Effect of Compatibilization in Injection-Molded Polycarbonate and Liquid Crystalline Polymer Blend

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ABSTRACT: The effect of compatibilizing polycarbonate (PC) and LC5000, a thermotropic liquid crystalline polymer consisting of 80/20% of hydroxybenzoic acid and poly(terephthalate) with a laboratory synthesized compatibilizer was studied. The compatibilizer was synthesized by transesterification of PC and LC5000 with the aid of a catalyst. The effect of compatibilization was investigated by studying the mechanical and morphological properties of injection-molded plaques with different thicknesses. Substantial improvement was observed in the mechanical properties after compatibilization. Significant enhancement in the fibrillation was also observed in the samples after addition of compatibilizer. The surface finish of the compatibilized samples was smooth and homogenous as compared to the uncompatibilized samples. The skin-core phenomenon in the tensile fractured surfaces was less obvious in the former samples, indicating better adhesion and homogeneity. These morphological studies showed that the mechanical properties enhancement lay in improved fibrillation and interfacial adhesion between the dispersed and major phases. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 568–575, 2002; DOI 10.1002/app.10308

Key words: liquid crystalline polymer; compatibilizer; interfacial adhesion

INTRODUCTION

In situ composites that comprise a thermoplastic and reinforcing liquid crystalline polymer (LCP) have been an area of considerable interest to researchers in the last few years.[1–8] Under favorable conditions, LCPs will develop fibrillar morphology leading to the enhancement of mechanical properties. Both engineering and commodity resins have been reinforced using various LCPs. However, most of the thermoplastics studied were incompatible with LCPs, causing the properties of the blends to fall short of expectations.

Reinforcement of PC with LCPs has been studied by many researchers.[9–12] Contradictory results on the reinforcement and other properties have been reported, and were attributed to the different inherent properties of the LCP and processing conditions, especially the elongational drawing of extrudates.[10–13] Poor interfacial adhesion, however, remained a major obstacle in achieving a highly reinforced blend. Hence, compatibilization of the blends seemed to be the necessary approach in overcoming the problem. Compatibilizing agents are block or graft copolymers possessing segments with chemical structures or

solubility parameters that are similar to those of the polymers being blended. Acting as polymeric surfactants, these agents reduce the interfacial tension, which promotes interfacial adhesion leading to the formation of a finer and more uniform distribution of the dispersed phase.[14] Better dispersion and adhesion result in improved mechanical properties of the compatibilized blend.[15–17]

Injection- molded LCP blends usually have low mechanical properties, frequently below the value calculated from the rule of mixture.[18,19] However, this processing method is one of the most widely used methods, and hence it would be very useful to be able to develop LCP blends with good mechanical properties by injection molding. The objective of this study is to investigate the effect of compatibilization on the mechanical and morphological properties of PC and LC5000 in injection molded samples. The compatibilizer used was synthesized by the controlled transesterification of PC and LC5000 with the aid of lanthanum catalyst. Hence, the compatibilizer, containing similar chemical structure units of both components, provided the physical interaction between the PC matrix and the LCP. The mechanical properties of the blends were determined using the Instron universal testing machine. The corresponding morphological studies were analyzed using a scanning electron microscope (SEM).

EXPERIMENTAL

The polycarbonate (PC3200) used in this project was kindly provided by Bayer. The TLCP used is from Unitika, Japan, and has the following composition: PHB/PET:80/20. For the preparation of the compatibilizer, lanthanum acetylactonate hydrate from Aldrich was used. The transesterification was controlled with the aid of an inhibitor—Ultranox 626A—kindly provided by GE Specialty Chemicals. The PC and LC5000 were used as received after 12 h of drying at 120°C under vacuum.

The synthesis of the compatibilizer was based on the work by Fiorini et al.[20,21] Based on their work, the synthesis conditions were optimized for our system. The blending temperature and time as well as the concentrations of all the materials for the synthesis of the compatibilizer reported below are the optimized condition. The blending of the compatibilizer was done in the Haake mixer with a rotor speed of 20 rpm. The blending

temperature and time were 270°C and 30 min, respectively. The composition of PC and LC5000 used were 15 and 85% by weight respectively with 0.02% by weight of catalyst and 0.3% by weight of inhibitor concentration. The compatibilizer was quenched immediately after mixing and dried. It was subsequently ground to fine granules prior to use. Fourier transform infrared (FTIR) and differential scanning calorimetry (DSC) runs were used to characterize the synthesized compatibilizer.

The melt blending of the blends was carried out using the Haake extruder at 270°C. Fifteen percent by weight of LCP was used throughout the study and the compatibilizer added was 5% by weight of the total blend. This ratio of compatibilizer to LCP was the optimized concentration. The extrudates were quenched and subsequently pelletized. The pellets were dried at 120°C for 12 h prior to use.

Injection molding was performed in the Manumold 77/30 injection molding machine at temperatures of 270–280°C. Mini tensile bars were cut from the injection molded rectangular plaques. Two molds for producing plaques with 1 and 4 mm thickness were used. The use of molds with different thicknesses allowed the effect of shear rate on the mechanical properties to be studied. The thicker mold will generate a lower shear rate during molding. The tensile testing was carried out at a crosshead speed of 5 mm/min and an extensometer, which was utilized to determine the specimen modulus, was removed at 1% strain.

Some mini tensile bars were cryogenically fractured in the longitudinal or transverse direction and the fracture surfaces were analyzed under the SEM.

RESULTS AND DISCUSSION

Compatibilizer Characterization

Figure 1 shows the FTIR absorption peaks of the compatibilizer with and without catalyst. The PC peaks have been subtracted from the FTIR trace of the blends. The two absorption peaks at wavelengths 1734 and 1717 cm^{-1}, indicated the aliphatic and aromatic ester groups in the LCP respectively. When the transesterification reaction progresses, the aliphatic ester group from the LCP will be exchanged with the aromatic group from the PC. Thus, the aromatic ester peak will become relatively larger compared to the ali-
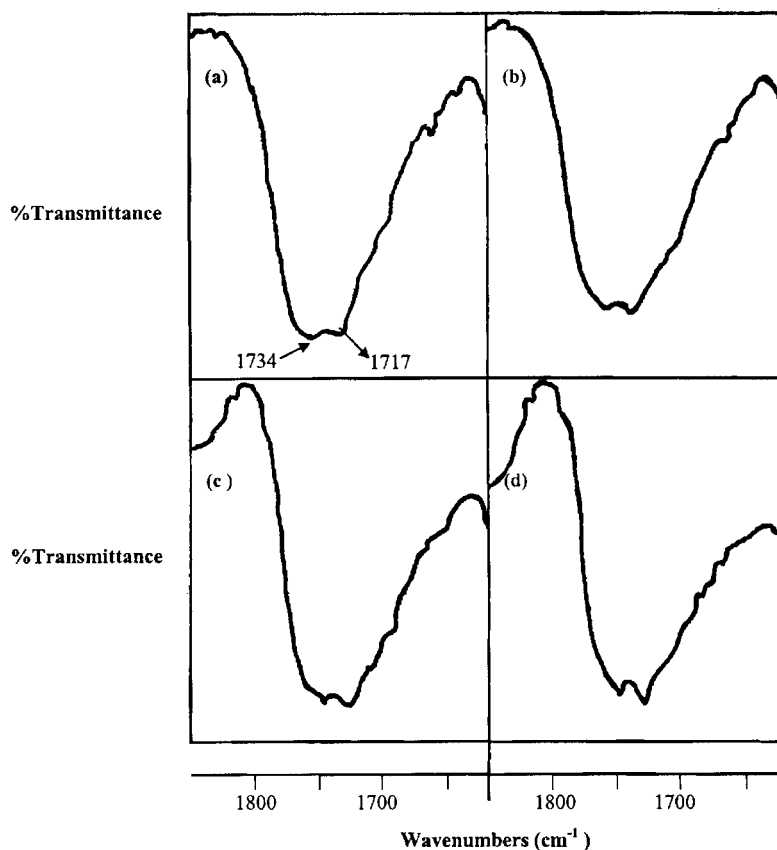
Figure 1   FTIR runs showing the increasing prominence of the aromatic group peak with addition of catalyst: (a) pure LCP, (b) 30 min mixing time without catalyst, (c) 3 min mixing time with catalyst, and (d) 30 minutes mixing time with catalyst.

phatic peak as the reaction proceeds. It can be seen from Figure 1 that, as the mixing time increased, the aromatic ester peak seemed to increase relative to the aliphatic peak. This implied the occurrence of transesterification between PC and LC5000.

The synthesis of compatibilizer without any catalyst showed a similar trend to that synthesized with catalyst but processed for a short mixing time of 3 min, in that although there was some changes in the intensity of the peaks, the changes were minor and less significant. In contrast, the aromatic ester peak outgrew the aliphatic peak notably in the preblend synthesized with catalyst and that had been mixed for longer than 3 min. These results implied that the synthesis of the compatibilizer required long mixing time (30 min) and with the aid of catalyst for transesterification to occur.

The transesterification reaction was further investigated using the DSC. (The T_g of the LCP could not be detected significantly for all the sys-

tems). Figure 2 shows the thermograms of the pure LCP and PC and the synthesized compatibilizer with and without catalyst at different mixing times. The T_g s of pure PC and LCP are 148 and 63°C respectively. In the absence of catalyst, mixing time has little effect on the reaction. This is why the T_g of the compatibilizer without any catalyst, which had been mixed for 30 min, did not change significantly. In contrast, the T_g of that with catalyst and longer mixing time shifted noticeably to the left (toward the T_g of the LCP), indicating increasing miscibility. However, for the compatibilizer synthesized with the aid of catalyst but mixed only for 3 min, the thermograms did not indicate any reaction, as the T_g remained unchanged. The above results again indicate that transesterification reaction seemed to occur only at sufficiently long mixing times of about 30 min with the aid of a catalyst. Hence, for subsequent work, the preparation of the compatibilizer will be based on 30 min blending time with the aid of catalyst.
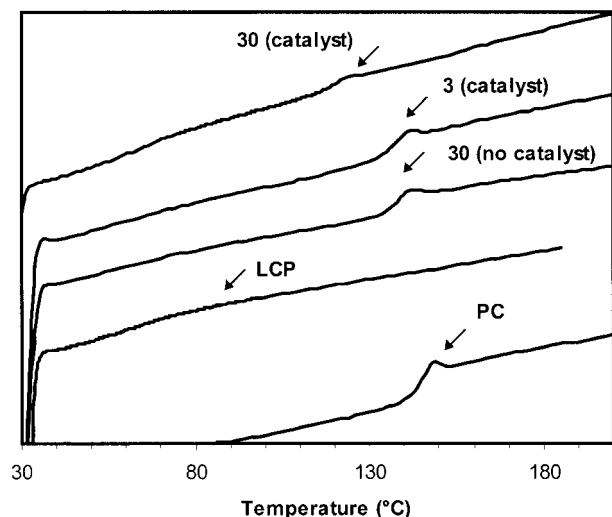
Figure 2 DSC thermograms of the compatibilizer produced with and without catalyst and at different mixing times. The arrow shows the T_g of the respective blends.

Morphological Properties of Blends

The morphology of the cryogenically fractured surfaces of the blends produced by injection molding of 4 mm plaque is shown in Figure 3. The uncompatibilized system showed a coarse, inhomogeneous, and irregular dispersion size of the LCP phase in the PC matrix in the core section. Generally, the LCP phase remained as spheres in both the compatibilized and uncompatibilized systems in the core, but the size of the dispersed LCP phase reduced remarkably with the addition of the compatibilizer. The average dispersion size for the compatibilized system was about 2.5 microns while those in the uncompatibilized system ranged from 1 to 15 microns. The large and irregularity of the LCP dispersion size in the uncompatibilized system indicated the incompatibility of the system. Due to the high interfacial tension in the incompatible blend, the dispersed phase tend to agglomerate and hence formed much larger particle size.

In the skin section of both the compatibilized and uncompatibilized systems, LCP fibrillation was observed. However, the fiber density was higher in the skin section in the former than that in the latter. The improved interfacial property induced by the compatibilizer enabled better transfer of viscous force during processing. Viscous force is necessary for the deformation of the dispersed phase in a blend.[22,23] Hence, fibrillation could occur more readily as observed in the better fibrillation in the compatibilized system.

It was also observed that delamination between the skin and core was very severe in the uncompatibilized system (Fig. 4). There is a distinct separation of the skin and core into two layers in the uncompatibilized blend, whereas in the compatibilized blend, the skin and core sections remained intact. These results indicated that there was better adhesion between the components in the compatibilized system. The better adhesion was also reflected by less fiber pull out in the compatibilized sample (Fig. 5). In the uncompatibilized blend, the fibers were easily pulled out from the matrix, as shown by the pores with smooth circumference that are remnant holes arising from extraction of fibers from the matrix. The better compatibility in the system after addition of compatibilizer was also reflected in the smoother and more homogenous surface finish (Fig. 6) in the specimen.

Mechanical Properties

The effects of interfacial adhesion as well as shear rate on the mechanical properties will now be considered. The effect of compatibilizer on the mechanical properties in the longitudinal direction is shown in Figure 7(a) and summarized in Table I. From the figure, it can be observed that addition of the compatibilizer significantly enhanced the mechanical properties of samples processed at both high and low shear rates. However, the samples processed at lower shear rate had inferior properties as compared to that processed at higher shear rate. For the 1 mm samples, addition of the compatibilizer increased the tensile strength by 17% over that for the uncompatibilized system. The tensile modulus was improved by 34%. The mechanical properties were higher than the calculated values using the rule of mixture. Both the ultimate tensile strength and modulus are about 1.3 times higher than that calculated using the rule of mixtures. However, less significant improvement was observed in thicker samples where the shear rate was lower, yielding lower degree of fibrillation. The tensile strength and modulus improved by 4 and 7% over that for the uncompatibilized system respectively. From the morphological studies, the enhancement can be attributed to better interfacial adhesion and fibrillation promoted by the compatibilizer.

The improvement of the mechanical properties in the transverse direction was even more drastic, again reflecting the better interfacial adhesion between the matrix and the dispersed phase. The

(a)

(b)

(c)

(d)
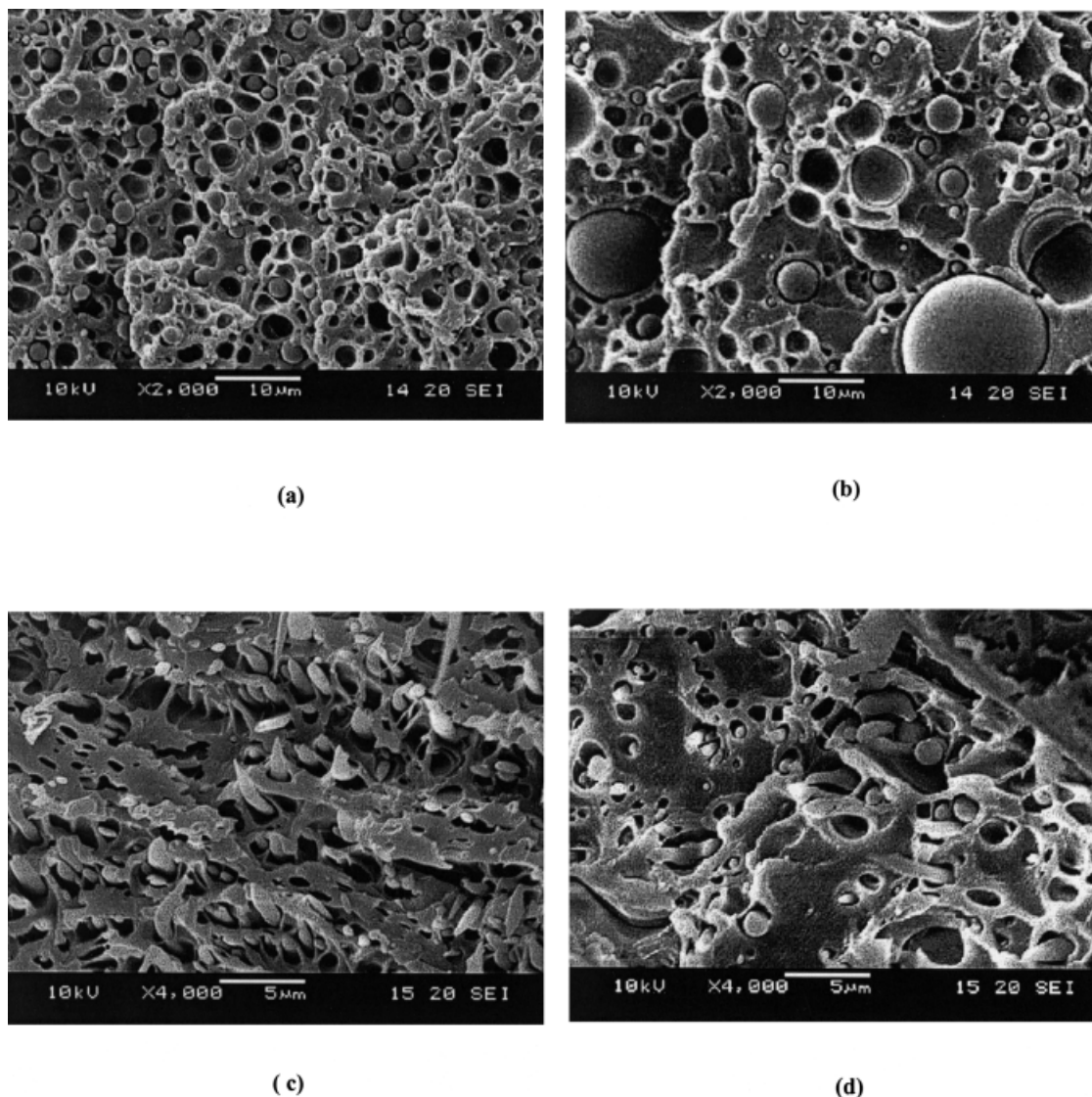
Figure 3   SEM micrographs of cryogenically fractured surfaces of (a) core of compatibilized, (b) core of uncompatibilized, (c) skin of compatibilized, and (d) skin of uncompatibilized blends.

skin region is LCP rich whereas it is PC rich in the core region. Due to the immiscibility of the two components, the bond between them is extremely weak. The interface would then act as defect, resulting in severe delamination between the skin and core. When a suitable compatibilizer is added, the delamination problem was diminished leading to enhanced mechanical properties especially in the transverse direction. From Figure 7(b) and Table I it can be seen that the tensile strength and modulus of the compatibilized system in the 1 mm samples were drastically enhanced by 71 and 120% respectively over that of the uncompatibilized system.

The better fibrillation and orientation in the compatibilized system did not jeopardize the transverse properties as often observed in fiber reinforced systems. Enhanced mechanical properties in the longitudinal direction due to the anisotropy in fiber reinforced systems normally have very poor transverse mechanical properties. However, in our compatibilized system the transverse properties were not compromised greatly by the enhancement in the longitudinal properties. The compatibilizer was able to cause a good adhesion between the two components, resulting in the possibility of load transfer during testing. Hence, the mechanical properties in the trans-
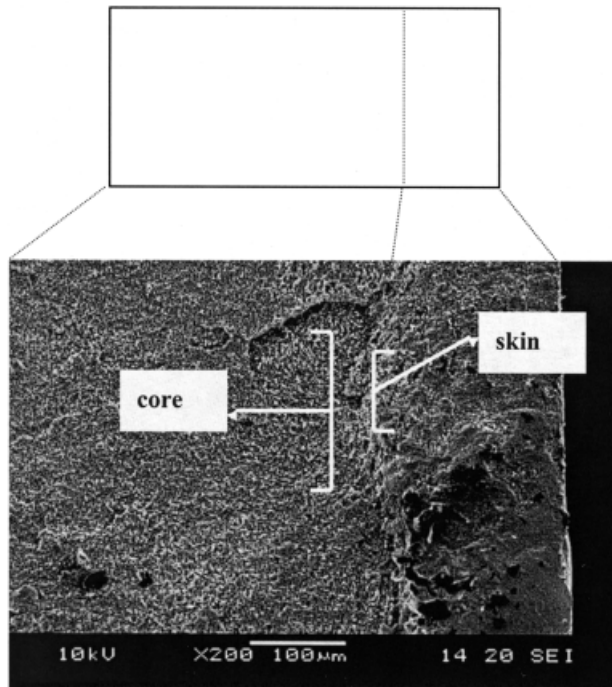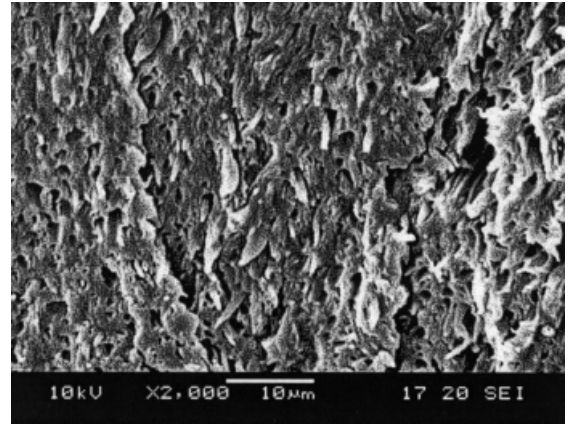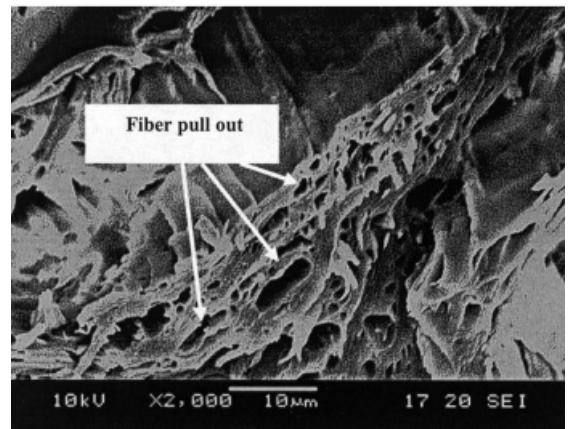
Compatibilized blend
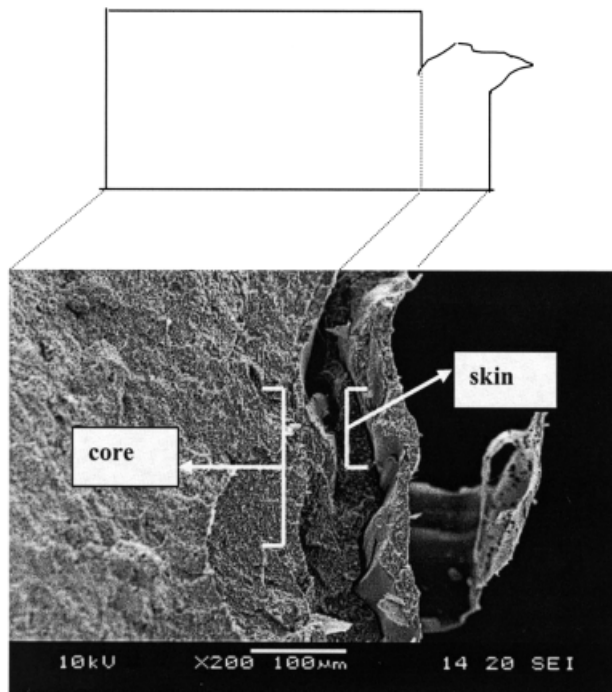
Uncompatibilized blend

Figure 4 Cryogenically fractured surfaces showing severe delamination between the skin and core sections in the uncompatibilized blend. The schematic diagram of the side view of the respective samples shows how the samples failed upon fracture.
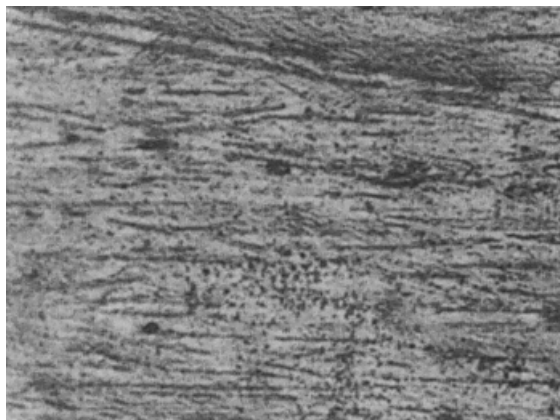

a) **Compatibilized blend**

(b) **Uncompatibilized blend**

Figure 5 Fracture surfaces (at room temperature) of (a) compatibilized and (b) uncompatibilized blends showing obvious fiber pull out leaving behind smooth pores in the latter system.

verse direction were much higher than that of the uncompatibilized system where the adhesion between the two components was very poor.

The enhancement of the mechanical properties in the transverse direction for the thicker sample was not as drastic though it was still significant. This is because the low shear rate did not allow much fibrillation and orientation to occur in both the uncompatibilized and compatibilized systems. Hence, the skin-core phenomenon was not as distinct in the thicker sample, causing the delamination to be less severe. This in turn caused the mechanical properties at the transverse direction to be relatively high in the thicker sample, even in

Compatibilized blend
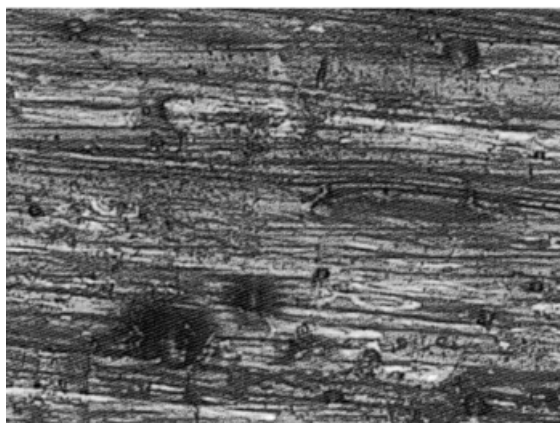
Uncompatibilized blend

Figure 6 Top surface finish of the samples showing a smoother surface for the compatibilized system indicating better homogeneity. Magnification 50×.

the uncompatibilized system. These observations suggest that the strength in the transverse direction is dominated by the bonding between LCP and PC phases, and the morphology or physical shape of the LCP phase plays a lesser role.

CONCLUSION

The addition of the synthesized compatibilizer into the PC/LCP blend caused significant improvements in the morphological and mechanical properties of the blends. The morphological studies indicated that compatibilization led to better fibrillation in the samples especially those pro-

cessed at a high shear rate. Interfacial adhesion between LCP and PC and overall homogeneity in the samples were also improved, and this was reflected in the good bonding between the skin and core regions and a more uniform LCP dispersion.

The tensile strength and modulus improved in both 1 and 4 mm thick samples. However, the properties of the compatibilized system in the 1 mm thick samples where the shear rate was greater were higher than in the 4 mm thick samples. Both the orientation and interfacial adhesion between the LCP and PC phases had a large
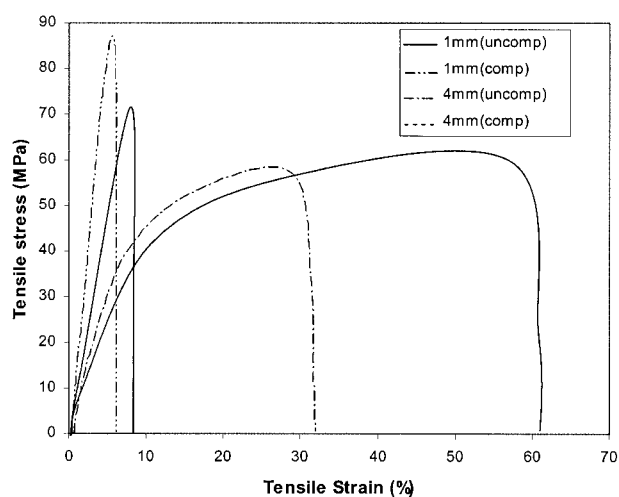
(a)
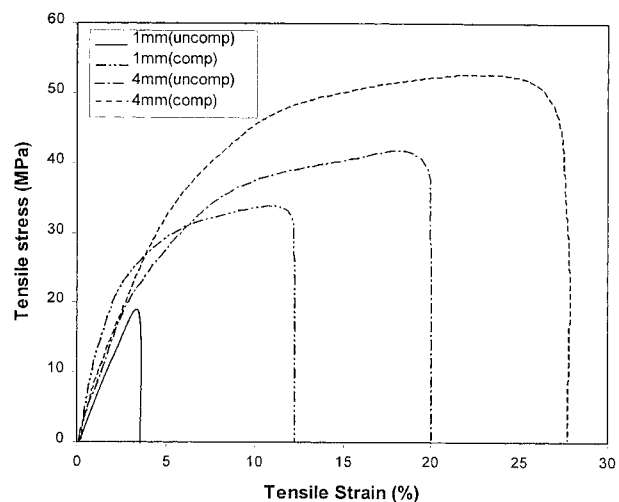
(b)

Figure 7 Stress–strain curves showing the effect of compatibilization on the mechanical properties of the blends processed at different shear rates. (a) In the longitudinal direction. (b) In the transverse direction.

Table I   The Longitudinal and Transverse Mechanical Properties of Compatibilized and Uncompatibilized Blends Processed at Different Shear Rates

	Longitudinal				Transverse			
	1 mm		4 mm		1 mm		4 mm	
	Tensile Strength (MPa)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Tensile Modulus (GPa)
Uncompatibilized blend	73.49	1.48	56.31	0.96	19.41	0.53	41.33	0.81
Compatibilized blend	85.71	1.98	58.93	1.03	33.11	1.17	51.56	0.89

influence on the performance of the blend. The ultimate tensile strength and modulus were improved by 17 and 34%, respectively, in the compatibilized 1 mm samples as compared to the uncompatibilized system. The mechanical properties were higher than the calculated values using the rule of mixture. Both the ultimate tensile strength and modulus are about 1.3 times higher than that calculated using the rule of mixtures.

The transverse ultimate tensile strength and modulus of the compatibilized 1 mm samples were also significantly enhanced by 71 and 120% respectively. The weakness in the transverse properties for the uncompatibilized system was due to delamination of the skin from the core section. In the compatibilized system, the delamination was greatly reduced, and hence the mechanical properties were enhanced.

It can be concluded that the synthesized compatibilizer was efficient and able to act as a physical "bridge" between the two components. This allowed higher viscous force transfer from the matrix to the LCP, and hence better fibrillation could occur.

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