

The Influence of a Copolymer as Adhesion Promoter for Polycarbonate and Liquid Crystalline Polymer Blends

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SYNOPSIS

The modification of the interface between polycarbonate (PC) and PetPhb60 was studied. The ester interchange reaction between the components of the 50% w/w mixture, responsible for the formation of molecular segments of intermediate affinity toward the parent polymers, has greatly affected the morphology of extrudate samples. The reacted compound was used in the ratio of 5% as compatibilizer in the formulation of the *in situ* composite between PC and PetPhb60, containing 10% of the reinforcing thermotropic liquid crystal polymer (TLCP). The effects of the adhesion promoter has been evaluated comparing the morphological features of melt-drawn fibers with the previous result concerning the fibers without the compatibilizer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In the 1990s, the plastic industry is experiencing its greatest advances in materials and processing. Along with the development of new high-performance resins, new trends are being established in the processing of composites and polymer blends. However, the addition of rigid fillers into a polymeric matrix continues to have an adverse effect on the processability.^{1,2} For reasons similar to those accounting for the excellent dimensional stability and the increased elastic modulus, the presence of solid filler results in a dramatic increase in the melt viscosity.

The enormous effort exerted by the industry in seeking new materials to be used as plastic modifiers has been rewarded with the discovery of the unique properties of the thermotropic liquid crystalline polymers (TLCP). Since the TLCPs can be processed in conventional equipment, they are prime candidates to produce high-stiffness and -strength fibers to be used as *in situ* reinforcing agents for high-performance thermoplastics.

Blending of TLCPs with thermoplastics, however, offers the possibility of exploiting many of the in-

triguing features of TLCPs. Several advantages can be accomplished by the addition of TLCPs to a polymeric mixture.³⁻¹¹ The rigid or semirigid molecules in the liquid crystalline state can easily orient if subjected to suitable processing conditions, i.e., elongation and/or converging flows and electric or magnetic fields.

Therefore, if the desired goal is to improve the mechanical properties of the hosting matrix, then an effective orientation of the molecules along the spinning direction of fibers ought to be accomplished by controlling the processing parameters, such as temperature, viscosity ratio between components, shear stress in the extruder, and spinning velocity. The formation of elongated fibers during the processing of the blends is the main reason for referring to this class of materials as "*in situ* composite."

Since the relatively rigid backbone molecules can be oriented in the nematic phase, the TLCP inclusions in the polymer matrix can elongate and the molecules can orient during the processing, retaining their orientation during the cooling down of the product. The orientation of the rigid blocks produces a manyfold increase of the elastic modulus of TLCP.^{12,15} In blends constituted by a random-coil polymer (matrix) and a nematic polymer (filler), the increase of mechanical properties depends on the composition of the blend and can be easily fore-

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seen, assuming a good adhesion between matrix and filler, on the basis of composite theory.^{12,16}

The excellent nonreactivity of TLCPs, however, is responsible for the poor adhesion between the filler and the matrix. The wide scientific literature³⁻¹² concerned with blends based on TLCP clearly indicated the need of a deep investigation into the interaction mechanism between the liquid crystalline phase and the matrix, the adhesion between the matrix and filler being a factor of dramatic influence in the success of a composite design. To transfer the stress between the interface, a chemical binding is desirable, but a careful balance between the factors limiting the chemical miscibility is necessary to prevent the formation of a homogeneous mixture in which the absence of the liquid crystalline fibers segregated from the matrix will eliminate the reinforcement effect. The relevant role of the chemical interactions and the control over the morphology during the processing of the *in situ* composite have been described by the authors.¹³ Also, in previous work by Carfagna et al.,¹⁷ the interfacial strength was calculated on the basis of the Kelly and Tyson theory¹⁸ in blends of polycarbonate and PetPhb60 and the adhesion between the polycarbonate and TLCP was found to be poor.

Because the phenomena relating the chemical interactions between the components of the blend and its physical-chemical properties are very complex, this research sought to understand the improvement in adhesion between the reinforcing phase and the hosting matrix as a result of the addition of a compatibilizer.

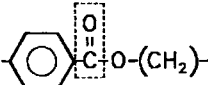
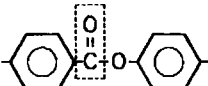
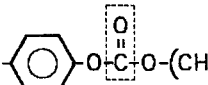
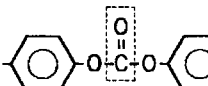
EXPERIMENTAL

The TLCP used in our investigation was kindly supplied by Tennessee Eastman Co. It is the well-known copolyester composed of 40 mol % of poly(ethylene terephthalate) and 60 mol % of poly(*p*-hydroxybenzoate), with an inherent viscosity of 0.68 dL/g and will be referred to as PetPhb60. The amorphous polymer used as hosting matrix is the bisphenol-A polycarbonate (PC), produced by

Table I Composition of the Polymeric Blends

	PetPhb60 (% w/w)	PC (% w/w)	Compatibilizer (% w/w)
PC/LC10	10	90	—
PC/LC10C	10	85	5
PC/LC50	50	50	—

Table II FTIR Absorption Bands of Selected Molecular Units

a)		1730 cm ⁻¹
b)		1740 cm ⁻¹
c)		1770 cm ⁻¹
d)		1780 cm ⁻¹

General Electric Co. with the trade name of Lexan, with an inherent viscosity of 0.42 dL/g.

The blends were prepared with the compositions listed in Table I. The polymers were vacuum-dried at 100°C overnight and homogeneously mixed in a Brabender at 260°C and 32 rpm for 10 min.

- DSC The transition temperature of the polymers and their blends were measured by differential scanning calorimeter (DSC), DuPont 910, at the scanning rate of 10°C/min.
- FTIR The spectroscopic investigation was performed on unsupported thin films by Nicolet Mod. 5 PC Fourier Transform Infra Red (FTIR) spectrometer at the resolution of 2 cm⁻¹.
- GPC The molecular weight and the molecular weight distribution was evaluated by a Polymer Laboratories gel permeation chromatographer (GPC). The system was calibrated using polystyrene standards. All samples were prepared as 0.2 wt % solutions in methylene chloride (CH₂Cl₂).
- SEM The morphology of the extrudates and drawn fibers was analyzed by Scanning Electron Microscope (SEM) using a Hitachi mod. S-2300. Sections of samples were obtained by fracturing them in liquid nitrogen.
- Fiber Spinning Spinning of the PC/PetPhb60 blend was performed by a rheometer, CEAST Rheoscope 1000, provided with a melt-spinning unit using a flat-entry die of the diameter of 1 mm and L/D of 10.

The Development of the Compatibilizer

A 50 wt % mixture of PC and PetPhb60, first dried overnight undervacuum, was mixed in a Brabender

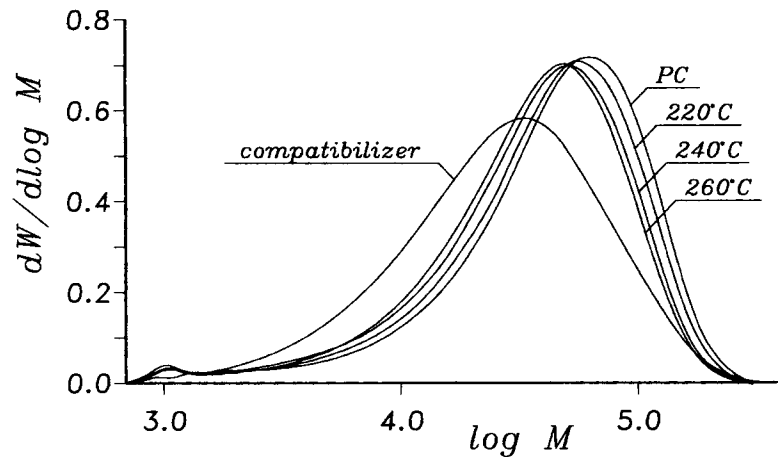


Figure 1 GPC chromatograms of unprocessed PC and PC extracted from the compatibilizer and from PC/LC10C blends processed at 220, 240, and 260°C.

in the molten state (260°C). Afterward the resulting blend was finely ground and the tetra(buthyl-*o*-titanate) (TBOT, as supplied by Aldrich) was added as an ester interchange catalyst, in the ratio of approximately 0.5 wt %. The mixture was heated at different reaction temperatures in the column of the

capillary rheometer. The extent of the interchange reaction was evaluated at the following temperatures: 220, 240, 260, and 275°C. The reaction time was 180 min in the case of the samples treated at 220, 240, and 260°C; for the temperature of 275°C, the reaction time was 210 min.

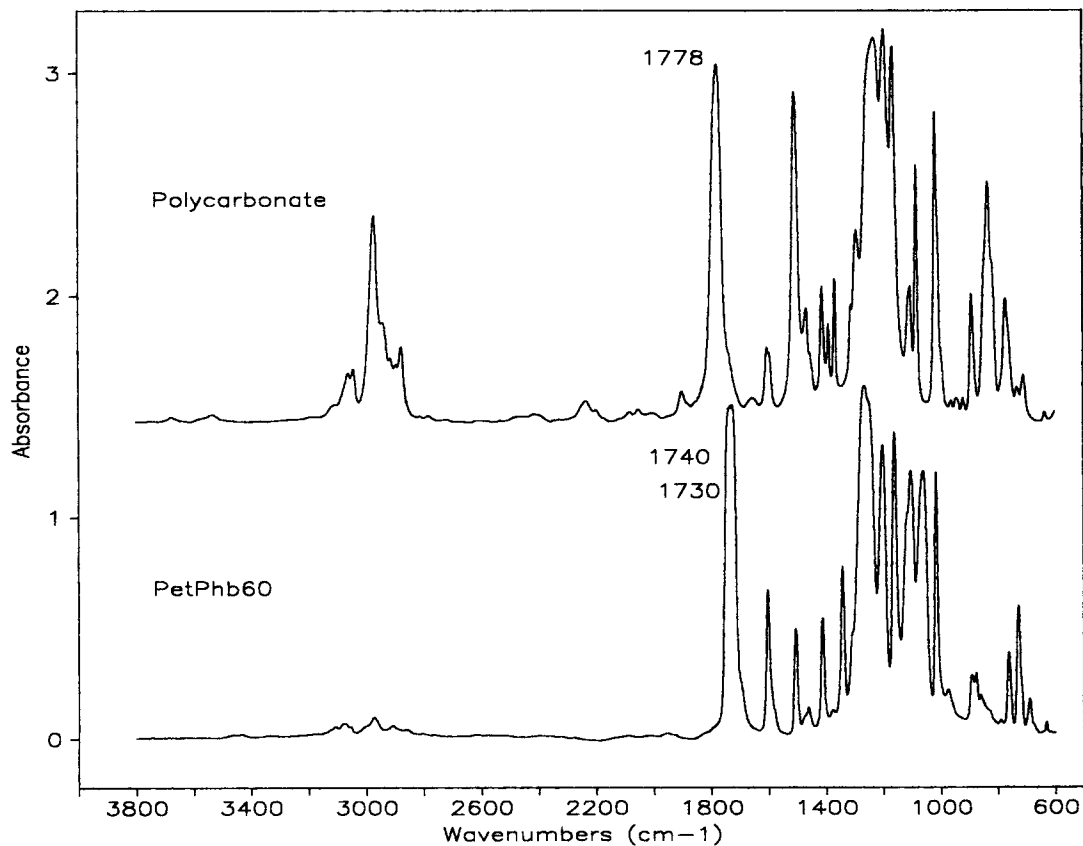


Figure 2 FTIR spectra of PC and PetPhb/60 pure polymers.

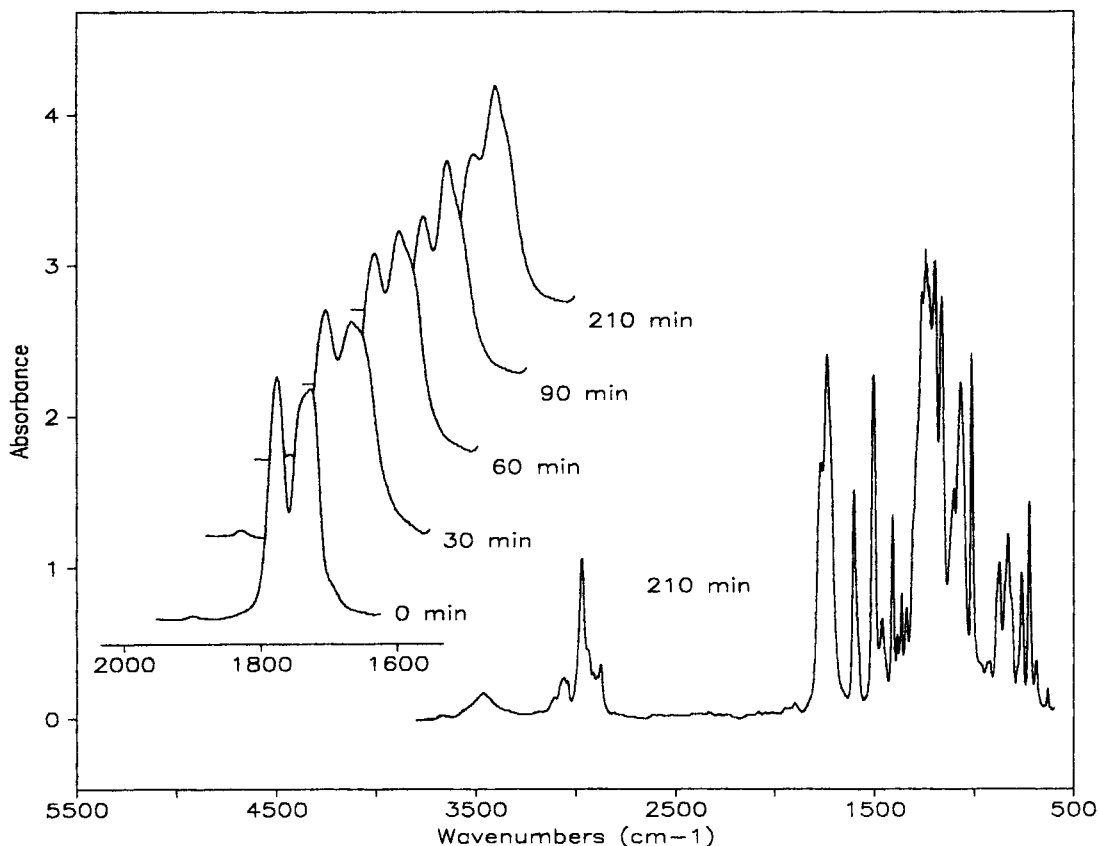


Figure 3 FTIR spectra of compatibilizer and PC/PetPhb60 (50% w/w) mixtures reacted for 0, 30, 60, 90, and 210 min at 275°C.

RESULTS AND DISCUSSION

The Ester Interchange Reaction

The exchange reaction between the ester and carbonate group in mixtures of PC and poly(ethylene terephthalate) (PETP) was the subject of both theoretical and experimental investigations.^{19,20} Four different functional groups resulted as a consequence of the combination of the PC and PETP moieties (see Table II). The degree of ester interchange was monitored by spectroscopic investigations. On the basis of chemical similarities between PETP and PetPhb60, we followed the same approach described in the literature for the analysis of ester interchange reaction of PETP.^{19,20}

The block distribution of the rigid moieties of the liquid crystalline polymer, composed mainly of *p*-hydroxy benzoic acid, determines a double-phase morphology. The calorimetric analysis evidenced the occurrence of two glass transitions. The first one at 72°C is associated with the presence of the PETP-rich phase, whereas the second one at 172°C is as-

sociated with the presence of the *p*-hydroxybenzoate-rich phase.^{12,21-23} The PETP-rich phase of PetPhb60 can react with the PC compound much in the same way as does pure PETP.

In Figure 1, the GPC chromatogram of the 50% blend (the compatibilizer) reacted for 3 h at 275°C is compared with the results obtained for unprocessed pure PC. The chromatograms show typical PC profiles with a decrease in molecular weight for the 50% blend ($M_w = 38,000$) with respect to the PC ($M_w = 58,000$).

The consequences of the addition of 5% w/w of the compatibilizer to the PC/LC10C blend was considered. Assuming a simple mixture rule to evaluate the elastic modulus, the adverse effect on the mechanical properties of the drawn fibers due to the reduction of the molecular weight of the compatibilizer is negligible, because of the low amount of compatibilizer in the blend. On the other hand, the decrease in the degree of polymerization of the compatibilizer can result in a benefit in terms of miscibility²⁴ with the other components of the mixture.



Figure 4 SEM picture of PC/LC50. Magnification of 2500X.

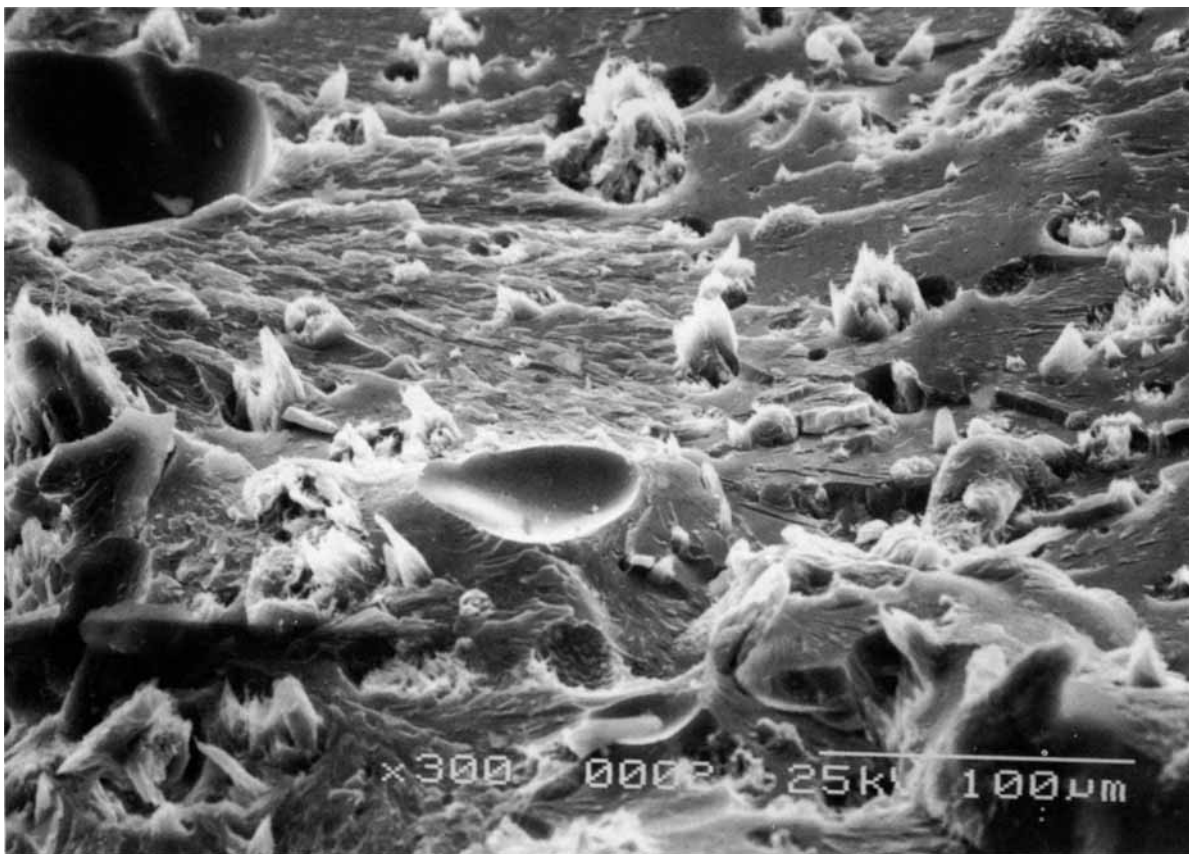
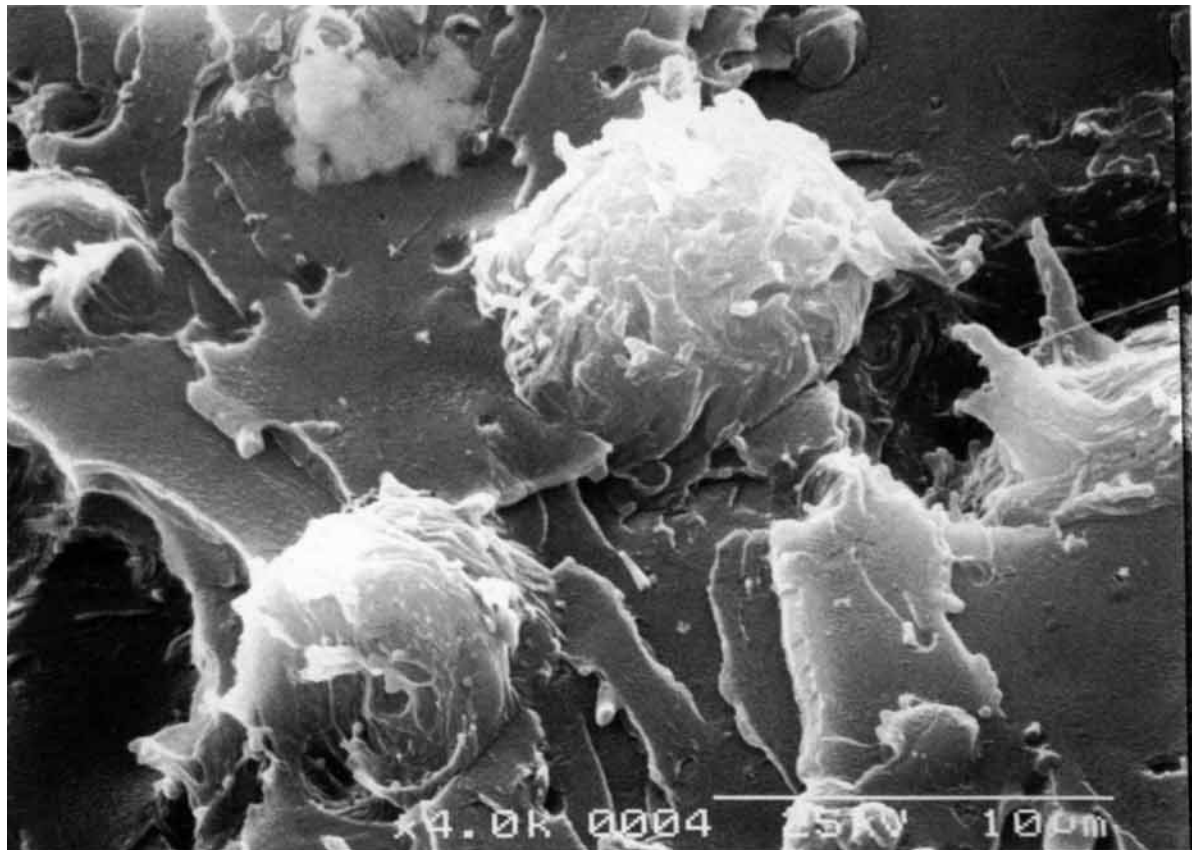
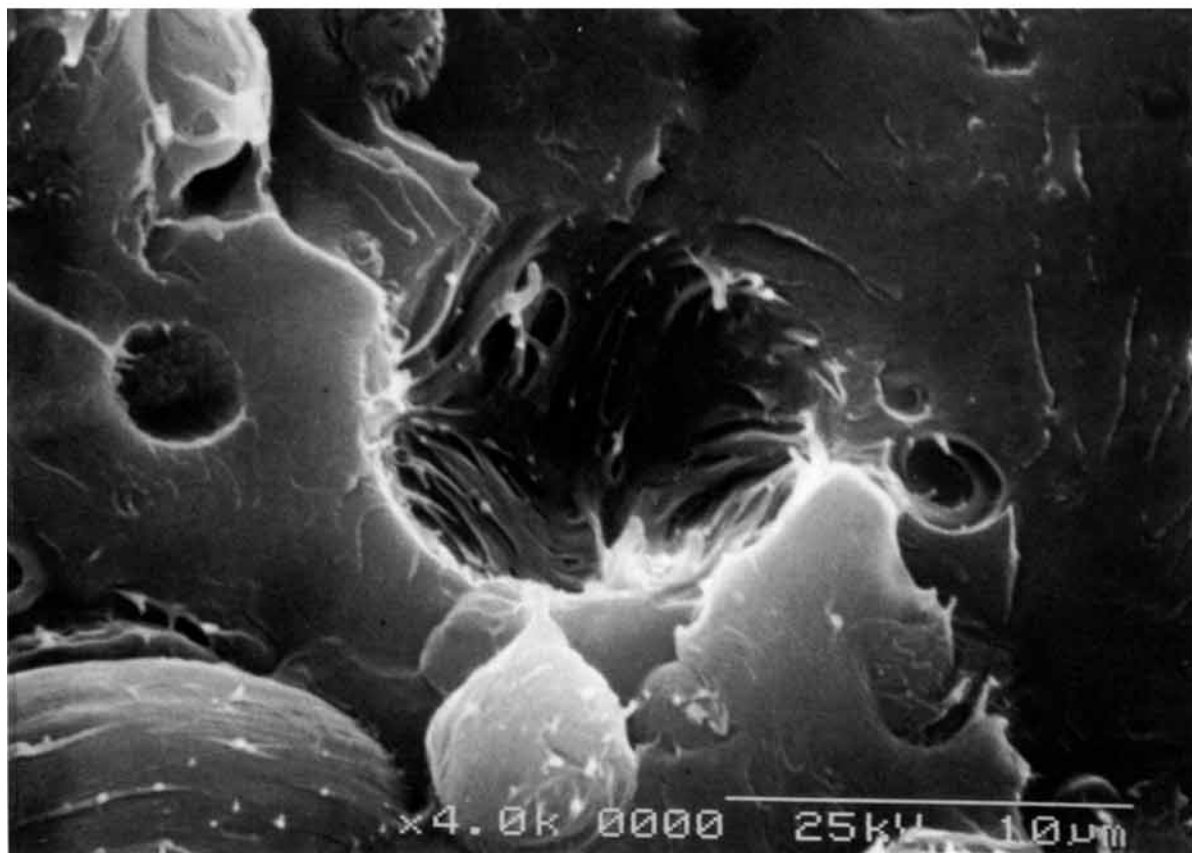


Figure 5 SEM picture of compatibilizer. General view at 300X.



(a)



(b)

Figure 6 (a) SEM picture of compatibilizer. Liquid crystalline particles embedded in the matrix. Magnification of 4000 \times . (b) SEM picture of compatibilizer. Imprint in the matrix of liquid crystalline particle. Magnification of 4000 \times . (c) SEM picture of compatibilizer. Interface between nematic inclusions and the matrix. Magnification of 8000 \times .

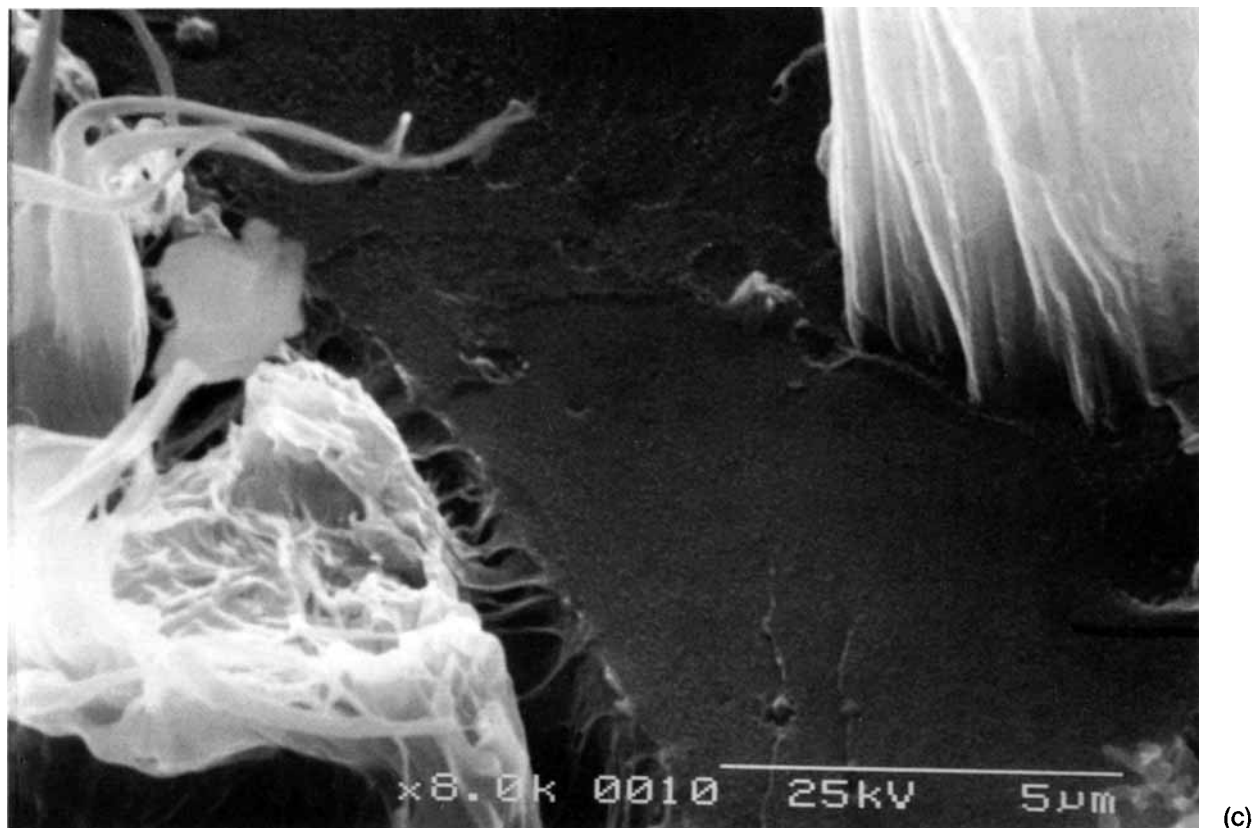


Figure 6 (Continued from the previous page)

The extent of the ester interchange reaction was investigated by FTIR characterization. Figures 2 and 3 show the spectra of the parent polymers and samples reacted, respectively, for 30, 60, 90, and 210 min at 275°C.

The evidence of group b (see Table II) in the nematic polymers, as a result of the condensation reaction between *p*-hydroxybenzoic acid units, makes the task of characterizing the interchange reaction a little more complex. In fact, the spectrum of PetPhb60 unveiled unresolved peaks at 1730 and 1740 cm^{-1} (see Table II), attributed, respectively, to the stretching of aliphatic and aromatic carbonilic esters of the terephthalic acid.²⁵ The aromatic carbonate band was found in the spectrum of PC at 1780 cm^{-1} . The analysis of the spectra in the wavenumber range between 1600 and 1900 cm^{-1} , presented in Figure 3, bears evidence of the occurrence of the reaction of ester interchange.

As the time increases from 0 to 210 min, the following can be observed: The relative intensity of the stretching bands of the aliphatic and aromatic esters (i.e., units a and b, respectively, in Table II) is reversed, whereas the absorption band of the carbon-

ate group continuously decreases. The regular increase in the amount of the aromatic ester group, replacing the aliphatic ester and the carbonate units, is therefore in accordance with the presumed reaction of ester interchange.

Morphological Characterization

The effectiveness of the interchange reaction in improving the adhesion between the reinforcing phase and the matrix was investigated by scanning electron microscopy. For the sake of clarity, the morphology of related systems are discussed side by side.

Let us first consider the blend without a compatibilizer (Fig. 4), referred to as PC/LC50. The appearance of the fracture surface of the drawn fibers evidence a complex morphology. The segregation of the components into well-identified zones is very clear. Because of the large amount of nematic polymer, several liquid crystalline droplets pool into a single fiber and a wide distribution results in the shape and dimensions of the nematic particles.

The elongational field experienced by the blend during the melt-spinning orients the rigid backbone

molecules in the TLCP-rich portion, much in the fashion as with pure TLCP drawn fibers.^{12,16} Otherwise, the matrix seems likely to be unaffected by the drawing operations.

The adhesion between the components of the mixture is very poor. The pullout of fibers from the matrix is clearly evident, and the smooth surface of the hole denotes the debonding between the reinforcing phase and the matrix. Therefore, the performance of the *in situ* composites are not optimized, since only a mechanical coupling between the different phases can be achieved.^{7,12,16} The morphology of the compatibilizer by itself, however, shows a much more intimate interconnection between the nematic inclusion and the surrounding matrix.

The general picture of the fracture surface of the compatibilizer is shown in Figure 5. The morphological features of the reacted mixture are quite intriguing. The appearance of gas voids is quite clear. The thermal degradation of the catalyst during the interchange reaction may be responsible of the release of alcoholic fragments, primarily, isopropyl alcohol.

Two distinctive features are recognizable at first glance in Figure 5: The pullout of fibers from the matrix is greatly reduced and there is a lack of small nematic droplets. The ester interchange reaction appears likely to induce a complete mixing of a substantial fraction of the liquid crystalline polymer into the amorphous matrix. As a consequence, the amount of the observed dispersed phase is invariably smaller than 50% for the samples analyzed. Furthermore, due to the dramatic increase of the mutual solubility, the chemical composition of the phases changes. The strong chemical interaction between the interface prevents the slippage of the fibers from the matrix, which leads to brittle rupture of the samples.

A section of Figure 5 is illustrated in Figure 6. The surface of the inclusion is much rougher [see Fig. 6(a)]. There is a continuity between the fiber and the matrix, and no separation is evident at all. The imprint in the matrix of the slipped particles is illustrated in Figure 6(b). The interesting pattern perfectly represents the shape of the particle that was occupying the site. The comparison with the

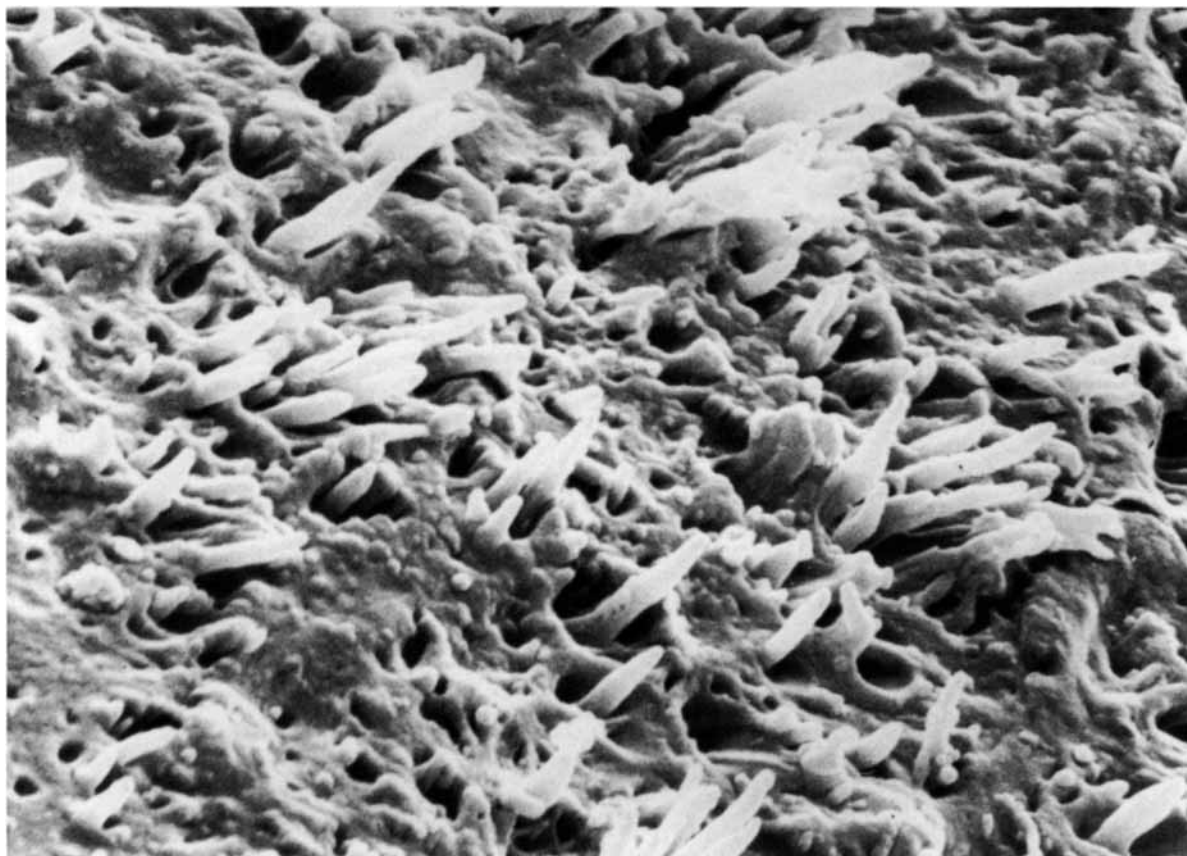
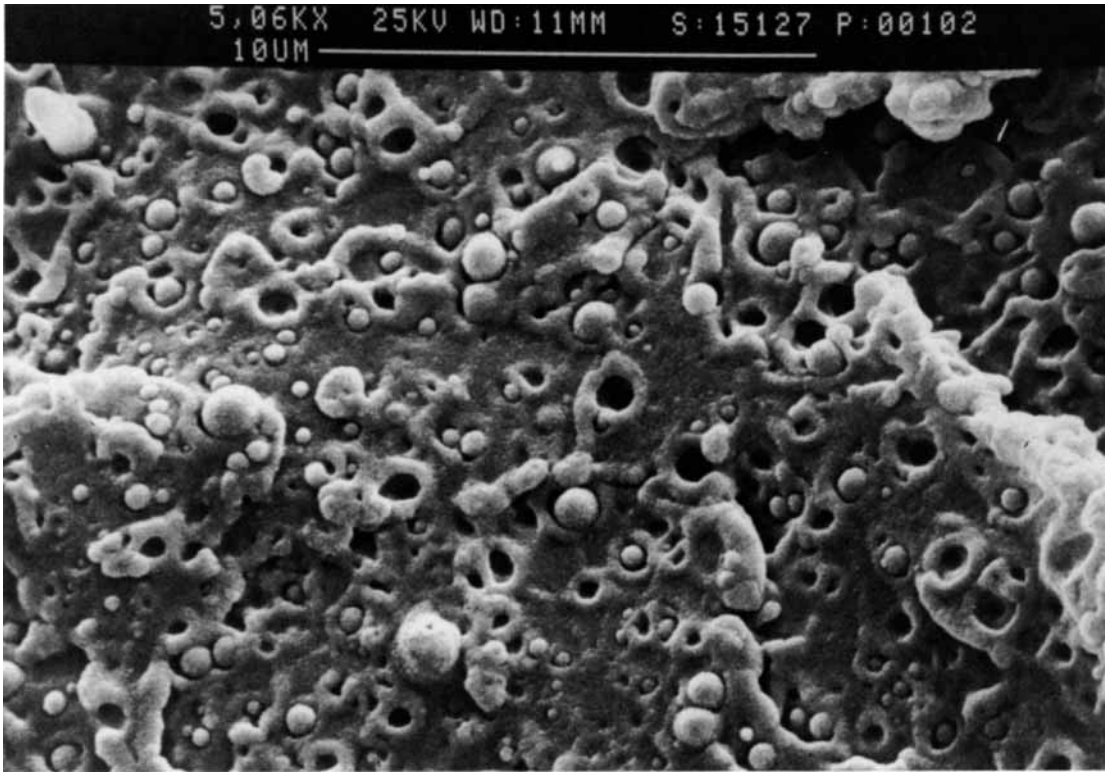
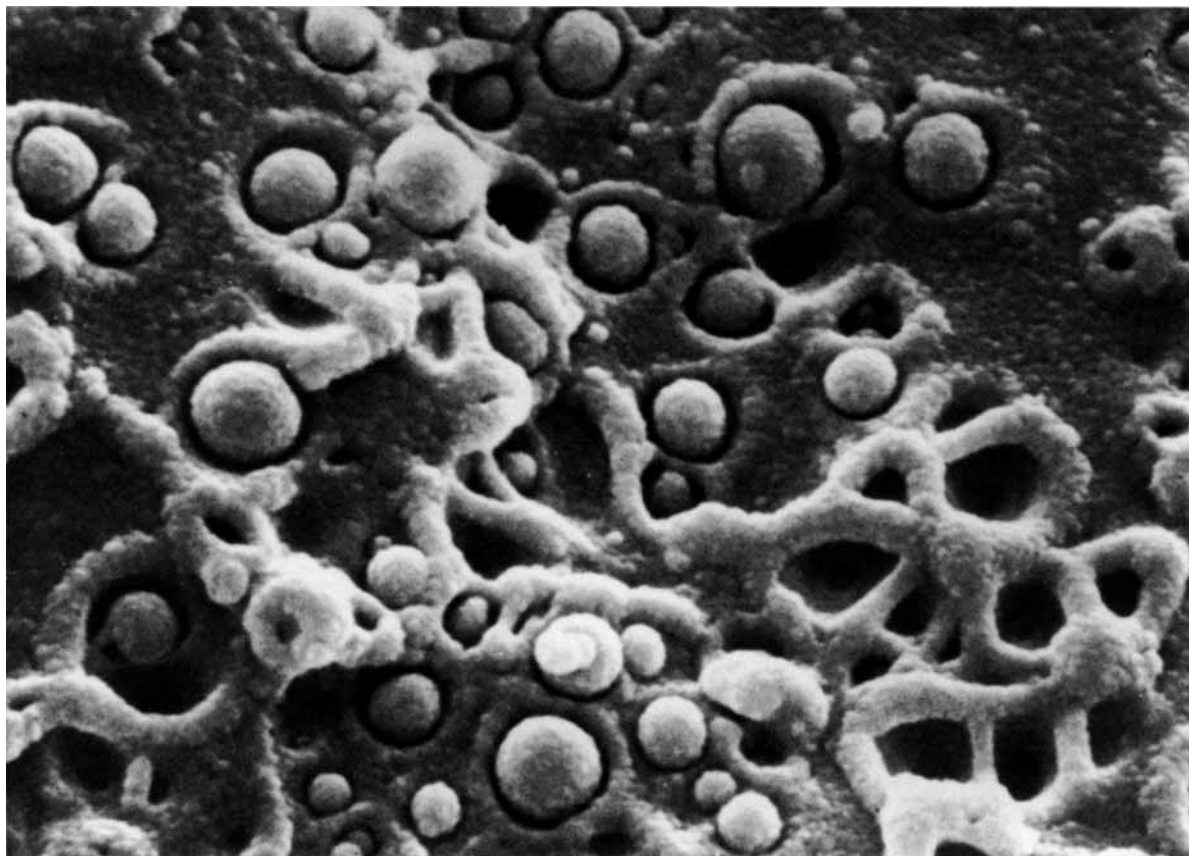


Figure 7 SEM picture of PC/LC10 blend. Spinning temperature of 210°C; draw ratio of 200; magnification of 5000×.



(a)



(b)

Figure 8 (a) SEM picture of PC/LC10 blend. Spinning temperature of 260°C; draw ratio of 200; magnification of 5000×. (b) SEM picture of PC/LC10 blend. Spinning temperature of 260°C; draw ratio of 200; magnification of 10,000×.



(a)



(b)

Figure 9 (a) SEM picture of PC/LC10C blend. Spinning temperature of 260°C; draw ratio of 20; magnification of 5000×. (b) SEM picture of PC/LC10C blend. Spinning temperature of 260°C; draw ratio of 20. A view at magnification of 15,000×.

smooth surface of the holes in the PC/LC50 blend (see Fig. 4) bears evidence of the strong adhesion achieved between the two polymers.

It should be noted that the diameters of the spherical inclusions in the fracture surface of the compatibilizer (Figs. 5 and 6) cannot be compared with the fiber diameters in Figure 4, because of the different geometries of the dispersed particles.

Morphology of the PC/LC10 and PC/LC10C Blends

Because we are concerned with the possibility of improving the adhesion between the reinforcing phase and the amorphous matrix with the aid of the compatibilizer, the morphological features of the blend containing 10 wt % of PetPhb60 were analyzed.

The basic appearance of the blends with and without the compatibilizer are very similar, but our attention will be focused upon some important differences. The shape and the molecular orientation of the PetPhb60 inclusions in the amorphous matrix for the PC/LC10 blends are governed by the spinning conditions. The viscosity ratio of the two components has been proven to be one of the main parameters affecting the load transfer from the matrix to the fibers.^{5,7,12,26}

At the lowest practical drawing temperature (210°C), the liquid crystalline droplets are elongated into fibrils with an average aspect ratio of 10 (Fig. 7). It has been shown that the elastic modulus of the PetPhb60 polymer can increase greatly, as a result of the orientation of the rigid backbone molecules in the nematic phase.^{12,15} When the drawing temperature is increased to 260°C (Fig. 8), the decrease in the viscosity ratio between matrix and PetPhb60 (Ref. 11) adversely affects its ability to propagate the elongational stress to the liquid crystalline inclusions. As a consequence, the droplets retain their spheroidal shape and the reinforcing effects are greatly reduced.

An analysis of the morphology of the amorphous matrix in the proximity of the TLCP inclusions can shed some light upon the fracture mechanism. Poor fiber/matrix adhesion causes the stress to be supported by the matrix and increases the stress gradient close to the fiber. The plastic behavior of PC allows the matrix to relax after the fracture and consequent fiber slippage, resulting in the formation of round-shaped contours of the preexisting holes containing the fibers (Fig. 8). Of course, very little, if any, reinforcement benefit will result. In the case

of the PC/LC10C blend, the amount of liquid crystalline polymer added is the same as in the previous sample. The fracture surface of PC/LCP10C specimens shows elongated fibers protruding from the matrix (Fig. 9).

To evaluate the degradation of PC by the presence of TBOT during the processing, the GPC chromatograms of the extracted matrix were analyzed (see Fig. 1). The chromatograms of PC/LC10C processed at 220, 240, and 260°C slightly differ from the pure PC curve, indicating that the degradation of the matrix during processing is of little relevance.

The effect of the compatibilizer during the melt drawing was evident by the formation of elongated fibers even at the drawing temperature of 260°C. Distinction between the elongated TLCP fibers (Fig. 9) and the round-shaped inclusions obtained for PC/LC10 fibers drawn at 260°C (Fig. 8) is clear. The improved stress transfer through the interface during the melt spinning of the fibers elongate the TLCP inclusions more effectively.

Analysis of the fracture surface in Figure 9 revealed that the binding between the fibers and the matrix was not complete since pullout was still evident to some extent. Additionally, the necking of the fibers emerging from the matrix may be the result of adhesion experienced during fracture, preventing the fiber pullout.

The surface of the TLCP fibrils is not as uniform as in the PC/LC10 samples. The presence of the compatibilizer affects the microrheology of the blend. The flow conditions are not steady and fluctuations result during the spinning procedures. As a consequence, the diameter of the blend fiber is affected as well. This results in the formation of fibers with a wide range of diameters.

The occurrence of strong interactions between the phases is evidenced by the lack of rounded edges around the hollows containing the TLCP. In this case, the strong adhesion across the interface determines a good load transfer from the fibers to the matrix.

The mechanical properties of the PC/LC10C blend fibers is worthy of further discussion. We would expect an improvement in the mechanical properties of the blend processed with the addition of the adhesion promoter. Unfortunately, the gas evolution during the mixing and melt-spinning of the fibers led to the formation of voids. The presence of these irregularities resulted in excessive data scatter and prevented both a meaningful evaluation of the mechanical properties of the undrawn and drawn fibers and comparison with results obtained from samples prepared without any compatibilizer.

CONCLUSIONS

It has been shown that the adhesion between matrix and reinforcing liquid crystalline inclusions can be improved by the addition of a suitable compatibilizer. In this case, the ester interchange reaction between the carbonate and the ester groups in the parent polymers has been practically adopted to produce the adhesion promoter. A small percentage of the compatibilizer was added to the blends and the results compared with previous investigations dealing with "in situ composites" based upon the same constituents.

Although the morphological characterization has proven the effectiveness of the adhesion promoter, the lack of homogeneity in the sample dimensions has prevented us to determine the mechanical properties of the fibers. Furthermore, the gas evolution resulting from the thermal degradation of the catalyst used to produce the compatibilizer led to the formation of voids and bubbles.

Further investigations may be devoted to the same subject, revealing the details of the compatibilization mechanism. The synthesis of copolymer suitable to be used as the compatibilizer directly from raw materials and the effects of different molecular weights and the distribution of rigid blocks along its molecular backbone ought to be investigated as well.

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