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Structure development of TLCP ternary blends during biaxial elongational flow

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Abstract

This study demonstrates the important role of the compatibilizer in blown films of a ternary blend of a thermotropic liquid crystalline polymer (TLCP (a poly(ester amide)), dispersed phase), a polyetherimide (matrix), and a poly(ester imide) (PEsI, compatibilizer). We investigated the morphology of the blown films via transmission electron microscopy and scanning electron microscopy, as well as optical microscopy. A stripe structure of TLCP phase was observed in the blown film, which evidently showed unequal biaxial deformation of the dispersed phase. The compatibilizer helped to deform the dispersed phase in the hoop direction as well as in the flow direction. It was evident that the amount of compatibilizer played a very important role in the dispersion and the deformation of the TLCP phase. It was found that 0.6 wt% of the compatibilizer was the optimum amount when 10 wt% TLCP was included. Coalescence of the TLCP phase was observed when excessive amount of the compatibilizer was used, resulting in a larger dispersed-phase size. The crystalline structure of the dispersed phase did not vary with the compatibilizer. A qualitative explanation of the effect of the compatibilizer on the deformation of the dispersed droplets is given based on simple droplet elasticity and interfacial tension. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Biaxial deformation; Thermotropic liquid crystalline polymer blend; Compatibilizer

1. Introduction

Deformation of the thermotropic liquid crystalline polymer (TLCP) domains dispersed in a matrix polymer into fibril shapes during processing produces a so-called in situ composite because of in situ shaping during processing [1–5]. Because such in situ composites can solve some problems that arise during the processing of conventional fiber-reinforced composites, such as increase in the melt viscosity, thermal degradation, poor dispersion of fibers, wear-out of processing machinery, and breakage of solid fibers, to name a few, they have attracted a great deal of interest. However, they also have some drawbacks. One of them is that most thermoplastics are incompatible with TLCPs. This incompatibility between the matrix polymers and the reinforcing TLCPs leads to poor interfacial adhesion, which brings about a reinforcing effect less than that expected from the law of mixtures [6]. Compatibility between the matrix polymers and the reinforcing TLCPs has been sought to obtain enhanced properties in in situ composites [6–10]. Compatibilization has been known to overcome the problems of poor dispersion and poor adhesion in blends. In recent years, a number of studies on blends of TLCPs with different conventional thermoplastics such as polyamides, polyesters, polycarbonates and polysulfones have been directed at determining the optimal reinforcing effects of TLCP domains to solve the incompatibility problem of in situ composites [11–18]. One way of compatibilizing an immiscible system is to use a third component as a compatibilizer or a coupling agent. In our previous study, we synthesized a poly(ester imide) which was used as a compatibilizer for a poly(ether imide) and a poly(ester amide) TLCP blend [7]. The experimental result revealed that the addition of an optimal amount of the compatibilizer reduced the size of the TLCP droplets and induced a fine distribution [7,9,13,14]. An excess amount of the compatibilizer, however, coalesced the dispersed phase (TLCP domains) [7,8]. Thus, the best mechanical properties were obtained when an optimum amount of the compatibilizer was used [7,9,19].

Among the problems of in situ composites, one of the worse is the poor performance in the transverse direction. Most previous studies have been concerned with deformations of TLCP domains in a uniaxial elongation process [1–6]. A drawback of this process is the high degree of anisotropy, which provides exceptional properties in the flow direction, but poor properties in the transverse direction

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[7–12]. Other ordinary processes, such as injection molding and extrusion, also produce products whose properties in the flow direction may be outstanding due to a deformed TLCP phase, but the anisotropy usually present is such that the transverse properties are grossly inferior [14]. One method of reducing this anisotropy is to use biaxial deformation. If biaxial deformation can be properly done without excessive deterioration of the properties in the flow direction, the polymers will have a wider range of applications.

Recently, some researchers have applied the film blowing process to obtain a more or less well-balanced in situ composite [20–23]. However, poor interfacial adhesion problem was still a problem. In this study, for the first time, we investigated the effect of a compatibilizer for a TLCP blend under biaxial deformation. A major goal of this study was to establish a basic understanding of the compatibilizer's role in the biaxial deformation process and to investigate the possibility of controlling the morphology.

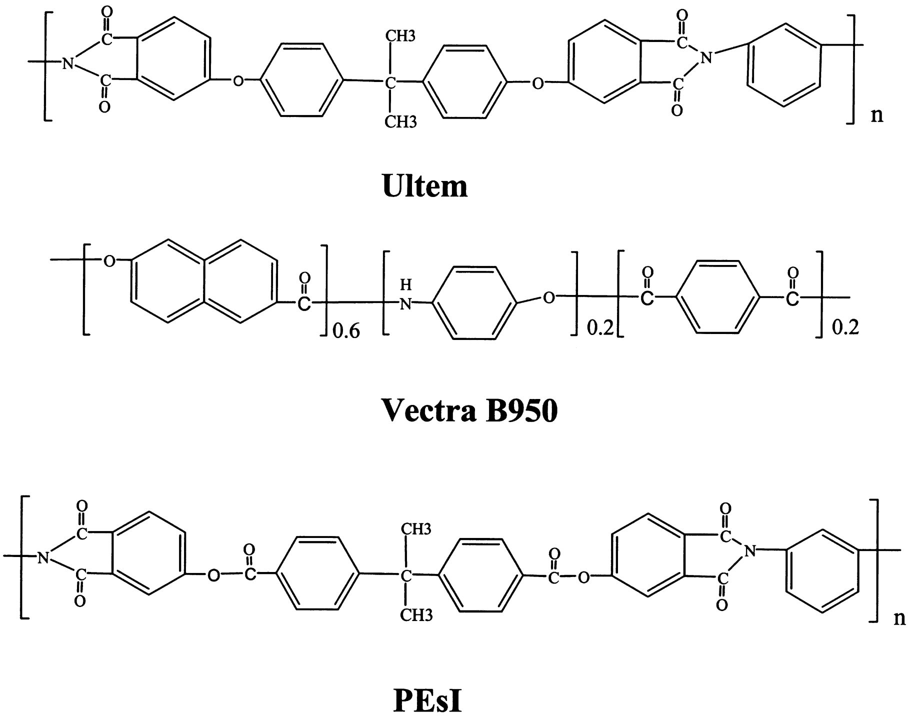
2. Experimental

2.1. Materials

The TLCP used was a copolyester amide of 6-hydroxy-2-naphthoic acid (60%), terephthalic acid (20%), and aminophenol (20%), commercially known as Vectra® B950 (VB) manufactured by Celanese Hoechst. This material has been used and characterized by many researchers. It was supplied in the form of pellets. Poly(ether imide) (PEI), commercially known as Ultem® 1000, an amorphous polymer made by GE, was used as the matrix. The compatibilizer used in this study was a poly(ester imide) (PEsI). Details of its synthesis scheme and miscibility with VB and PEI were fully described in our previous study [7]. Scheme 1 shows the chemical structures of these polymers.

2.2. Blending and extrusion

The pellets of PEI and VB were dried in a vacuum oven at 120°C for at least 24 h before use, and steps were taken during processing to minimize exposure to atmospheric moisture. The TLCP content was kept at 10 wt%. The TLCP content should be at least 25 wt% for the best mechanical performance [6], but it was kept at 10 wt% in this study for other reasons. The amount of PEsI was kept to less than 1.5 wt% [7]. Blending was carried out in a 42 mm Bravender twin-screw extruder (AEV651) at a fixed rotation speed of 20 rpm. At the end of the extruder, a connector and an annular die (Bravender No. 8) were attached for film blowing. The annulus had a slit thickness $h_0 = 1$ mm and an inner radius $a_0 = 26$ mm. The apparatus was also equipped with an adjustable film tower with a guide, nip and take-off rolls, and a Bravender torque winder onto which the sheet was subsequently wound. The extrusion temperatures of the feeding zone, transporting zone, melting zone, and die were set as 240, 330, 330, and 335°C, respectively. The connector was also wrapped with a heating band. The temperature of the connector and the annular die were set as 330°C. The die temperature could not be varied to a large extent because of the solidification in the narrow annular gap at lower temperatures and because of insufficient



Scheme 1.

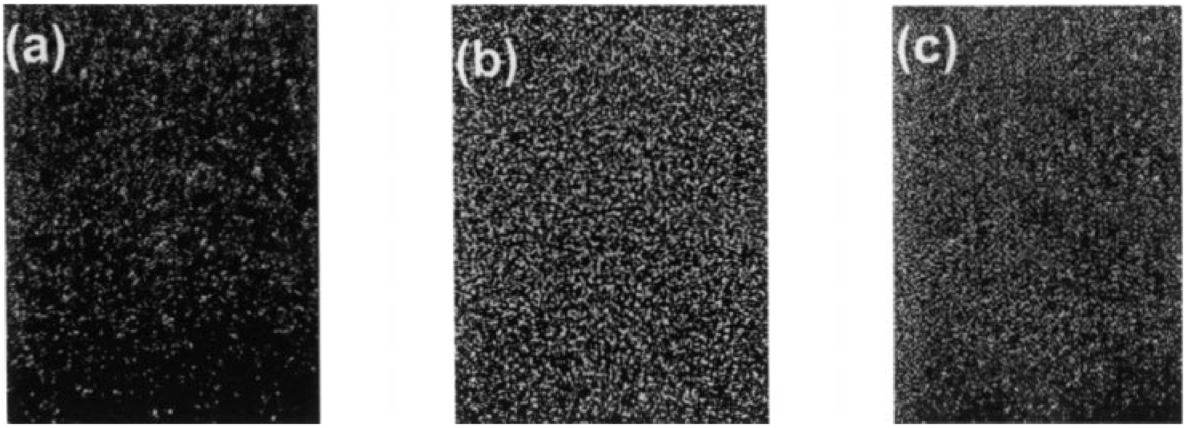


Fig. 1. Crossed polarized optical micrographs (400 times magnification) of the blown films: (a) binary-blend film; (b) ternary-blend film with 0.6 wt% PEsI; and (c) ternary-blend film with 1.3 wt% PEsI.

melt strength at higher temperature. The blown parison was encircled with a Teflon bag to keep a hot atmosphere, which could prevent early solidification, around it. The major adjustable parameter was the pressure of the nitrogen blown into the bubble. The blow-up ratio (ratio of the diameter of the final bubble to that of the annulus) was controlled in the range of 1–3. Although both the thermal history and the deformation history have a significant effect on the final structure in and the final properties of the blown film, we could not vary them over a wide range because the processing window was quite narrow for the same reason as the die temperature. By the same token, cooling air was not used in this study. For removal of the anisotropy, use of a counter-rotating annular die is desirable [23], but our equipment had only a non-rotating die. This should be pursued in the future.

2.3. Scanning electron microscopy (SEM)

Observations of the composite film morphologies were performed on a Hitachi S-2500 model. The samples were fractured in liquid nitrogen and were coated with gold to enhance the phase contrast.

2.4. Transmission electron microscopy (TEM)

The specimens for TEM were cryoultramicrotomed using a Reichert Ultracut S (Leica) microtome equipped with a diamond knife. Sections (50 nm thick) were obtained at −100°C. A transmission electron microscope (JEM 1200 EXII, JEOL) operating at 100 kV was utilized to observe the specimens. The specimens were stained with ruthenium tetroxide (RuO_4) vapor.

3. Results and discussion

In an effort to provide a support for the compatibility of the blend, the morphologies of the binary and the ternary blends were first investigated. Fig. 1 shows polarized micrographs of the blends. The samples were heated to 320°C, maintained for 3 min at that temperature, and then cooled in a hot stage. Since the thickness of the film was relatively thick for optical microscopy, the image of the crystalline zone is not very clear, but it definitely shows that ternary blends have a more uniform and finer dispersion of TLCP phase due to the effect of the compatibilizer. Fig. 2 shows the surface morphology of the blown films. The surface of

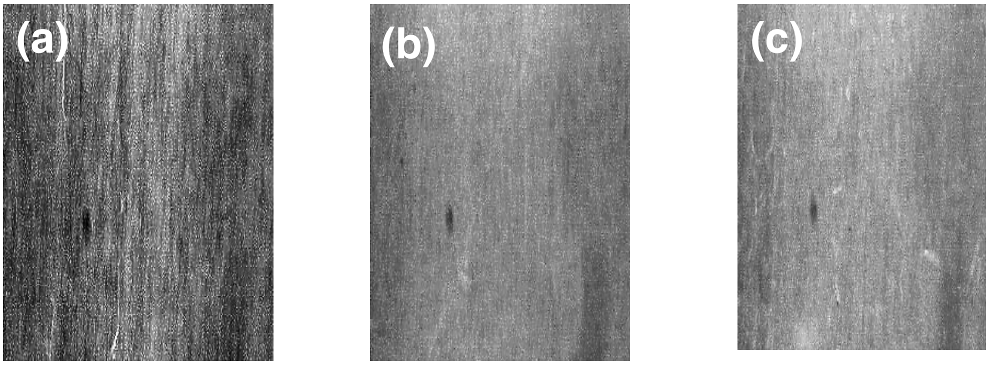


Fig. 2. Surface morphology of the blown films: (a) binary-blend film; (b) ternary-blend film with 0.6 wt% PEsI; and (c) ternary-blend film with 1.3 wt% PEsI.

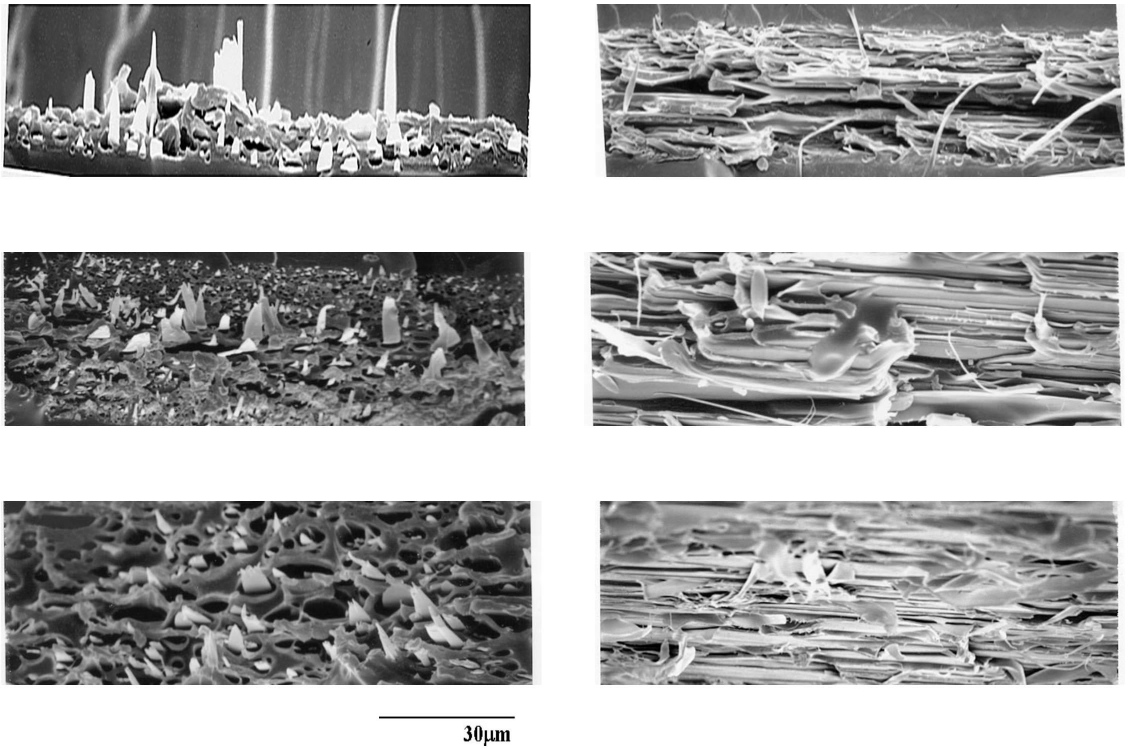


Fig. 3. SEM micrographs of the fractured surfaces of binary-blend films (1000 times magnification). Surfaces are fractured normal to the flow direction (left column) and parallel to the flow direction (right column). Blow-up ratios are 3, 2, and 1 from top to bottom. Film thicknesses are 0.2, 0.4, and 0.6 mm, respectively.

the binary blend is more rugged and rougher due to the relatively larger size of the TLCP phase while the surface of the ternary blend is smooth and uniform due to the fine dispersion of the TLCP phase by the compatibilizing action.

SEM shows more vividly the microstructure of the blown film. Figs. 3–5 show the fractured surfaces of the binary and the ternary blends both in the machine direction (flow direction) and the normal direction (thickness direction). Several factors are worth noting.

First, the micrograph of the binary blend film displays poor adhesion between the two phases, which leads to an open ring around the TLCP phase and to holes formed by pulling out the TLCP domains during the fracturing process. The surface of uncompatibilized binary blend, which is fractured normal to the flow direction, shows relatively large TLCP domains, indicating a poor dispersion (Fig. 3, left column). In contrast, the TLCP phase in the ternary blends (Fig. 4, left column and 5, left column) is more evenly distributed and finer in size than that of the binary blend. The fracture is seen to occur more within the TLCP phase in the compatibilized blend, and not many open rings exist around the TLCP domain, reflecting a better binding between the two phases because of the compatibilizer's existence at the interface. All the SEM images show that a broad distribution exists in the size of the dispersed domains. All of the dispersed TLCP domains are deformed into stripes due to biaxial elongation. This is obviously different from shear flow. In shear flow, it is known that as the shear rate is varied, a critical minimum drop size exists [24–27]. As explained later, a decrease in the interfacial tension due to the compatibilizer allows small droplets to deform easily. For blends containing 1.3 wt% PEsI, the size of the TLCP phase is bigger than that of the blend containing 0.6 wt% PEsI. In our previous study on uniaxial deformation of the TLCP phase in a ternary blend of PEI, VB, and PEsI, we observed an optimum amount of compatibilizer for the best mechanical properties and for uniform dispersion of the TLCP phase [7]. For a TLCP phase content of 25 wt%, a maximum reduction in the dispersed domain size was observed when 1.5 wt% of the compatibilizer was added to the blend. This amount corresponds to 0.6 wt% for VB content of 10 wt%. Thus, our ternary blend containing 0.6 wt% PEsI would be optimum. When the amount of the compatibilizer exceeds the optimum quantity, the excess compatibilizer tends to coalesce the dispersed TLCP phase [7]. The flocculation and the coalescence of the TLCP phase result in a less uniform dispersion and a bigger VB domain. Dispersed VB domains are not even homogeneous; they include the compatibilizer, which acts as a defect in the VB phase. As a result, when excess compatibilizer was added, the mechanical properties of the blend became even worse than those of a binary blend [7,14]. Details of the physical properties of biaxially deformed in situ composites are reported elsewhere [28].

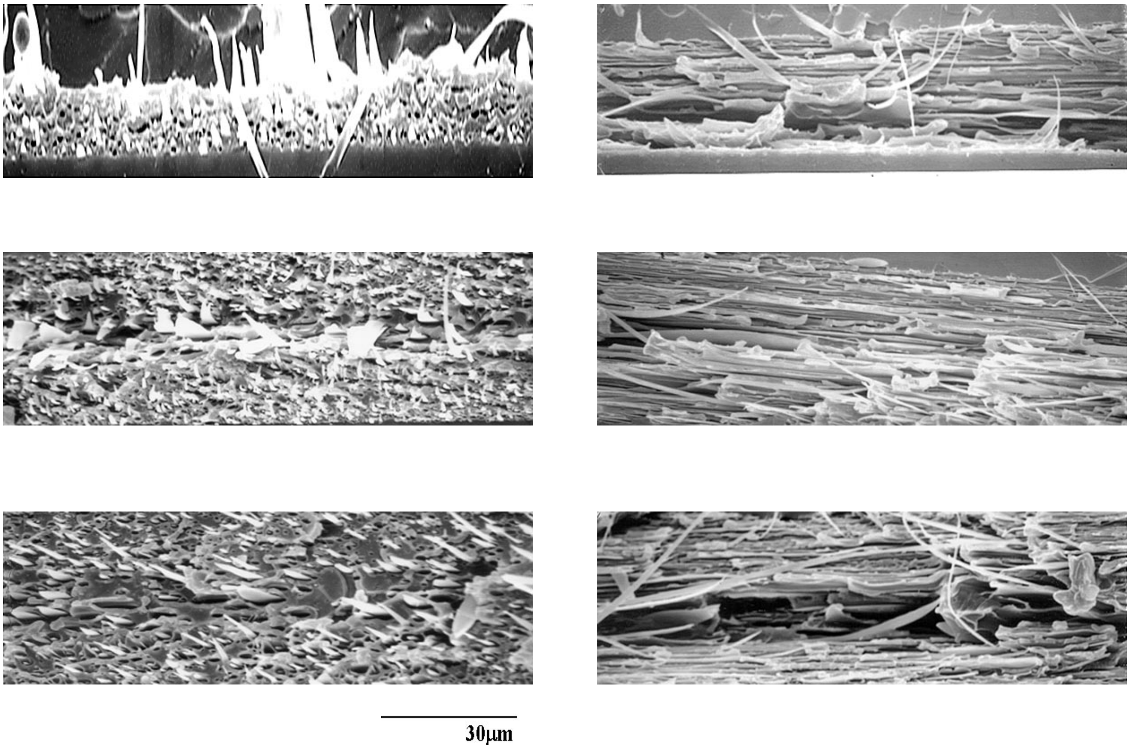


Fig. 4. SEM micrographs of the fractured surfaces of the ternary-blend films with 0.6 wt% PEsI (1000 times magnification). Surfaces are fractured normal to the flow direction (left column) and parallel to the flow direction (right column). Blow-up ratios are 3, 2, and 1 from top to bottom. Film thicknesses are 0.2, 0.4, and 0.6 mm, respectively.

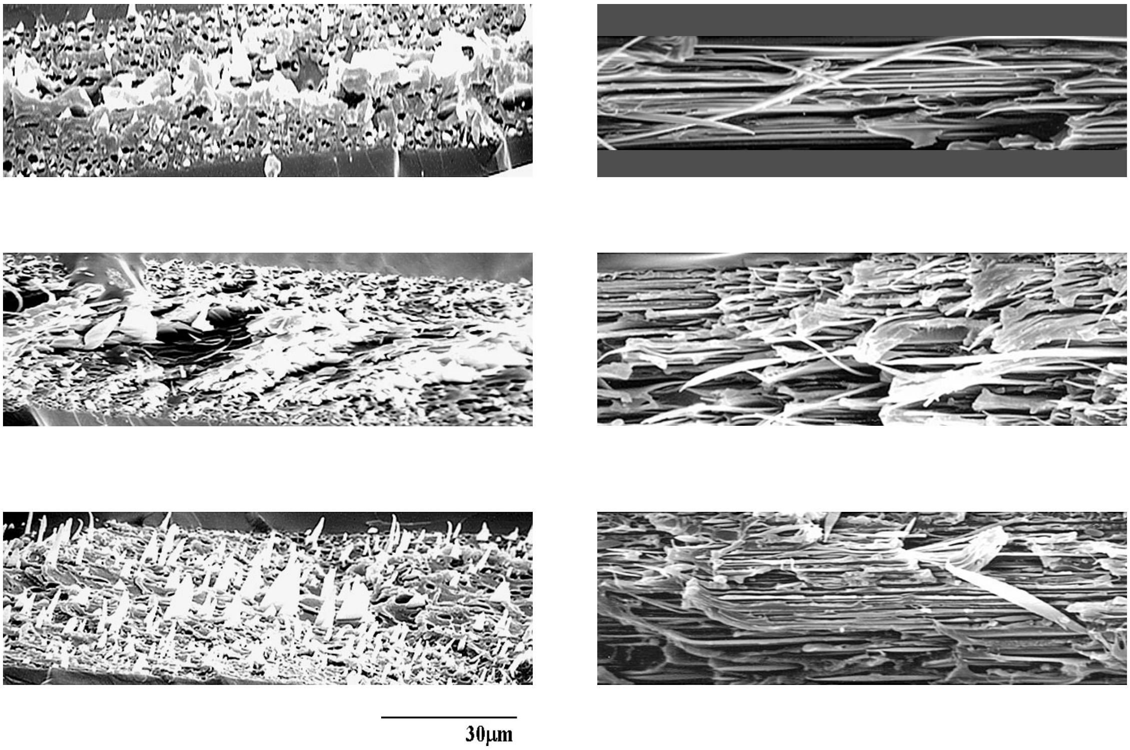


Fig. 5. SEM micrographs of the fractured surfaces of the ternary-blend films with 1.3 wt% of PEsI (1000 times magnification). Surfaces are fractured normal to the flow direction (left column) and parallel to the flow direction (right column). Blow-up ratios are 3, 2, and 1 from top to bottom. Film thicknesses are 0.2, 0.4, and 0.6 mm, respectively.

Second, the TLCP phase in blown films can be seen to be mostly elongated in the flow direction (unequal biaxial deformation) which indicates that more deformation occurred in the flow direction owing to strong pulling at take-up unit, and also to be flattened in the plane of the film (Figs. 3–5). This is an evident difference between uniaxial deformation (extrudate drawing), equal planar biaxial deformation, and unequal biaxial deformation (film blowing). Occasionally, fibers of submicron size are seen, but most of the dispersed VB phase is deformed into flat stripes rather than fibrils due to the biaxial deformation in the film blowing process. The high blow-up ratio leads to more deformation than low blow-up ratio in the radial direction; hence, flatter stripes are observed. Large flat stripes are more abundant in the middle of the blown film than in the inner and the outer surface regions. This can be ascribed to shearing action inside the die. In the absence of wall slip, high shearing deforms the dispersed phase in the flow direction near the wall whereas almost no shearing or very slight shearing occurs in the middle of the flow [29]. When the melt comes out from the die, the less deformed VB phase in the middle can be deformed more in the hoop direction to produce flatter stripes in the middle section. For the blown films in this study, the holes opened by the pulling out of the TLCP phase are ellipsoidal rather than circular. Ternary blends show flatter stripes than binary blends. Good adhesion at the interface by the compatibilizer allows the dispersed VB phase to be deformed in the circumferential direction (hoop direction) as well as in the flow direction. The numerous large matrix voids generated in binary blends by the pulling-out the stripes reveal poor interfacial adhesion between the matrix and the dispersed phase, whereas the reduction in the number of such voids in ternary blends indicates good adhesion. The ternary blend containing 0.6 wt% PEsI shows more uniform deformation in both the flow direction and the hoop direction than the ternary blend having 1.3 wt% PEsI. This is confirmed by TEM, as shown below.

Third, the SEM micrographs of blown-film samples broken parallel to the flow direction reveal that the layers formed by the dispersed stripes are thinner for the compatibilized blends due to a more uniform and fine distributions of the TLCP phase (right column figures of Figs. 3, 4 and 5). In a non-compatibilized blend, the long TLCP stripes are bundled together. Also, the stripe surfaces look clean and smooth along the flow direction, which indicates poor adhesion between the TLCP phase and the matrix. In contrast, the compatibilized blown-film containing 0.6 wt% PEsI exhibits finer and thinner stripes with rough and rugged surfaces. This definitely indicates good adhesion between the TLCP stripes and the matrix phase. However, the TLCP domains coalesce when excess PEsI is added. Thick bundles of stripes appear as excess PEsI is added (1.3 wt% PEsI, Fig. 5, right column), but their surfaces were still rough due to strong interactions.

Fourth, the skin–core texture in which the core remains relatively undeformed is absent in the blown films. This is due to the biaxial elongational deformation, which proceeds during the film blowing process.

Fifth, thinner films have large blow-up ratio, which is defined as the ratio of bubble radius to that of the die radius after the film radius reaches to the steady state. The radial direction deformation rate increases with the blow-up ratio. SEM micrographs display more deformed (wider) TLCP phase with thin films of larger blow-up ratio.

TEM images of the binary and the ternary blends are given in Fig. 6; the VB phase appeared as separate domains dispersed in the PEI matrix. The binary blend has relatively large domains while the ternary blend of 0.6 wt% PEsI shows more finely dispersed VB spheroids in the matrix. It should be noted that all the dispersed VB domains are ellipsoidal rather than spherical, which is again ascribed to the biaxial deformation occurring in the film blowing process. On the other hand, the TEM image of the ternary blend with 1.3 wt% PEsI clearly shows the coalescence of the particles. In Fig. 6D (a magnification of Fig. 6C), PEsI is seen to reside at the interface between the PEI and the VB, and due to the coalescence, the domain size of the VB phase is much larger. These TEM images also demonstrate the importance of using an optimum amount of the compatibilizer. Elsewhere, it is evidently shown that the morphology observed in the ternary blends is responsible for the significant improvements in the mechanical properties of those blends especially in the hoop direction when an optimum amount of compatibilizer is added [28].

SEM and TEM micrographs show that the size and the shape of the dispersed phase vary with the addition of a compatibilizer. This can be explained by the force balance in a droplet. In polymer blends, deformation and the final shape of the dispersed phase are the result of a dynamic equilibrium between the forces from the matrix (the shear stress and the elasticity of the matrix) and the resisting force (the elasticity of the droplet and the interfacial tension). This can be expressed by the following equation:

$$\eta_{\mathrm{m}}\dot{\gamma} + N_{1\mathrm{m}} = \mathit{\Gamma}/r + N_{1\mathrm{d}} \Rightarrow n_{\mathrm{m}}\dot{\gamma} + (N_{1\mathrm{m}} - N_{1\mathrm{d}}) = \mathit{\Gamma}/r \quad (1)$$

where η_{m} is the viscosity of the matrix, $\dot{\gamma}$ the shear rate, $\mathit{\Gamma}$ the interfacial tension, r the radius of the droplet, and $N_{1\mathrm{m}}$ and $N_{1\mathrm{d}}$ the first normal stresses of the matrix and the TLCP droplet, respectively. Since the film blowing process is a biaxial extension process, it does not have any shear deformation. Thus, we define a new capillary number, Ca^{E}, (the elastic capillary number) as

$$Ca^{\mathrm{E}} = (N_{1\mathrm{m}} - N_{1\mathrm{d}})/(\mathit{\Gamma}/r) \quad (2)$$

which is the ratio of the elastic force on the droplet to the interfacial tension. Dispersed particles are deformed when $Ca^{\mathrm{E}} > 1$. This is clearly the case for PEI/VB blends [30]. Addition of the compatibilizer reduces the interfacial tension, and also the size of the dispersed phase. However, elongational flow can deform small particles [7,21,28]. Hence, the compatibilized blends have smaller dispersed-phase

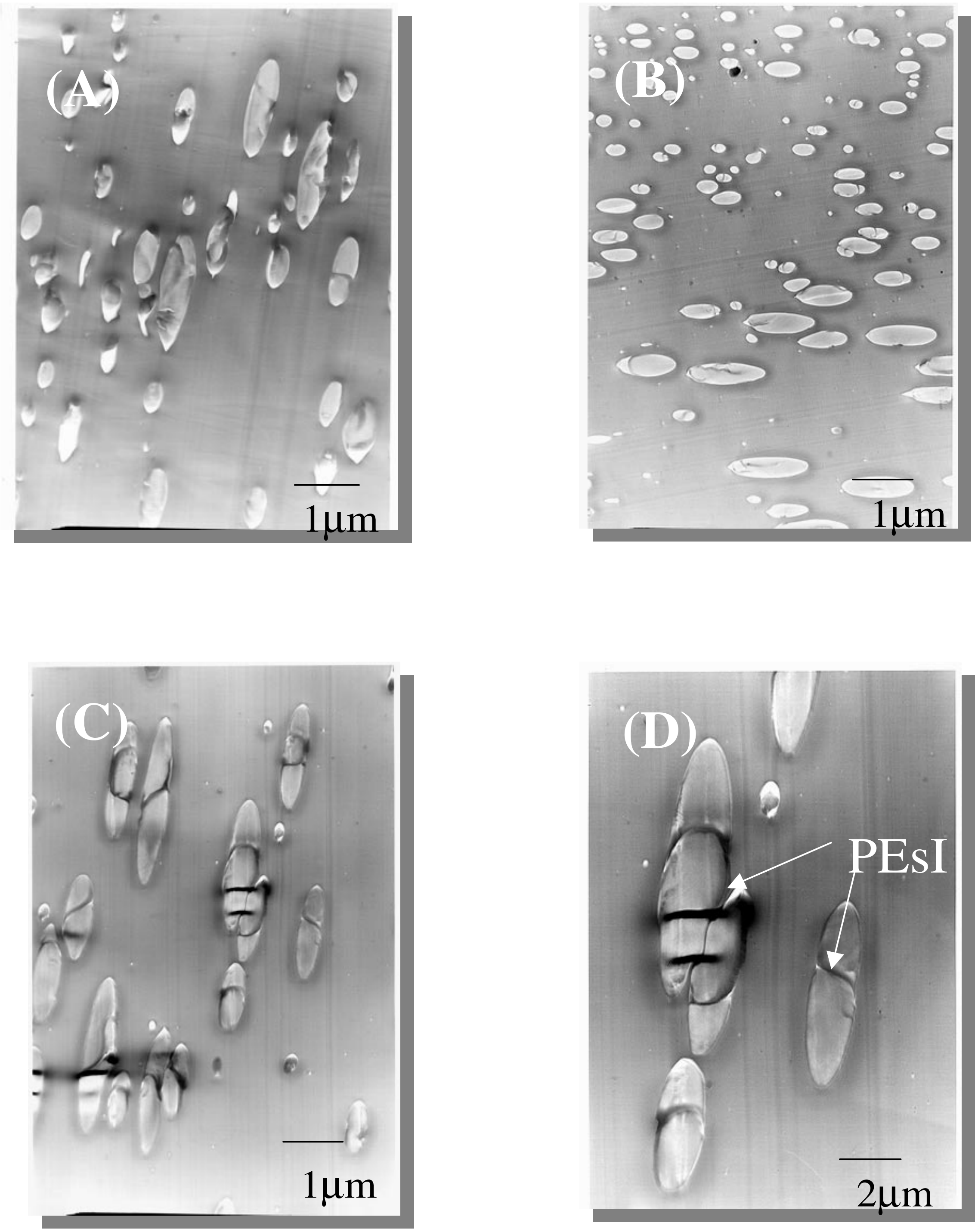


Fig. 6. TEM images of the blown films: (A) binary- blend film; (B) ternary-blend film with 0.6 wt% PEsI; and (C) ternary-blend film with 1.3 wt% PEsI. (D) Enlarged picture of (C).

regions, but they are deformed (Figs. 3–5). This deformation happens outside the die exit, and the normal stresses exerted by the matrix on the drop make stretching in parallel and perpendicular directions to the flow direction. According to Levitt and Macosko's experimental results on the droplet deformation [25], the widening of the drop is inversely proportional to the ratio of the drop and matrix elasticities, $G_r = G_d/G_m$ where G_d and G_m are the elastic modulus of the droplet and the elastic modulus of the matrix, respectively. Based on the simple assumptions that stretching in the hoop direction is much larger than that in the thickness direction and that the second normal stress difference is proportional to the first normal stress difference, Levitt and Macosko obtained an approximate equation for the thickness of a droplet after deformation [25]

$$0.6(G_m - G_d) \approx \Gamma/R_n^{max} \tag{3}$$

Thus,

$$R_n^{max} = \Gamma/(0.6(G_m - G_d)) \tag{4}$$

where Γ is the interfacial tension and R_n^{max} is half the maximum thickness. Addition of a compatibilizer decreases the interfacial tension; hence, R_n^{max} decreases. Since the thickness is inversely proportional to the width of the droplet, reduced thickness means increased width (widening in the hoop direction). In the film blowing process, therefore, reduction of the interfacial tension by the compatibilizer induces more deformation of the droplet in the hoop direction. Also, deformation due to large blow-up ratio leads to more deformation in the hoop direction, hence the compatibilized TLCP phase of better adhesion is more deformed and becomes thinner and wider in hoop direction.

4. Conclusions

The experimental results provide some insights into the importance of morphology control in two-dimensional in situ composites (blown films) by the compatibilizer. Addition of the compatibilizer leads to improved adhesion, better stress transmission, reduced interfacial tension, hence, finer dispersion of the TLCP phase. The skin–core morphology normally observed in extrudate of TLCP blends is absent in biaxially oriented films due to the elongational deformation in the film blowing process that deforms the TLCP phase uniformly in the hoop direction as well as in the flow direction. Biaxial deformation produces flat stripes rather than round fibrils. Addition of the compatibilizer enhances the adhesion at the phase boundary, and allows better stress transfer and easier deformation.

It should be emphasized that the final particle size of the dispersed phase depends on the amount of added compatibilizer. Coalescence during the blending process occurs when an excessive amount of compatibilizer is used, resulting in larger particle sizes. This was manifest in the TEM images. Distribution of the particle sizes in the dispersed phase was generally broad.

In shear flow, it is known that as shear rate is varied, there is a critical minimum drop size for deformation. Deformation of a small drop can be achieved in elongational flow. The SEM images of the biaxially blown films show that most of the dispersed phase is deformed into stripes and that reduction of the interfacial tension helps not only the deformation in the flow direction but also that in the hoop direction. The film morphology includes large stripes in the middle section and these are due to the shearing action in the die. Adding a proper amount of compatibilizer induces a finer dispersion of the TLCP phase. On a microscopic scale, more deformation in the hoop direction occurs for a larger blow-up ratio. The SEM images show films containing stripes whose biaxial orientations become more apparent with the addition of the compatibilizer, which widens the stripes. Thus, from a processing point of view, it is highly desirable to have the proper (optimum) amount of the compatibilizer for the best dispersion, the most deformation of the dispersed phase, and the best properties. Excessive compatibilizer coalesces the dispersed phase. This conclusion is consistent with our previous study of uniaxially drawn in situ composite [7]. This study also shows a certain similarity as well as a clear difference between uniaxial deformation and biaxial deformation. Reduction of the interfacial tension by adding a compatibilizer helps the biaxial deformation both in the hoop direction and in the flow direction.

Acknowledgements

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