A Study on Blends of Liquid Crystalline Copolyesters with Polycarbonate. III. Mechanical Properties of Compatibilized Blends

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ABSTRACT: Blends of liquid crystalline poly(oxybenzoate-*co*-oxynaphthalate) (Vectra A950) and polycarbonate (PC) were prepared by adding a compatibilizer to the two polymers in a melt-blending process. The compatibilizer was based on controlled transesterification between synthesized poly(oxybenzoate-*co*-terephthalate) (40/60) and PC. The compatibilizer exhibited birefringence, and its thermal property was analyzed by differential scanning calorimetry. The maximum increase in tensile modulus and tensile strength of these compatibilized Vectra blends were 24% and 54%, respectively, as compared with those of binary Vectra blend without compatibilizer resulting from an injection-molding process. The tensile properties of the compatibilized Vectra blends decreased once the concentration of the compatibilizer exceeded 2 phr. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1527–1533, 1997

Key words: liquid crystalline polyester; blends; tensile modulus

INTRODUCTION

Blends of liquid crystalline polymers (LCPs) and engineering plastics have been studied extensively. Their major advantage is the possibility of the inclusion of a rigid-rod (liquid crystalline) polymer in an isotropic matrix for forming *in situ* composites, as described by Kiss.[1] Additionally, the LCP can reduce the overall viscosity of the blend and serve as a processing aid, as evidenced by the work of several groups.[2,3] Liquid crystalline polymer chains are very stiff and of rigid-rod nature. The mixing of a rigid-rod polymer with a flexible-coil polymer is not favorable in thermodynamics. Consequently, phase separation of the LCP blend occurs during processing, where high stress and high temperature exist.[4] The homogeneity of a polymer blend determines the mechanical properties of the blend. From this view, the compatibility of liquid crystalline polymer and engineering polymer is a major obstacle in LCP blends' application. Introducing some kind of interaction between these two dissimilar polymers is necessary to improve their compatibility. The previous work by our group was concerned with the compatibility by the transesterification between polycarbonate (PC) and liquid crystalline poly(oxybenzoate-*co*-ethylene terephthalate) (POB-PET, 40/60).[5] The main result was that the compatibility between the two polymers increased with ester exchange reaction. However, as transesterification continued the blend converted first to block copolymer and finally to random copolymer.[6] When the blends were in the form of random copolymer, the benefits of adding LCP to the matrix polymer were lost. We also attempted to control the ester exchange reaction with inhibitors,[7] but had limited success when both LCP concentration and high temperature exposing time increased. Therefore, this *in situ* compatibilization of binary liquid crystalline polymer blends suffered the drawback of not having consistent mate-

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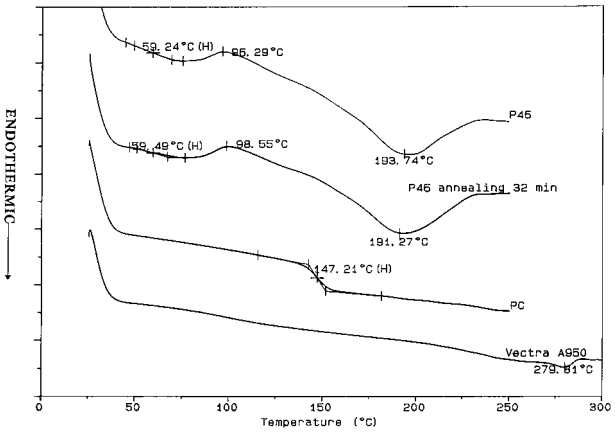

Figure 1 The DSC curves of PC, Vectra A950, P46, and P46 annealed at 260°C for 32 min.

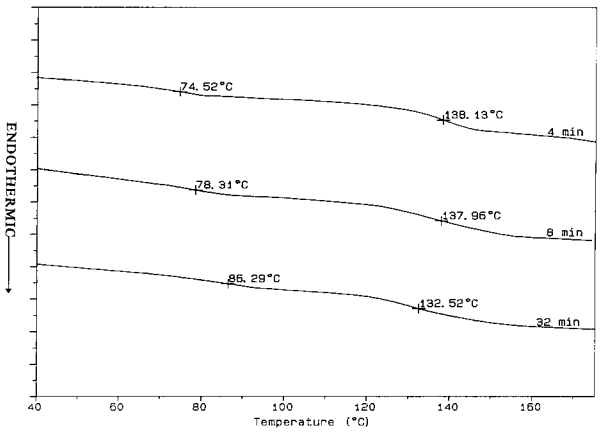

Figure 3 The DSC curves of solution blends of P46/PC annealed at 260°C for different times.

rial properties as ester exchange continued during further processing.

These results lead us to explore the possibility of developing a compatibilizer based upon controlled transesterifiaction between a matrix polymer and a second liquid crystalline polymer. After controlled transesterification, a polymer containing both liquid crystalline and flexible-coil structures would form. This resultant polymer can have better interaction between matrix polymer and reinforcing LCP due to similarities in the two chemical structures. The polymer (compatibilizer) can be added to matrix polymer and reinforcing liquid crystalline polymer, and partially miscible ternary blends can then form. In this study, we used two liquid crystalline copolyesters. The one with higher flexible-coil copolyester (POB-PET, 40/60) content is designed to carry out transesterification with polycarbonate for forming a compatibilizer. The other, with higher rigid-rod molecule content (POB-PNA, 73/27), is intended for reinforcing polycarbonate matrix. We are interested in the mechanical properties of LCP blends consisting of PC, reinforcing LCP, and the compatibilizer. Previously we studied the effect of the compatibilizer based on limited transesterification between POB-PET (60/40, 40 mol % PET) with PC, and found increased tensile strength as well as impact properties in these ternary blends.[8] Since the transesterification took place mostly among PC and the PET segments in the POB-PET copolymer, we wondered if the mechanical properties of these ternary blends can be further enhanced by having greater interaction (transesterification among 60 mol % PET and PC).

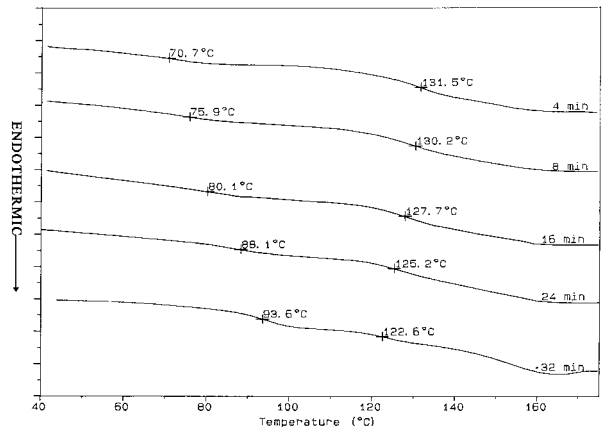

Figure 2 The DSC curves of P46/PC (60/40) blend after being melt-mixed for different times at 260°C.

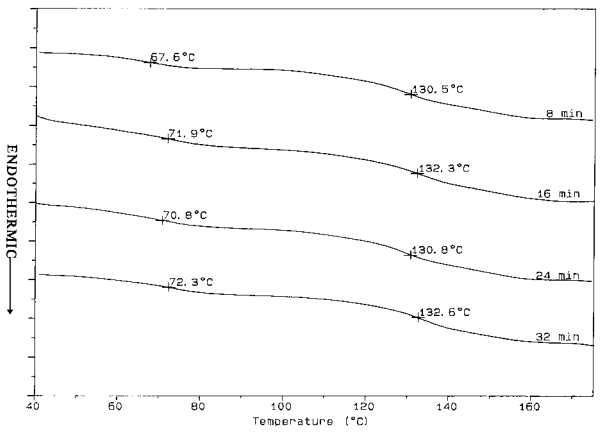

Figure 4 The DSC curves of inhibited P46/PC (60/40) blend being melt-mixed for different times at 260°C.

EXPERIMENTAL

Materials

Liquid crystalline POB-PET with composition 40/60 in molar ratio was synthesized in our laboratory following the method as described in the literature.[9] The POB-PET (40/60) is termed P46 in this paper. PC was purchased from General Electric. The trade name of the PC is Lexan 121, and its molecular weight (M_w) = 158,900. The above two polymers were used for preparing a compatibilizer. The reinforcing LCP was poly(oxybenzoate-*co*-naphthalate) with a composition of 73/27, trade named Vectra A950, obtained from Hoechst Celanese Corp., USA.

Methods

Compatibilizer

The method of preparing melt blends has been described in our previous two papers.[4,6] Blends were prepared by mixing P46/PC at a weight ratio of 60/40 in a Brabender mixer at 260°C. The solution blend of 60/40 P46/PC was prepared by dissolving 2 g of polymers at the proper weight ratio in a 100-cm^3 mixed solvent of 50/50 phenol/tetrachloroethane by weight. Then the solution was precipitated in a 10-fold volume of methanol. The precipitated polymers were washed 4 times in hot methanol. The blend was dried in a vacuum oven at 100°C for 4 days prior to a thermal analysis. Thermal analysis of the blend at different times was carried out with a Dupont 2910 differential scanning calorimeter. The samples were heated from 30°C to 260°C at a heating rate of 20°C per min. At 260°C the samples were annealed for 1 min. Subsequently, the samples were cooled to 170°C and annealed for 10 min. The samples were quenched to 25°C and heated again to 275°C at the same heating rate. The differential scanning calorimetry (DSC) curves of the samples were taken the second time when the samples were heated at the rate of 20°C per min. Without annealing, the DSC curves of the blends did not exhibit separate crystallization (from P46) and glass transition (from PC).[10] Annealing at 170°C for 10 min avoided the problem by allowing the sample to crystallize. For controlling ester exchange in the blend, 0.5% triphenyl phosphate was added into a blend consisting of 60/40 P46/PC as described in out previous paper.[6] The inhibited P46/PC (60/40) blend was used as a compatibilizer in this study. The intrinsic viscosities of the P46/PC blend and the inhibited P46/PC blend were measured by dissolving them in a mixed solvent of tetrachloroethane/phenol 50/50 wt/wt. Polarizing optical microscopy on the melt blends at different mixing times was also carried out with a Carl Zeiss Axiophot microscope.

Blends Preparation

The pellets of the compatibilizer were ground into powder. The compatibilizer, Vectra, and PC were mixed in a container, then fed into a twin-screw extruder maintained at 300°C. The twin-screw speed was 80 rpm. To understand the effect of the concentration of the compatibilizer, three compositions were made: 20/80/2, 20/80/3, and 20/80/5 for Vectra/PC/compatibilizer. A blend with a composition of 20/80 Vectra/PC was made for comparison. These blends were molded with a Toshiba IS55EPN injection-molding machine. The melt temperature was 300°C and the molding-process cycle time was 30 s. Tensile tests were performed according to ASTM D638 at 23°C using a Testometric Micro 500 machine. Reported data were obtained at a crosshead speed of 1.3 mm/min. Unnotched I-Zod tests were performed according to ASTM D256 specification. For each data point, six specimens were tested and the average value was taken.

RESULTS AND DISCUSSION

The thermal analysis curves of P46, Vectra A950, and PC are shown in Figure 1, where the glass transition temperature (T_g) and the melting temperature (T_m) of P46 were 59.24°C and 193.74°C, respectively. The crystallization temperature (T_c) for P46 was 96.29°C. The T_g of the P46 has been attributed to the presence of a PET-rich phase in P46.[11] To check its thermal stability, P46 was annealed at 260°C for 32 min. After the annealing, the T_c and the T_m of P46 had changed only about 2°C. Vectra A950 has a melting point of 279.81°C. Thermal gravity analysis of these three polymers that were annealed at 260°C for 32 min showed no appreciable weight loss. The thermal analysis of the blend P46/PC (60/40) at different blending times is shown in Figure 2. All these thermograms displayed two T_gs. The lower T_g represents the amorphous phase of P46 in the blend, whereas the higher T_g stands for the PC component in the blend. After 4 min blending, the two T_gs were about 60.8°C apart. As the blending time in-

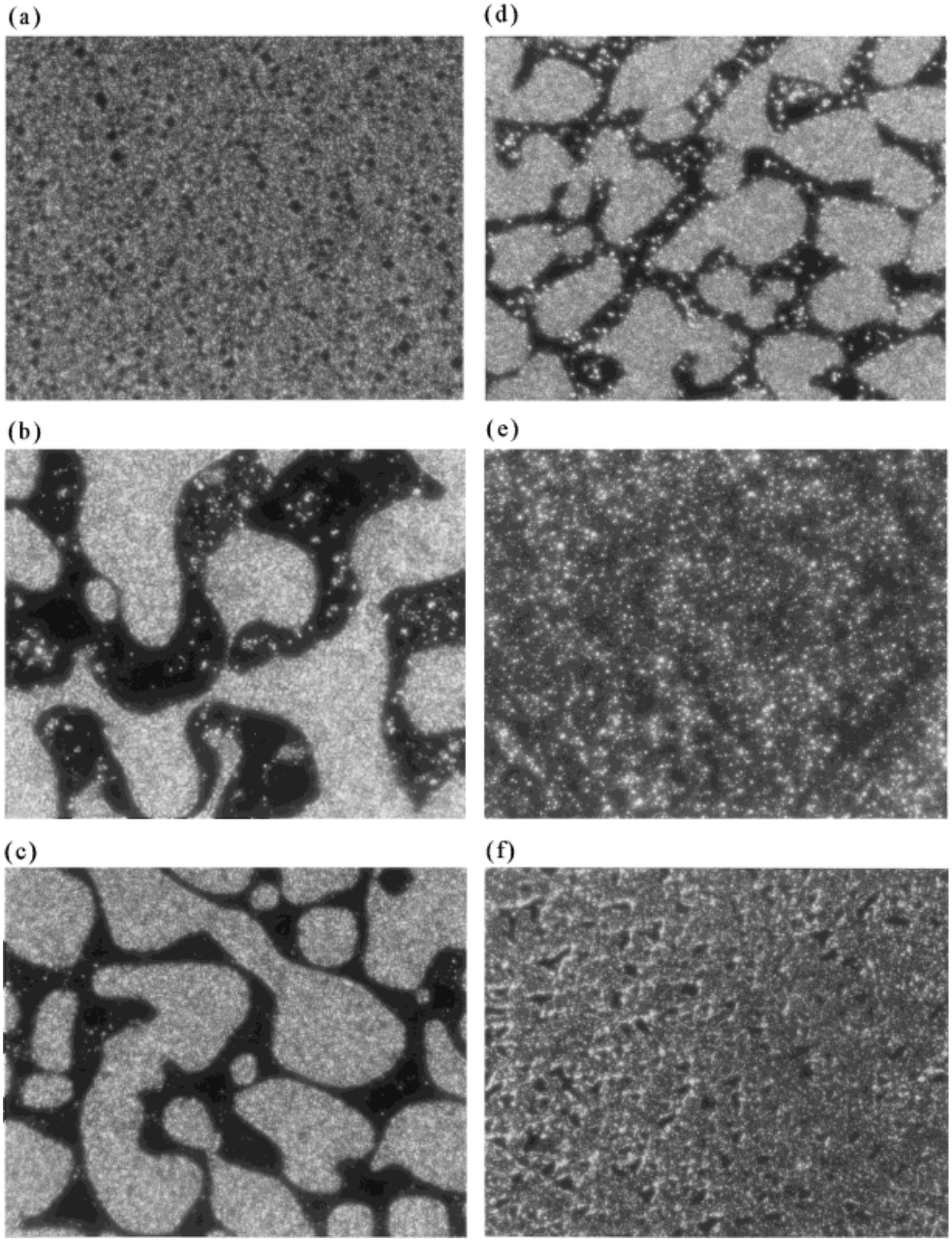

Figure 5 The birefringence pattern of (a) P46, (b) 60/40 P46/PC melt-mixed for 4 min, (c) 60/40 P46/PC melt-mixed for 8 min, (d) 60/40 P46/PC melt-mixed for 16 min, (e) 60/40 P46/PC melt-mixed for 32 min, and (f) inhibited 60/40 P46/PC melt-mixed for 16 min.

creased to 8 min, the two T_gs became 54°C apart. After 32 min blending, the two T_gs were 29°C apart. The same trend can be observed in thermal analysis of the solution blend of 60/40 P46 and PC, as shown in Figure 3. In Figure 3, the two T_gs are about 63°C apart after 4 min annealing at 260°C, then 46°C apart after 32 min annealing. Therefore, this phenomenon of reduction in the difference between the two T_gs with annealing time was mostly not a result of morphological effect. It can be explained by the occurrence of an increase in the compatibility between the amorphous phase of P46 and PC. For the inhibited blend, the two T_gs remained 60°C apart for 32 min blending time, as shown in Figure 4. This represents that the ester exchange between PC

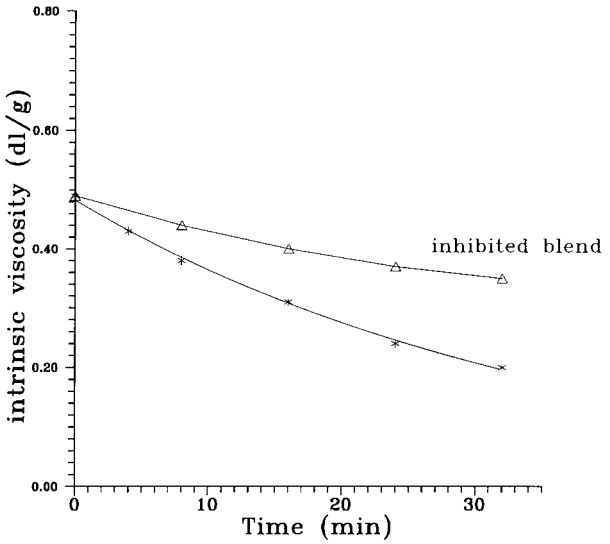

Figure 6 The changes in the intrinsic viscosity of 60/40 P46/PC melt blend and inhibited 60/40 P46/PC melt blend with mixing time.

and the amorphous phase of P46 has been effectively stopped.

Further evidence of the inhibition effect can be confirmed through the birefringence pattern exhibited by the compatibilizer. In Figure 4(a), the birefringence pattern of the biphasic P46 can be observed. Figure 4(b–e) shows the transition of the birefringence pattern of the 60/40 P46/PC blend. The dark areas in the pictures represent the isotropic phase in the blend. The overall area of the isotropic phases spread with blending time. The birefringence of the blend almost disappeared after 32 min of thermal treatment, as shown in Figure 5(e). The compatibilizer retained much of the liquid crystalline characteristics under inhibition, as shown in Figure 5(f). Transesterification led to chain scission of polymer molecules. Inhibition effect can also be checked by the change in the intrinsic viscosity (I.V.) of the blend, which decreases with the blending time as shown in Figure 6. After 32 min annealing at 260°C, the I.V. of the blend dropped to 41% of its original value. For the same thermal treatment, the I.V. of the inhibited blend became 73% of its original value.

The tensile and the impact properties of the injection-molded ternary blends are listed in Table I, which shows that the tensile modulus and tensile strength of the 20/80 Vectra/PC binary blend are about 8% and 11% higher than that of the neat PC, respectively. Once 2 phr compatibilizer is added to the Vectra blend, the increase in tensile modulus and tensile strength can be as high as 24% and 54%, respectively, as compared with those of binary Vectra blends. However, the tensile modulus of the blend decreases when the compatibilizer concentration is greater than 2 phr. This corresponds to the fact that better adhesion between Vectra and PC in the 2-phr-compatibilizer case was observed in the scanning electron microscopy (SEM) micrographs displayed in Figure 7. In Figure 7(a), the fractured surface of the 20/80 Vectra/PC blend displays uneven breaking. In Figure 7(b–d), the interfacial distance between the Vectra droplet and the PC matrix increase with the compatibilizer concentration, indicating decreasing adhesion. This might be explained by the theory that critical micelle concentration has been reached for the 2-phr-compatibilizer case,[12] in which compatibilizer itself aggregates rather than attaching to the interface between PC and Vectra droplets. The impact strength of the blends decreases with the increasing tensile strength for these ternary blends, as listed in Table I. This can be explained by the fact that LCP fibers embedded in the matrix had a preferred orientation in the tensile direction as a result of the injection-molding process. The better alignment of these LCP fibers in the tensile direc-

Table I The Tensile and Impact Properties of Injection-molded Tensile Bars from Various Blends Followed ASTM D256 Specifications

Blend	Tensile Modulus (N/mm^2)	Ultimate Tensile Strength (N/mm^2)	Impact (ft lbs in^{-1})
PC	1391.2	56.74	[a]
PC/Vectra (80/20)	1504.4	63.38	12
PC/Vectra/comp. (80/20/2)	1873.8	97.61	7.47
PC/Vectra/comp. (80/20/3)	1753.5	91.10	7.72
PC/Vectra/comp. (80/20/5)	1712.4	90.80	7.83

[a] Exceeding test range.

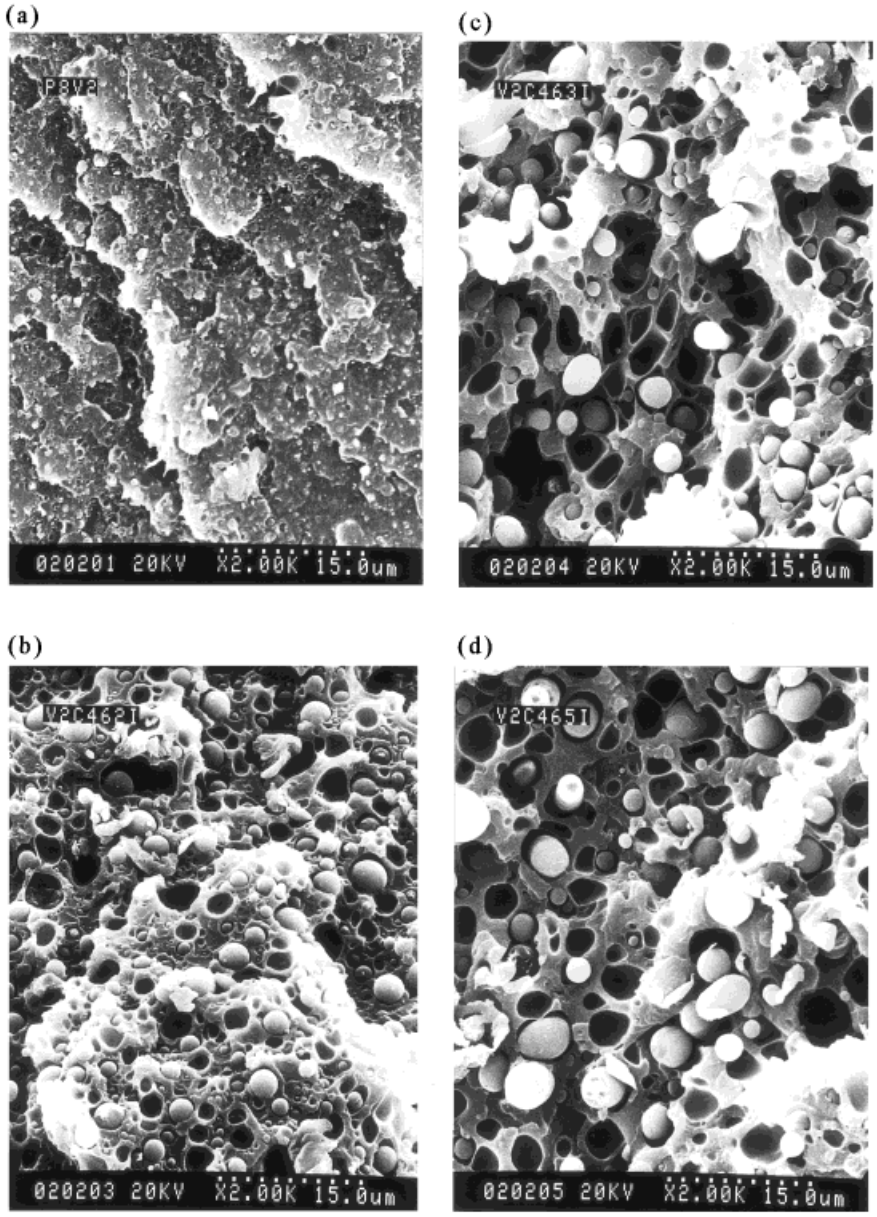

Figure 7 SEM micrograph of fractured surface of injection-molded tensile bar from (a) 20/80 Vectra/PC blend, (b) 20/80/2 Vectra/PC/compatiblizer, (c) 20/80/3 Vectra/PC/compatiblizer, and (d) 20/80/5 Vectra/PC/compatiblizer.

tion caused weak mechanical properties in the transverse direction.

CONCLUSION

The compatibilized, wholly aromatic Vectra/PC (20/80) blend displayed enhanced tensile properties, such as a 24% increase in modulus and 54% increase in strength as compared with those of the binary Vectra blend even under the injection-molding process. The compatibilizer was prepared based on a controlled transesterification between synthesized POB-PET (40/60) copolymer and PC, to which a phosphate compound was added as an inhibitor. The tensile properties of these blends decreased with increasing compatibilizer concentration when the compatibilizer's concentration exceeded 2 phr. The impact strength of these compatibilized

Vectra blends decreased with increasing compatibilizer concentration.

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