluene (a ratio of EB liquid to toluene of 1 : 3 was used). The temperature of the EB/toluene solution was increased to 100°C and preliminary prepared sodium caprolactamate was added. The copolymerization reaction was completed after 3 h at 100°C under intensive mixing. The reaction product was then precipitated in acetone and washed at least three times. The obtained copolymer was dried under vacuum at room temperature. The obtained product was extracted using toluene and formic acid to remove unreacted EB and homopolyamide 6, respectively.

Blend preparation

Polymerization-prepared blends

The preparation of polymer blends by the method of ϵ -caprolactam anionic polymerization was carried out in two separate reactors as follows. The liquid ϵ -caprolactam monomer was first purified from humidity at a temperature of 100°C under vacuum and subsequently the purified ϵ -caprolactam was divided into two parts. In one reactor the triblock copolymer PA6-*b*-EB-*b*-PA6 was dispersed in ϵ -caprolactam; then, TDI and EB elastomer were added to the reaction medium. In the second reactor, the sodium caprolactamate was prepared using metallic sodium at a temperature of 100°C under nitrogen flux. The temperature of the two reactors was then increased to 140°C, a temperature at which the anionic polymerization of ϵ -caprolactam was carried out. The contents of the two reactors were then mixed together in one reactor at a temperature of 140°C during 1 min. After that, the content of the reactor was poured into a mold and annealed during 2 h at a temperature of 170°C. At the end of the annealing process the mold was allowed to cool down to room temperature at a cooling rate of 2.5°C/min.

Extrusion-melt prepared blends

Homopolyamide 6 and neat EB elastomer were melt-blended using a midi-extruder (DSM Research). It is a

conical corotating fully intermeshing twin-screw extruder having a mixing capacity of about 15 cm³. All blends were prepared under nitrogen flux at a temperature of 240°C, a screw speed of 100 rpm, and during a mixing time of 10 min.

For all the blend systems investigated, the following composition was maintained: PA6 phase: 85 wt %, EB elastomer phase: 15 wt %. The compatibilizer content was also kept constant at a concentration of 6 wt % with respect to the total amount of the blend.

Phase morphology characterization

The polymer blend test specimens were cryofractured in liquid nitrogen and the fracture surfaces were examined using a Philips XL-20 scanning electron microscope. The EB elastomer dispersed phase was etched in toluene at 50°C for 20 h, dried, and then coated with a gold layer before microscopic observation. Leica QWin image analysis software was used to calculate the particle size of the dispersed phase on several SEM micrographs.

Viscoelastic and mechanical testing

Dynamic mechanical thermal properties (storage modulus, loss modulus, and loss factor) of PA6 and its blends with EB elastomer were measured using a DMA 2980 (TA Instruments, Inc.) in the dual cantilever beam mode at a frequency of 1 Hz and a heating rate of 3°C/min. Notched Izod impact tests were performed at room temperature according to ISO-180 on Zwick 5110 apparatus. The samples, having dimensions of 65 × 6 × 4 mm³, were machined from the bulk polymer blends. A notch shape of 0.1 mm width and an angle of 45° was used. An average of five specimens were used for each sample.

RESULTS AND DISCUSSION

The phase morphology of the polymerization-prepared blends depends mainly on the initial state of the dispersion of EB elastomer particles in the ϵ -caprolactam monomer before the start-up of polymerization. The addition of a compatibilizer or its generation *in situ* is expected to improve the interfacial adhesion between the phases and prevents the undesired coalescence of EB particles. The particle size of the EB elastomer minor phase is controlled by the extent of mixing of the EB phase in ϵ -caprolactam monomer. In the absence of compatibilizer, which in the EB/ ϵ -caprolactam fulfills the role of a surfactant that stabilizes the dispersion and also prevents the coalescence before polymerization is completed, the average particle size of the dispersed phase is 12 μ m.

Scanning electron microscopy was used to examine the phase morphology generated in PA6/EB elas-

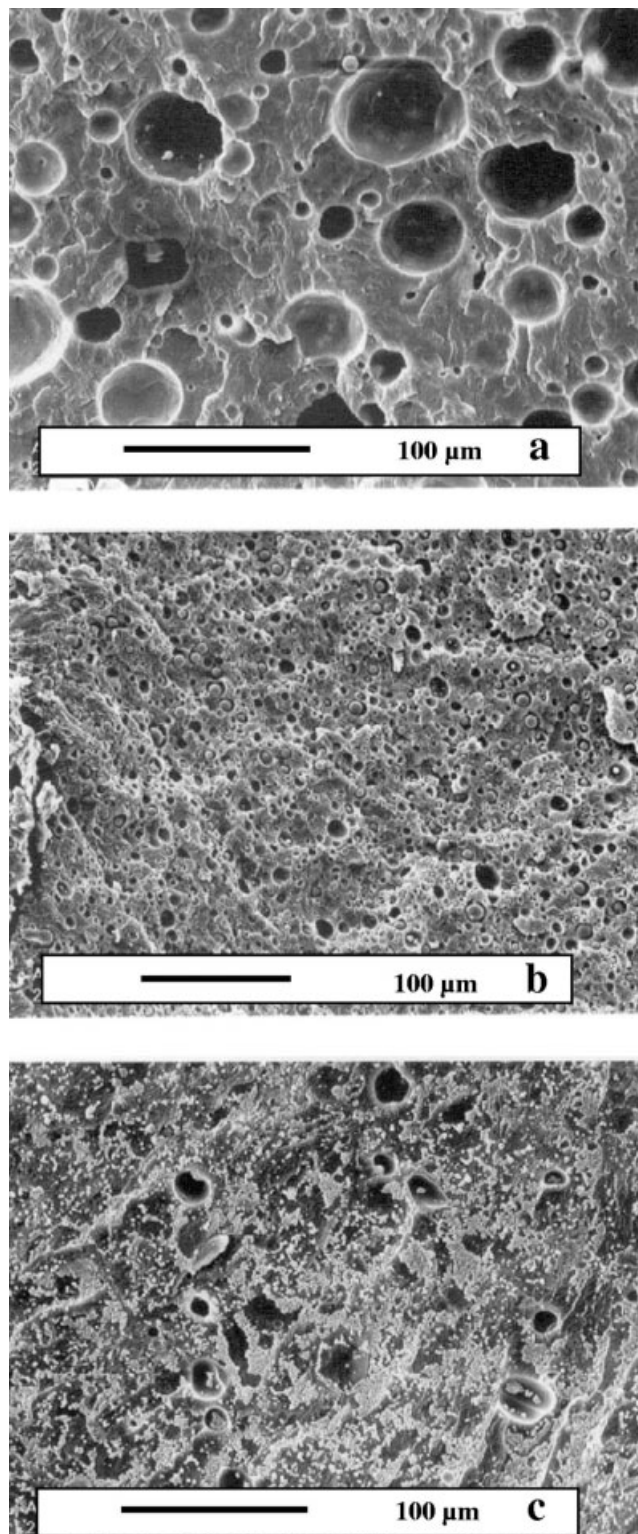


Figure 1 SEM micrographs of etched surfaces of (a) non-compatible PA6/EB—OH (85/15), (b) compatibilized with the premade triblock copolymer PA6/EB—OH/copolymer (79/15/6), and (c) *in situ* compatibilized PA6/EB—NCO (85/15) polymerization-prepared blends.

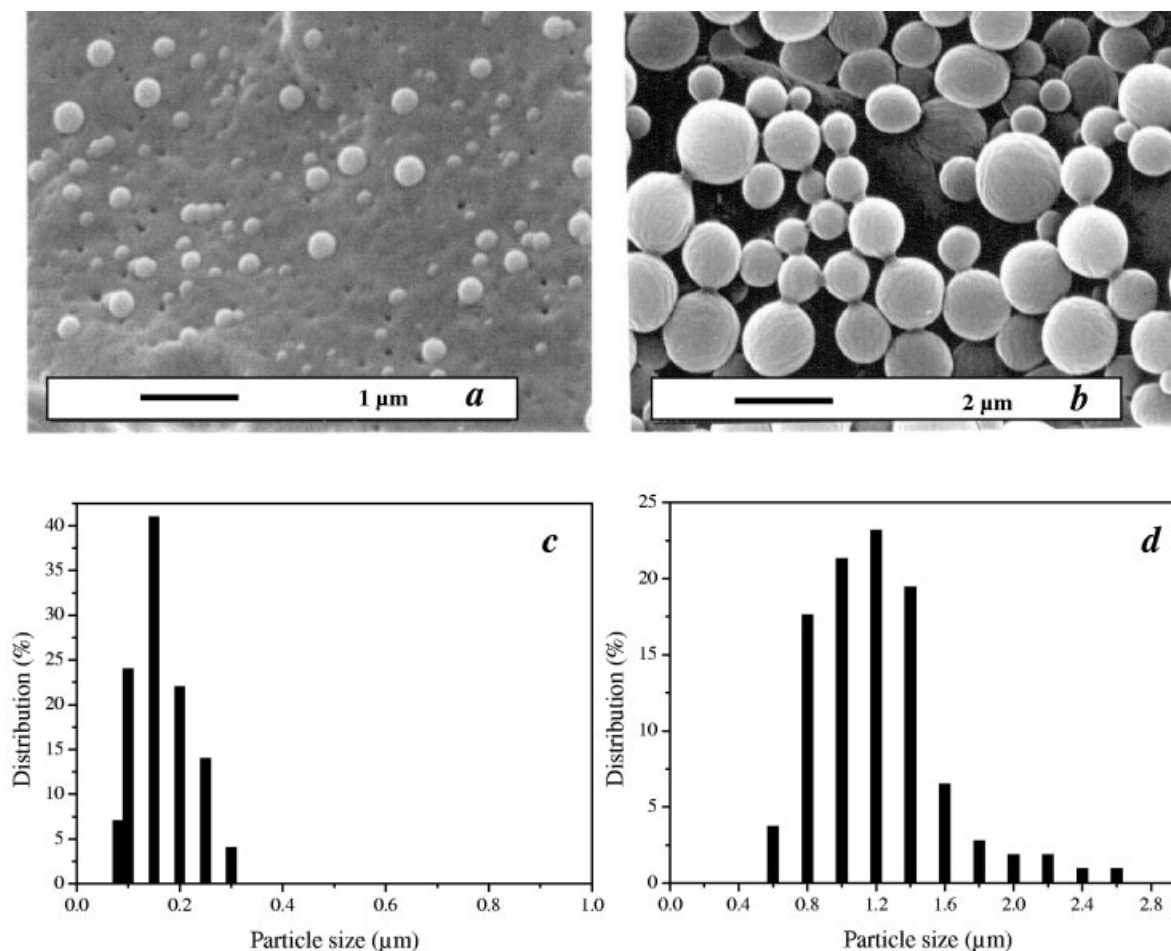


Figure 2 (a) High magnification of Figure 1(b); (b) high magnification of Figure 1(c); (c and d) particle size distribution of blends shown in Figure 1.

tomers blends. Figures 1(a–c) represent the phase morphology of cryogenically fractured and etched surfaces of PA6/EB-OH (85/15), PA6/EB-OH/copolymer (79/15/6), and PA6/EB-NCO (85/15) polymerization-prepared blends. In the PA6/EB-OH (85/15) blend [Fig. 1(a)] it is not expected to form a significant amount of PA6-*b*-EB block copolymer because the reaction time allowed for the formation of homopolyamide 6 using TDI and Na-caprolactamate is much shorter (ca. ~ 1–3 min) than the time necessary to convert the hydroxyl groups of EB-OH to -NCO groups (~ 3–5 h).

In the absence of any compatibilizing agent, i.e., when ϵ -caprolactam is polymerized in the presence of less reactive EB elastomer (slow reaction kinetics with respect to the short time allowed), it was difficult to maintain a stable particle size of the EB phase in ϵ -caprolactam monomer. Particle coalescence was observed, which results in undesired EB phase coarsening in ϵ -caprolactam just before polymerization start-up. The consequences of the coalescence-induced phase coarsening are clear in the blends after polymerization is completed (1–3 min). As shown in Figure

1(a), an average particle size of about 12 μm with a very broad size distribution results from this blend. It is also noticed that the shape of the particles has deviated from an expected spherical form because of the altered coalescence process due to polymerization of ϵ -caprolactam. A close observation of the picture also reveals few small particles, which were generated by the small amount of PA6-*b*-EB copolymer produced. One has to note that a negligible amount of copolymer cannot be avoided. One can also observe that, after etching the EB phase using toluene at 50°C during 20 h, no attached (to PA6 phase) particles are found. This is a good indication of the negligible formation of EB-*b*-PA6 copolymer compatibilizer.

The SEM pictures of compatibilized PA6/EB-OH blend via premade 6 wt % EB-*b*-PA6-*b*-EB copolymer [Fig. 1(b)] and that of the *in situ* compatibilized PA6/EB-NCO (85/15) blend obtained by anionic polymerization of ϵ -caprolactam [Fig. 1(c)], respectively, show a very significant particle size reduction compared to Figure 1(a). Indeed, the addition of 6 wt % of triblock copolymer to PA6/EB-OH blend results in homogeneously distributed and finely dispersed elastomer

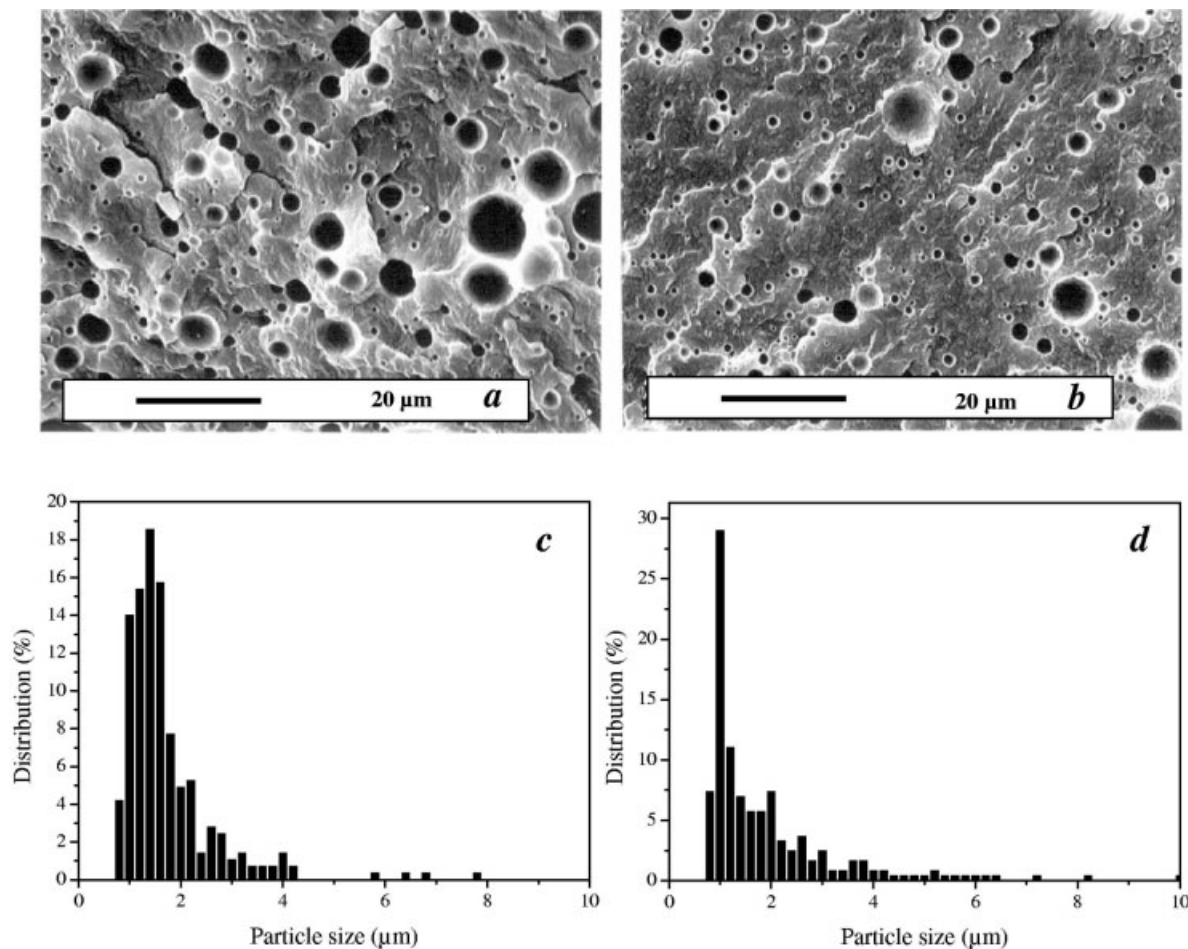


Figure 3 SEM micrographs of etched surfaces of (a) noncompatibilized PA6/EB—OH (85/15), (b) extrusion-prepared blends compatibilized with the premade triblock copolymer PA6/EB—OH/copolymer (79/15/6), and (c and d) particle size distribution, respectively.

particles. The particle size is considerably reduced by a factor of about 100 with respect to the uncompatibilized blend.

A substantial difference in phase morphology of the PA6/EB—NCO blend *in situ* compatibilized by the generation of PA6-*b*-EB block copolymer compared to the premade copolymer modified blend was observed [Fig. 1(c)]. The particle size is larger (1 μm) than that of the premade copolymer compatibilized blend (0.14 μm). After solvent etching, almost all elastomer particles remain attached to the PA6 matrix in the case of the *in situ* compatibilized blend [Fig. 1(c)], whereas, in the other case (premade copolymer), a large majority of particles were removed.

Magnified SEM pictures of Figures 1(b) and (c) are represented in Figures 2(a) and (b), respectively. It can be seen that a narrower particle size distribution is obtained when a premade copolymer is used [compare histograms in Figs. 2(c) and (d), respectively], whereas interconnected elastomer particles are produced in the case of *in situ* compatibilized blend [compare Figs. 2(a) and (b)]. The *in situ* formed copolymer

is certainly able to induce a very diffuse interface, as it is directly generated at the PA6/EB interface; it forms real physical bridges between the EB neighboring particles. In the case of premade copolymer, there exists a restriction to its efficient location at the interface; it is not expected to form bridges between the EB particles. It is important to mention that the nonability of toluene solvent to dissolve the particles that are visible in Figure 2 is certainly an indication that the copolymer forms a layer on EB particles in which the EB segment of the copolymer is completely miscible with the EB phase and that the PA6 block remains as a continuous protecting outer shell on these particles (preventing solvent internal diffusion).

In the case of the extrusion melt-prepared blends (prepared for comparison purposes), a completely different situation of phase morphology development is observed. The SEM pictures as well as the particle size distribution of PA6/EB elastomer blends compatibilized using extrusion blending are given in Figure 3. The blend of Figure 3(a) is compatibilized by PA6-*b*-EB copolymer *in situ* generated via reaction between

isocyanate groups of EB-NCO phase and amine end groups of the polyamide phase. The blend of Figure 3(b) is compatibilized via melt-extrusion blending using a premade PA6-*b*-EB-*b*-PA6 triblock copolymer. In both cases the apparent particle size of the EB elastomer phase is larger (1.6–1.8 μm) than that of the polymerization made blends described in Figures 1 and 2 (0.14 and 1 μm). These results clearly indicate that the polymerization-prepared blends are much more efficiently compatibilized than the extrusion-prepared ones.

To confirm further the generation of PA6-*b*-EB copolymer during the polymerization process, the obtained blends were investigated using the dynamic mechanical analysis. In the absence of any chemical interactions, the physically blended PA6 and EB pure components are expected to exhibit two transitions corresponding to thermal transitions of the pure constituents: PA6 and EB. The temperature dependence of the storage modulus (G') and loss factor ($\tan \delta$) for

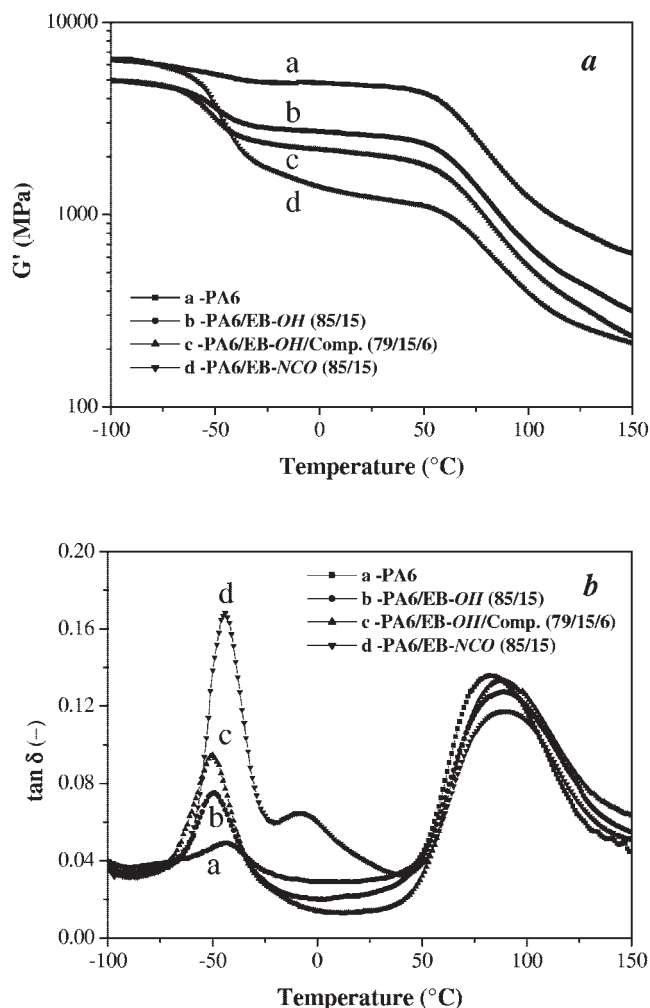


Figure 4 (a) Storage modulus (G') and (b) loss factor ($\tan \delta$) as a function of temperature for PA6 and its polymerization-prepared blends.

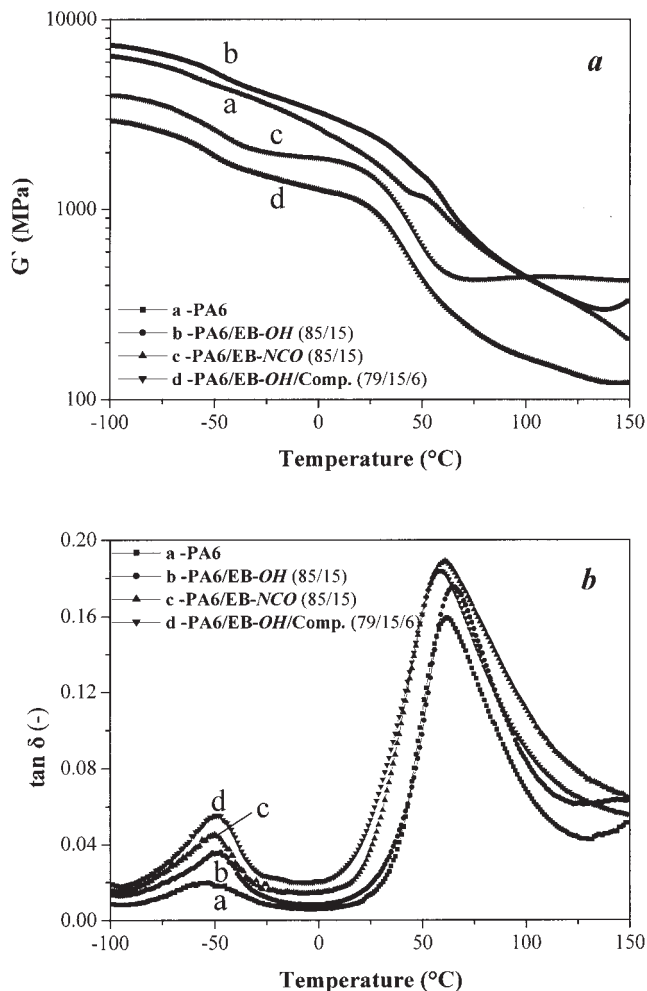


Figure 5 (a) Storage modulus (G') and (b) loss factor ($\tan \delta$) as a function of temperature for PA6 and its extrusion-prepared blends.

pure PA6, noncompatibilized, compatibilized with premade triblock copolymer, and *in situ* compatibilized polymerization-prepared blends are presented in Figures 4(a) and (b), respectively. As expected PA6 has a relatively higher modulus compared to its blends with EB elastomer [Fig. 4 (a)]. The blends of PA6 and EB elastomer exhibit two main transitions corresponding to those of the pure components, i.e., PA6 and EB elastomer as illustrated in Figures 4(a) and (b). The $\tan \delta$ versus temperature curve of PA6/EB-NCO blends (curve d) prepared by polymerization of ϵ -caprolactam in the presence of EB-NCO and *in situ* reactively compatibilized by the formed PA6-*b*-EB copolymer exhibits an intermediate transition between that of the elastomeric EB phase and that of PA6 phase. This additional transition located at -8°C is ascribed to the generation of a PA6-*b*-EB diblock copolymer having a low molecular weight and forming a layer around the EB phase inducing a more diffused interface.^{15–18} An additional indication for the forma-

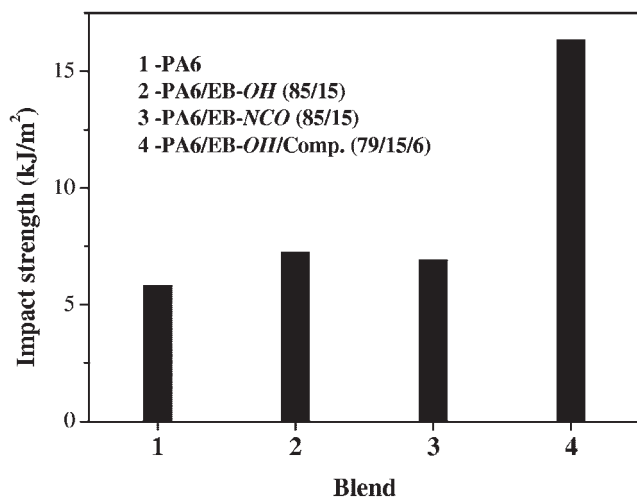


Figure 6 Notched Izod impact strength for PA6 and its polymerization-prepared blends at room temperature.

tion of PA6-*b*-EB block copolymer is the shift of the T_g of the EB phase to relatively higher temperatures (-44°C ; note that T_g of pure EB is -50°C). The non-compatible blends (curve b) and the ones compatibilized using the premade triblock copolymer (curve c) show two distinct transitions situated at the same temperatures as the T_g s of EB elastomer and PA6 phases. This indicates the nonexistence of an intermediate molecular structure. As expected, the $\tan \delta$ and storage modulus of the melt-extrusion prepared blends (Figure 5, curves b, c, and d) do not exhibit any transient or peculiar thermal transition compared to those of pure PA6 (curve a). No significant shift in the glass transitions of EB and PA6 is observed.

The notched Izod impact properties of the samples investigated at room temperature are presented in Figure 6. It can be seen that for the compatibilized polymer blend with the finely dispersed phase morphology a high impact toughness is obtained. Efficient compatibilization promoting a narrow interface is necessary because a PA6/rubber blend is known to deform by a process of rubber cavitation. The notched Izod impact strength of the blend compatibilized with premade triblock copolymer is found to be significantly higher (16 kJ/m^2) than that of neat PA6 (6 kJ/m^2), noncompatibilized, or that of the *in situ* reactively compatibilized blends (7 kJ/m^2). This might be due to a complex interrelation between the particle size and the interparticle distance, which was not easy to establish in this investigation.

CONCLUSION

A model investigation on phase morphology development in polymer blends based on an EB dispersed

phase in a PA6 matrix prepared by ϵ -caprolactam anionic polymerization processes is presented. For comparative purposes the same blends in composition and components have been melt-mixed using a twin-screw extruder at 240°C . The designed blends were investigated with respect to their phase morphology development using electron microscopy, dynamic mechanical analysis, and notched Izod impact tests. A finely dispersed EB elastomer phase was generated in a PA6/EB blend designed via the anionic polymerization of ϵ -caprolactam in the presence of EB elastomer. The substitution of the hydroxyl end groups of the EB chains to isocyanate groups allowed their use as a macroactivator for ϵ -caprolactam anionic polymerization. This also allowed the generation of EB-*b*-PA6 diblock copolymer acting as a compatibilizing agent.

This approach of developing PA6 based blends via polymerization of ϵ -caprolactam in the presence of ethylene-butylene elastomer was shown to be much more efficient than the extrusion prepared blends in terms of particle size reduction. It is also a fast process that can be transferred to a RIM process application. This approach can be adapted to include the use of more viscous rubber phases than the EB elastomer used in the present investigation.

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