Rheological and Physical Properties of *In Situ* Composite Based on Liquid Crystalline Polymer and Poly(ethylene 2,6-naphthalate) Blends

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ABSTRACT: The *in situ* composites based on poly(ethylene 2,6-naphthalate) (PEN) and liquid crystalline polymer (LCP) were investigated in terms of thermal, rheological, and mechanical properties, and morphology. Inclusion of LCP enhanced the crystallization rate and tensile modulus of the PEN matrix, although it decreased the tensile strength in the PEN-rich phase. The orientation effect of this blend system was composition and spin draw ratio dependent, which was examined by Instron tensile test. Further, the addition of dibutyltindilaurate (DBTDL) as a reaction catalyst was found to increase the viscosity of the blends, enhance its adhesion between the dispersed LCP phases and matrix, and led to an increase of mechanical properties of two immiscible blends. Hence DBTDL is helpful in producing a reactive compatibilizer by reactive extrusion at the interface of this LCP reinforced polyester blend system. The optimum catalyst amount turned out to be about 500 ppm, when the reaction proceeded in the 75/25 PEN/LCP blend system. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2448–2456, 1999

Key words: liquid crystalline polymer; poly(ethylene 2,6-naphthalate); *in situ* composite; tensile modulus; spin draw ratio; thermoplastics

INTRODUCTION

Poly(ethylene 2,6-naphthalate) (PEN) has attracted the attention of many researchers because of their excellent mechanical properties, including high tensile strength, high modulus, good gas barrier properties, and thermal stability. Compared with poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), PEN-containing rigid naphthalate units offer the added advantage of higher glass transition temperature (T_g); for example, the T_g of PEN is 120°C, which is higher than that of PET about 40°C. High thermal stability characteristically makes this kind of naphthalate polymer more useful for a broad range of applications such as magnetic tape, medical parts requiring steam sterilization, and hot food containers.[1,2]

On the other hand, thermotropic liquid crystalline polymers (TLCPs) are well known for their unique mechanical and rheological properties.[3] Due to their rigid molecular structure, they can easily be oriented in the melt state by an elongational flow field to form a threadlike or rodlike phase. When processed in the liquid crystalline state, these materials generally possess excellent physical properties in the direction of orientation.

An area of special interest has been the use of LCP in isotropic polymer blends.[4–6] However, the potential advantages of LCP properties in polymer blends have not yet been fully exploited. For example, the potential exists to obtain the fine and uniform microfibrillation of LCP with a large aspect ratio in thermoplastics and to improve the interfacial adhesion, dispersion, and compatibility between immiscible thermoplastic and LCP. Most of the thermoplastics studied so far are incompatible with usual LCP. The potential to apply the advantages of LCP such as high strength and high modulus, high thermal stability, high dimensional stability, low dielectric constant, low coefficients of thermal expansion, low moisture pick-up, and so forth to *in situ* composites recently has been shown to be achieved by reactive extrusion.[7–10] An *in situ* composite produced by reactive extrusion can solve some problems that arise during processing, such as phase separations containing the formation of the skin-core morphology for the immiscible *in situ* composite, and it displays greatly improved performance such as good interfacial adhesion and compatibility as compared with a conventional binary blend.

In recent years, generating interfacial adhesion and compatibility of the *in situ* composite has been attempted by introducing new techniques such as long flexible spacer,[11,12] block copolymer,[13–15] functional groups that have a chemical structure similar to the compounded polymers to modify the surface of binary blends,[16,17] reactive extrusion,[18,19] and addition of a third component having functional groups such as a maleic anhydride group[20] or incorporation of the LCP miscible with the matrix polymer. Of these techniques, reactive extrusion provides the most attractive approach to the development of an *in situ* composite system. In this respect, Hong et al.[21,22] and Baird et al.[20] have investigated the effect of the third component or a compatibilizer on the physical properties of the immiscible *in situ* composite system. They observed that the key factors to property improvement are good interfacial adhesion, less phase separation, and more uniform LCP distribution. In particular, our recent interest is to expand the application area of the *in situ* composite featuring better physical properties, which can be obtained through a transesterification reaction between ester groups[23] and other reactions.[18,19] It has also been shown that a catalyst, such as DBTDL, can be used to induce compatibility of PEN/TLCP. Many authors[23–25] reported that the transesterification reactions occur in the blend of PET or PBT and polycarbonate at high elevated temperatures with long residence time.

The purposes of this study are (1) to investigate the interrelationships among the processing, structures, and physical properties of PEN/LCP blends by adding a reaction catalyst; (2) to promote the reactive extrusion in a very short residence time; and (3) to enhance the physical properties of the immiscible PEN/LCP blends.

EXPERIMENTAL

The TLCP used in this work is LC5000 produced by Unitica Co. It is composed of 80 mol % of *p*-hydroxybenzoic acid (PHB) and 20 mol % of poly(ethylene terephthalate) (PET). As a matrix polymer, PEN was obtained from Mitsubishi Co. The material had a reported melting temperature of 270°C and an inherent viscosity of 0.61 (dL/g) (in phenol/tetrachloroethane mixture, 60/40 w/w, at a concentration of 0.25 g/dL at 25°C). DBTDL, used as a reactive catalyst, was obtained from Aldrich Co. PEN and LC5000 pellets were dried in a forced convection oven at 120°C for 24 h prior to compounding. The contents of TLCP in the PEN blends were varied as 3, 5, 10, and 25 wt %. The amount of DBTDL was 500 and 1000 ppm (to the total resin weight of PEN and LCP).

The formulated components were compounded using a Brabender twin-screw extruder at 290°C, while the hopper was purged with dried nitrogen gas. Melt spinning experiments were carried out using a Rosand capillary rheometer (model RH7-2). Capillary radius and length were 1 and 16 mm, respectively. Strands leaving the die exit were directly quenched in air and drawn with a take-up machine. The draw ratio was determined by dividing the capillary diameter (D) by the diameter of as-spun fiber (D_0) [D/D_0].

Thermal properties were investigated with a Du Pont Thermal Analyzer Differential Scanning Calorimeter (DSC) 2100 in a nitrogen atmosphere. The heating rate and cooling rate were each 10°C/min. Dynamic mechanical thermal analysis of the PEN/LCP blends was carried out with a Dynamic Mechanical Thermal Analyzer (Mk-III, Rheometric Scientific Co.) using bending mode. Measurements were performed on rectangular samples obtained by a Minimax molder model CS-183 MMX (CSI Co.) at 290°C. The heating rate was 5°C/min at a frequency of 1 Hz in the range of approximately 50–200°C. Rheological
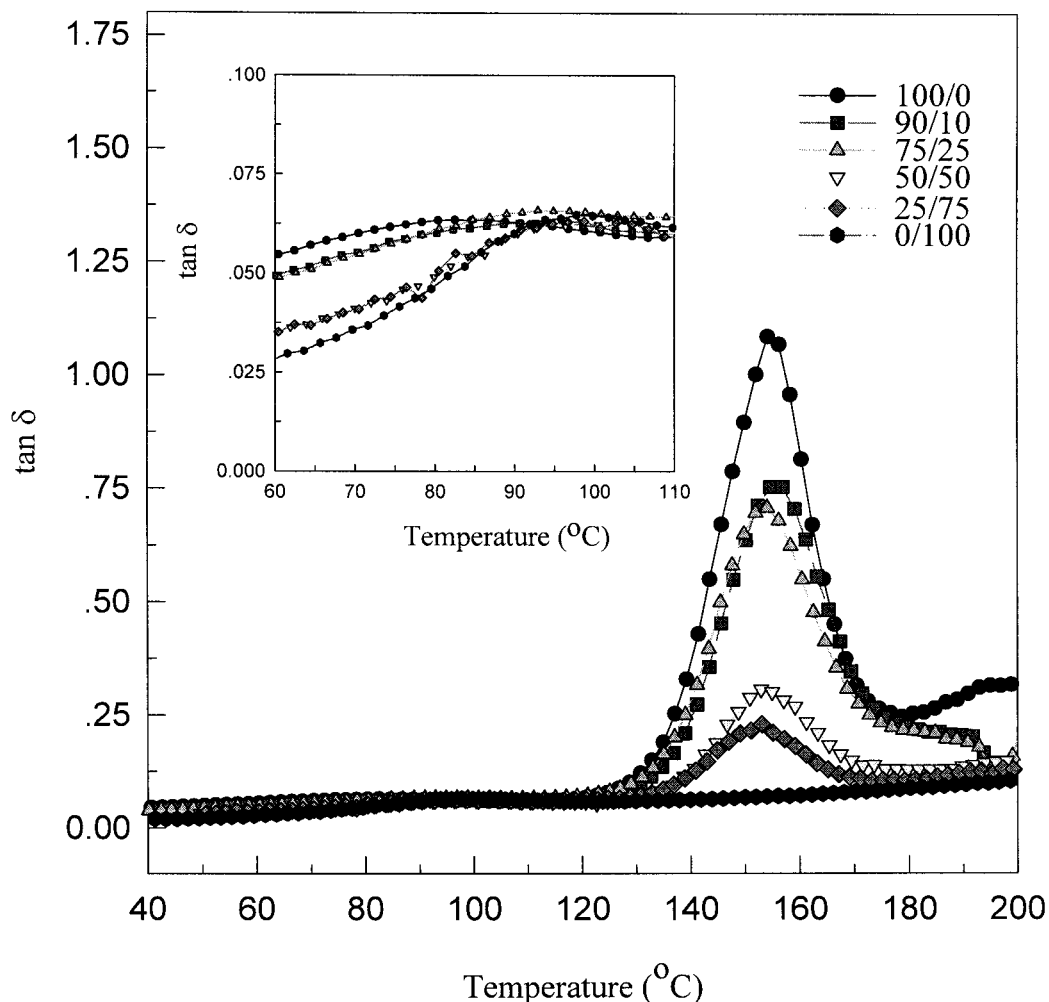
Figure 1   Glass transition temperature of PEN/LCP blends as a function of LCP content.

measurements were carried out using a Rosand capillary rheometer at 290°C. Tensile properties were measured with an Instron tensile tester (model 4201) at room temperature. In this experiment, gauge length and crosshead speed were 30 mm and 5 mm/min, respectively. Scanning electron microscope (SEM) observations of the tensile fractured surfaces of blend fibers were performed by Hitachi SEM (model S-4200).

RESULTS AND DISCUSSION

Thermal Behavior

Thermal transition behavior of polymer blends may provide important information concerning compatibility as well as crystallization behavior.
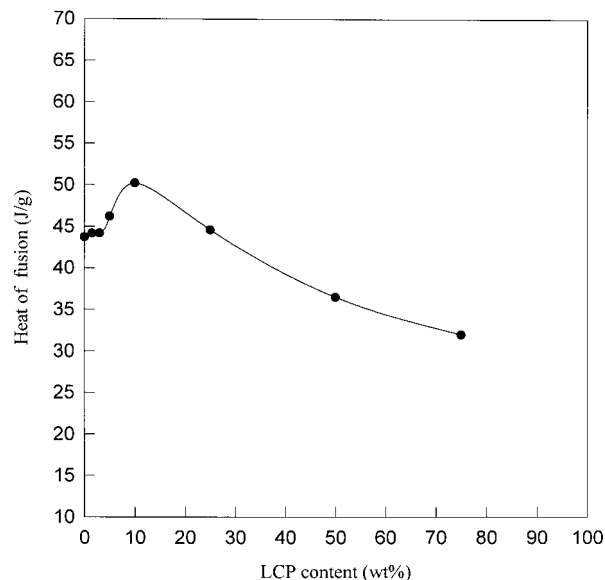
Dynamic mechanical thermal analysis was used to investigate different transitions occurring in PEN/LCP blends, results of which are shown in Figure 1. The tan δ versus temperature curve of PEN/LCP blends exhibits two distinct peaks, typically characteristic of an immiscible two-phase system.[26,27] The high T_g (at ~154°C) comes from the PEN-rich phase, whereas the low one (at ~99°C) is due to the LCP (PHB80/PET20)-rich phase, respectively. This peak is related to the motion of PET segments in the PHB-rich phase; similar results were reported by Benson and Lewis.[28] The height of the tan δ peak decreased with increasing LCP content.

Dynamic mechanical storage moduli of PEN/ LCP blends are shown in Figure 2. Pure LCP exhibited a large storage modulus. It was slightly
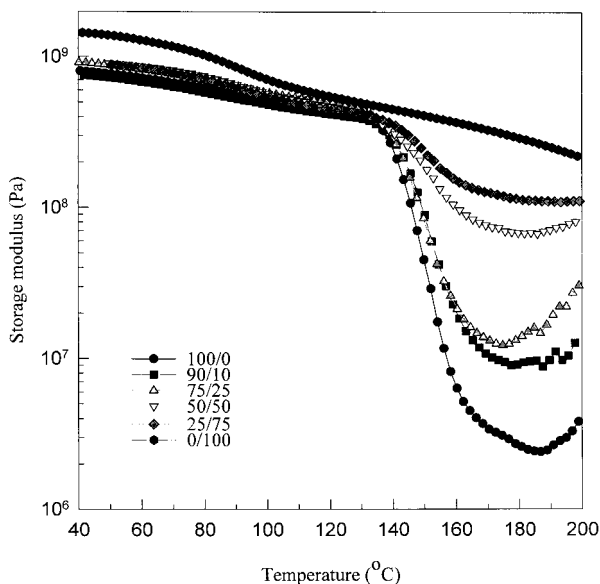
Figure 2 Storage modulus (E') of PEN/LCP blends as a function of LCP content.

Figure 3 Heat of fusion of PEN/LCP blends as a function of LCP content; based on the mass of PEN in the blends.

decreased with increasing temperature, due to the rigid molecular structure of the blends; the storage modulus decreased remarkably, however, with increasing temperature, especially at the vicinity of the glass transition temperature of the PEN. It was found that the LCP reinforced the PEN matrix. Based on the DMTA results alone, however, it is difficult to determine the role of LCP (PHB80/PET20) because the percent crystallinity of the PEN/LCP blends could also vary from system to system. The heat of fusion and the

crystallinity of the PEN/LCP blends were measured by DSC. Table I gives the relevant numerical data. The heat of fusion and crystallization for the PEN/LCP blends have been normalized with respect to LCP content. Figure 3 shows the heat of fusion as a function of LCP content for PEN/LCP blends. The heat of fusion showed a maximum at about 10 wt % of LCP, and it was decreased with increasing LCP content. That is the 10 wt % system had a heat of fusion of (based

Table I Thermal Properties of PEN/LCP Blends

Composition PEN/LCP	T_g[a] (°C)	T_{cc}[b] (°C)	ΔH_{cc}[c] (J/g)	ΔH_{cc}^{*}[d] (J/g)	T_m[e] (°C)	ΔH_m[f] (J/g)	ΔH_m^{*}[g] (J/g)
100/0	122	201	40.04	40.04	269	43.71	43.71
98.5/1.5	121	178	31.10	31.57	269	42.38	44.16
97/3	121	174	31.34	32.30	269	42.90	44.2
95/5	121	171	31.60	33.26	268	43.92	46.2
90/10	121	169	27.87	30.97	269	45.23	50.2
75/25	122	169	22.04	29.39	269	33.48	44.6
50/50	118	169	11.96	23.92	265	18.26	36.52
25/75	118	169	10.71	42.34	264	8	32

[a] T_g, glass transition temperature.
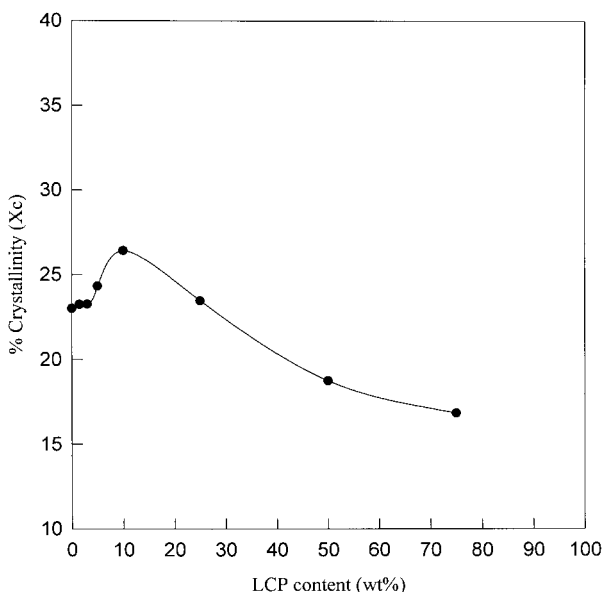[b] T_{cc}, cold crystallization temperature.
[c] ΔH_{cc}, heat of cold crystallization of the blends.
[d] ΔH_{cc}^{*}, heat of cold crystallization based on the mass of PEN in the blends.
[e] T_m, melting temperature.
[f] ΔH_m, heat of fusion of the blends.
[g] ΔH_m^{*}, heat of fusion based on the mass of PEN in the blends.

Figure 4 % Crystallinity of PEN/LCP blends as a function of LCP content; based on the mass of PEN in the blends.

on the mass of PEN in the blends) 50 J/g compared to 43.71 J/g for the PEN control. This initial increase of heat of fusion may be indirect evidence of an increase in percent crystallinity of the blends. Further, it indicates that the addition of small amounts of LCP enhanced the formation of crystallites or the crystallization process.[27,29]

Figure 4 shows the crystallinity as a function of LCP content for PEN/LCP blends. The crystallinity of PEN/LCP blends X_c showed a maximum at 10 wt % of LCP and then decreased at higher LCP content. The addition of small amounts of LCP enhanced the formation of crystallites. The values of X_c can be calculated from $X_c = \Delta H_m/\Delta$, where (PEN) = 190 J/g is the heat of fusion calculated for 100% crystalline PEN.[30] It should be noted that the crystallinity calculated by this method is an apparent value. It can be considered only as a measure of the amount of crystalline phase, and not necessarily a description and regularity of the lamellas.[27] The cold crystallization temperatures as a function of LCP content for PEN/LCP blends are shown in Figure 5. The PEN had a cold crystallization temperature peak at 201.72°C with a heat of cold crystallization of 40.04 J/g. This transition was shifted down to 178°C in the 1.5 wt % system, and heat of cold crystallization was reduced (based on the mass of PEN in the blends) to 31.57 J/g. This effect was more pronounced for the 10 wt % system, which indicates that it is an

efficient nucleating agent for PEN matrix. The ability for LCP to perform as nucleating agents has been observed in several other systems.[31] If the nucleating effect occurs during the fiber-spinning process, we can expect an enhanced mechanical performance by the reduction of the crystalline domain size and uniform distribution of PEN/LCP blends.[20–22] This tendency was reported by Hong et al. for PET/LCP blends.[22]

Rheological Properties

For LCP, most of the orientation and texture generated during the fabrication process are maintained in the final solid state unless the residence time in the capillary is longer than the relaxation time of LCP. Consequently, it is very important to understand the rheological behavior of LCP for the interpretation of the interrelationships among the processing, structure, and physical properties of PEN/LCP blends. However, a number of fundamental questions about the difficult analysis of the microstructure of LCP remain unsolved; that is, thermal history and shear viscosity. Similar problems can occur in the polymer blends containing LCP.

Figure 6 shows the shear viscosity behaviors of PEN/LCP blends measured from the capillary rheometer with LCP content. The blend containing higher LCP content results in lower viscosity, as expected. This shows that LCP can be used as a processing aid. This phenomenon is a general
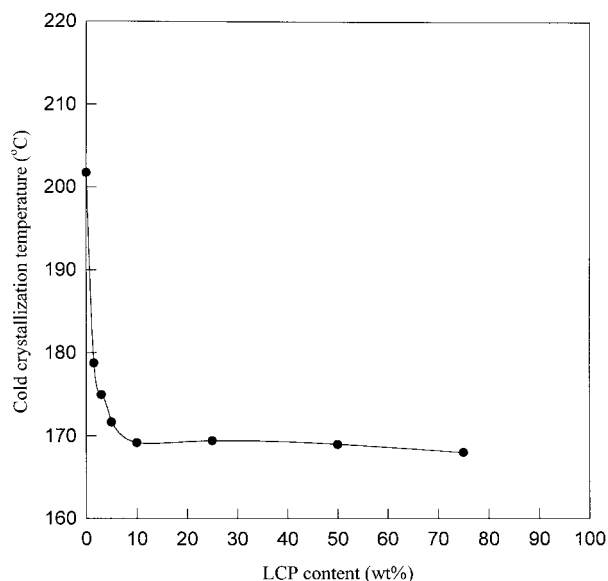
Figure 5 Cold crystallization temperature of PEN/LCP blends as a function of LCP content.
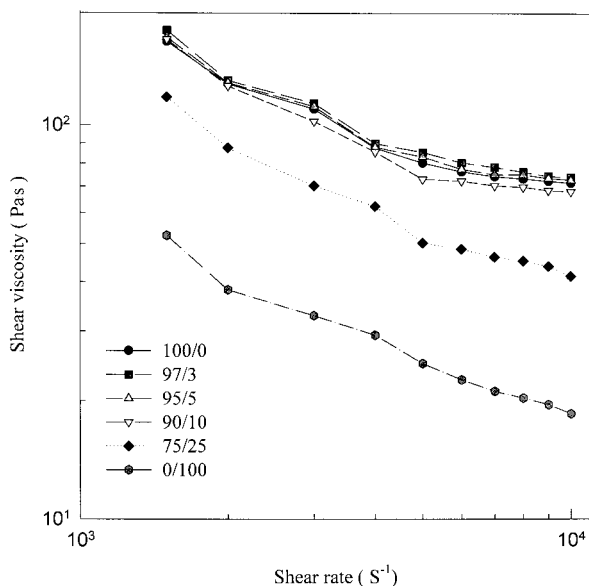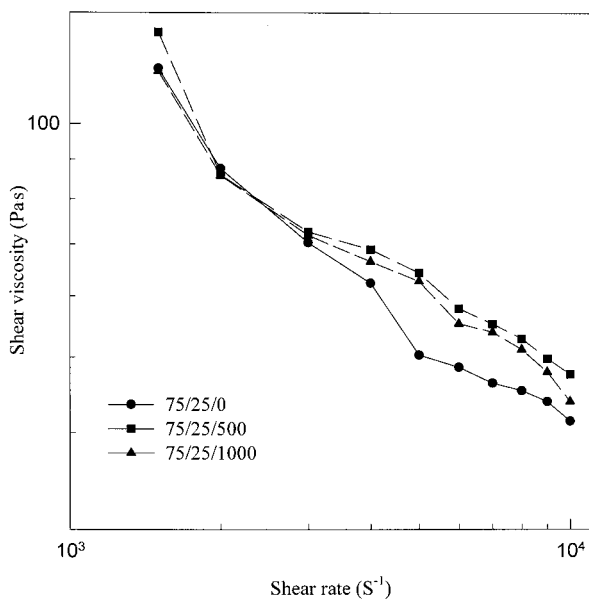
Figure 6 Shear viscosity behaviors of PEN/LCP blends with various LCP content at 290°C.
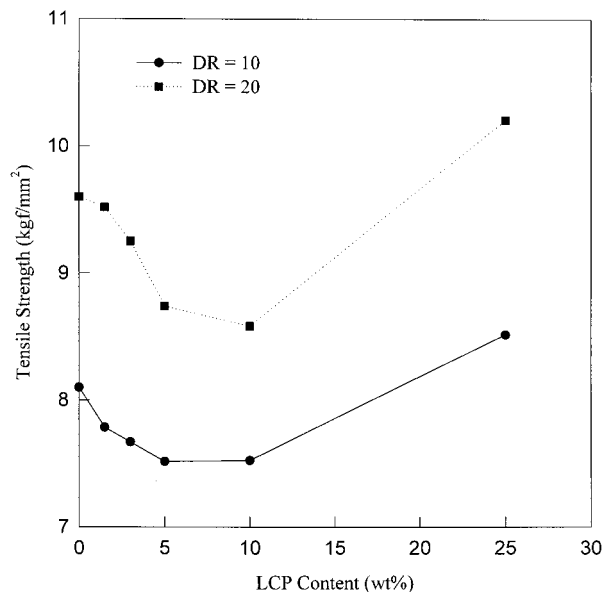
Figure 8 Tensile strength of PEN/LCP blends as a function of LCP content at draw ratios 10 and 20.

tendency of polymer blend systems containing LCP. On the other hand, as shown in Figure 7, for the 75/25 PEN/LCP blend containing 500 ppm of DBTDL used as reaction catalyst, the viscosity of the blend is slightly higher than that of 75/25 PEN/LCP blend without catalyst. This is attributed to the increase of the interfacial adhesion between dispersed LCP phase and PEN matrix.[32]

When more DBTDL was added (1000 ppm), the viscosity of the PEN/LCP blends decreased a little, even though it was still higher than that of the system with no added catalyst, which may be due to a reduction of molecular weight.[23,33] Details are under investigation and will be reported in the future.
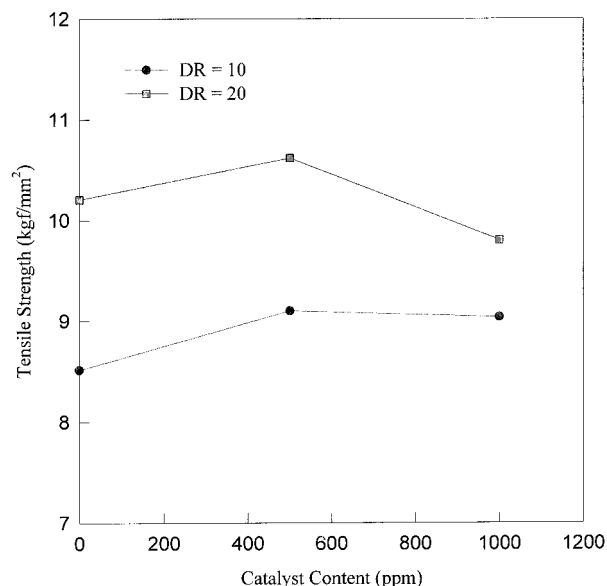
Mechanical Properties

Since thermotropic LCP has recently been utilized in applications requiring high modulus and strength, much effort has been made both to improve the processability and to develop the desired mechanical properties of semicrystalline polymers through *in situ* reinforcement technology. Tensile strength and modulus for several PEN/LCP blend fibers drawn at 290°C are plotted versus LCP content, as shown in Figures 8 and 9. The mechanical properties of PEN/LCP blend fibers are affected significantly by draw ratio due to the microfibrillation and orientation of dispersed LCP domains. The abrupt drop-off in tensile strength of the as-spun fibers at a certain content of LCP is indeed striking, whereas the modulus is enhanced by the incorporation of the liquid crystalline polymer. However, this phenomenon is not foreign to blends having liquid crystalline components. Brody observed that a 3% liquid crystalline additive to PET reduces spin orientation, and called it windup speed suppression (WUSS).[34] If

Figure 7 Shear viscosity behaviors of 75/25 PEN/LCP blends with various catalyst content at 290°C.
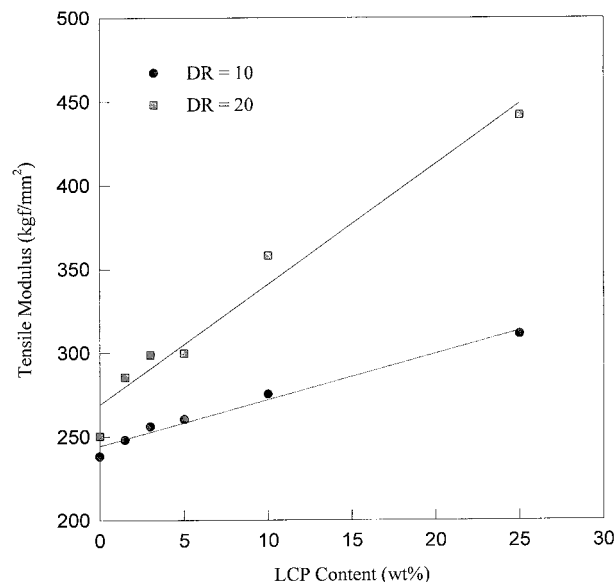
Figure 9 Tensile modulus of PEN/LCP blends as a function of LCP content at draw ratios 10 and 20.

Figure 10 Tensile strength of 75/25 PEN/LCP blends as a function of catalyst content at draw ratios 10 and 20.

the preceding premise is accepted, the low tensile strengths of the blend fibers can readily be explained, at least for the 90/10 PEN/LCP blend composition. An orientation suppression would lead to low-tensile-strength values.[34] It is worth mentioning that PEN/LCP blend fibers displayed extremely low melt viscosity. In our previous studies, we found that droplet deformation can be increased by any of the following factors: an increase in the medium viscosity, extension rate, or dispersed LCP droplet size; or decrease in interfacial stress.[16] As previously described, to overcome fiber-spinning problems due to the drastic drop-off in viscosity, it was decided to use a PEN resin with higher intrinsic viscosity (i.v.). This can be explained by the fact that the viscosity of the matrix PEN was too low to deform and break the spherical particles of the dispersed LCP phase.[35] Blends of the higher i.v. (high-molecular-weight) PEN resin showed a higher melt strength and modulus in the processing.[33]

Figures 10 and 11 describe the effect of DBTDL on the tensile strength and tensile modulus for the 75/25 PEN/LCP blend fibers at draw ratios 10 and 20. As expected, addition of DBTDL slightly enhances the mechanical properties of the blends at the particular content. The optimum amount seems to be about 500 ppm at draw ratio 20. However, the mechanical properties deteriorate when the amount of catalyst exceeds the optimum usage level. From the previous relationships be-

tween the rheological properties and the mechanical properties, it can be discerned that the interfacial adhesion and the compatibility between two phases of PEN and LCP were enhanced; hence, DBTDL can be used as a catalyst to produce reactive compatibility in this blend system. This suggests the possibility of improving the interfa-
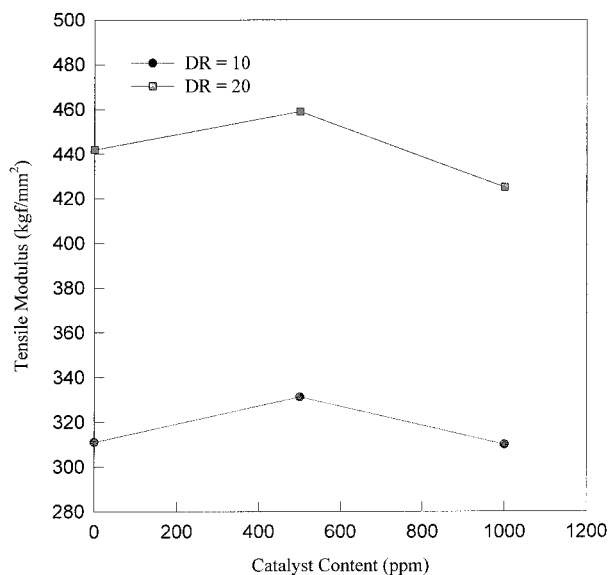
Figure 11 Tensile modulus of 75/25 PEN/LCP blends as a function of catalyst content at draw ratios 10 and 20.

cial adhesion between the immiscible polymer blends containing LCP by reactive extrusion processing at a very short residence time. As we see later from structural analysis data, the slightly enhanced mechanical properties of PEN/LCP blend fibers result from the formation of the fibrillar LCP structure and the reduction of the crystalline domain size and uniform distribution of LCP domains.

Morphology

As a rule, the mechanical properties of the *in situ* composite are greatly influenced by the resultant morphology. First, the LCP domains must be uniformly dispersed within the matrix. Second, the dispersed LCP domains must be effectively deformed during the fabrication process to raise the aspect ratio high enough to play the role of reinforcement. Third, good interfacial adhesion between two incompatible phases is essential for high-performance properties. In this respect, addition of the DBTDL as a reaction catalyst into the 75/25 PEN/LCP blend is expected to enhance the interface adhesion by reactive extrusion in the PEN/LCP blends, and these results were observed by SEM. Figure 12 shows the SEM photomicrographs of the PEN/LCP blend fibers system after Instron tensile test at a draw ratio of 20. The PEN/LCP blend fibers consist of two phases, the structure of which is composition-dependent. At 10 wt % LCP content, the LCP is dispersed as ellipsoidal particles; whereas at 25 wt % LCP content, the LCP is dispersed as fibrils or rodlike structures. In all cases, the major phase forms the matrix and the minor phase is segregated into dispersed phases.

CONCLUSIONS

Improving blend compatibility should increase the interfacial adhesion between the different components and the mechanical performance. Therefore it is important to control the interrelationships among the processing, structure, and physical properties for the immiscible blend and to improve the interfacial adhesion and compatibility by reactive extrusion. Blends made by reactive extrusion based on PEN, LC5000, and DBTDL used as a transesterification reaction catalyst have advantage over general binary PEN/LCP blends in the fabrication of *in situ* composites in terms of desired properties. The modulus of
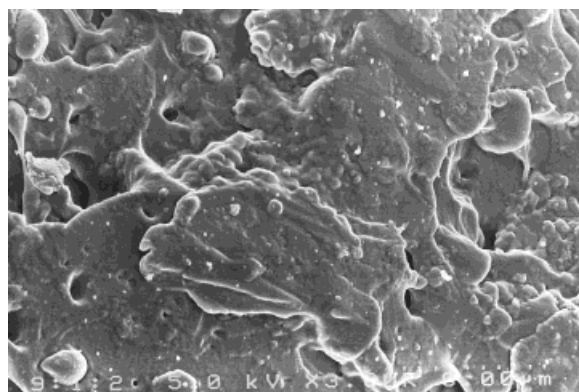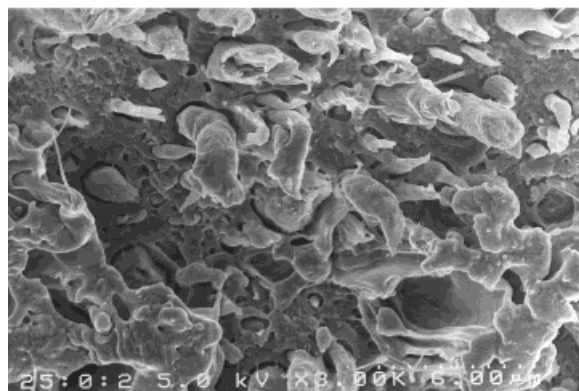
Figure 12 SEM fractographs of LCP blended fibers with draw ratio 20 after Instron tensile test. (a) 90/10, (b) 75/25.

the blends follows an additive rule with increasing the content of LCP in the PEN/LCP blends. The strength, however, shows an abrupt drop-off at a certain content of LCP. Addition of DBTDL used as a reaction catalyst was found to slightly increase the viscosity of the blends, enhance its adhesion with the matrix, and lead to increase of physical properties of two immiscible phases in a short residence time.

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