

# Mechanical, Morphological, and Thermal Properties of Poly(ethylene 2,6-naphthalate) and Copolyester LCP Blends

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**ABSTRACT:** Binary blends of a liquid crystalline polymer (LCP) and poly(ethylene 2,6-naphthalate) (PEN) were melt blended and injection molded. The mechanical properties were studied as a function of LCP content. Both the ultimate tensile strength and Young's modulus are higher than the theoretical values predicted by the rule of mixtures and they display a synergistic behavior at 70 wt % LCP content. However, the tensile strength decreases with LCP content and Young's modulus remained unchanged at lower LCP contents (10 to 30 wt %). The poor mechanical property is attributed to the immiscibility between PEN and LCP and the fibrillation behavior of LCP as revealed by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) results. However, LCP and PEN are found to be partially miscible at higher LCP content, ascertained by DSC and dynamic mechanical analysis (DMA). This is attributed to the transesterification reaction between PEN and PET moiety in the LCP molecules. SEM micrographs reveal a skin/core morphology in the tensile bars, that is, the LCP is better oriented in the skin than in the core region. At lower LCP content, the dispersed LCP phase is spherical in the core and ellipsoidal in the skin, with long axes oriented in the flow direction. DSC studies show that the crystallization rate is significantly enhanced by the presence of LCP up to 50 wt %, where the LCP acts as a nucleating agent for PEN crystallization. The melting temperature decreases with LCP content, probably as a result of imperfect crystals formed in the presence of LCP heterogeneous nucleating centers and the increasing miscibility between LCP and PEN. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 477–488, 2001

**Key words:** liquid crystalline polymer; poly(ethylene-2;6-naphthalate) (PEN); blend; *in situ* composite; morphology

## INTRODUCTION

In recent years, numerous studies on LCP/isotropic thermoplastic blends have been carried out

because of the growing industrial interest in the LCP fibril formation in the matrix during processing. The isotropic thermoplastic components used cover all the plastic families, ranging from commodity polymers (polyethylene,<sup>1,2</sup> polypropylene,<sup>3,4</sup> polystyrene<sup>5,6</sup>) and engineering plastics (polyamides,<sup>7,8</sup> polyesters<sup>9–11</sup>) to advanced specialty polymers (polyetherketone,<sup>12,13</sup> polyphenylene sulfide<sup>14,15</sup>).

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As for polyester/LCP blends, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) have been widely studied. The LCP used in the blends can be divided into two categories: one that possesses a rigid wholly aromatic structure such as hydroxyl benzoic acid and hydroxyl naphthoic acid (HBA–HNA) copolyester (Vectra from Hoechst Celanese),<sup>16–18</sup> and the other contains a flexible structure such as PHB–PET–polyesters (Rodrun LC series from Unitika).<sup>19–23</sup>

In the blends of Vectra/PET, studies indicated that Vectra and PET are immiscible and there is no transesterification reaction between them. But these rigid LCP molecules can act as a nucleating agent, which promotes crystallization of the PET. The mechanical properties of the blends can be improved by both LCP fibrillation and a significant increase in the crystallinity of the PET matrix. Liang et al.<sup>16</sup> reported that the mechanical properties of the as-spun blend fibers of Vectra A900/PET could be improved by heat treatment because of a striking increase in the crystallinity of the PET matrix. On the other hand, PET and the more flexible LCP such as PHB–PET copolyester are miscible or partially miscible because of the transesterification between PHB–PET and PET under the conditions of high blending temperatures,<sup>24</sup> prolonged mixing time,<sup>25</sup> or in the presence of catalyst.<sup>19</sup> The transesterification hinders the crystallization process of PET and results in a decrease in the crystallization temperature, heat of crystallization, melting point, and the heat of fusion of the PET matrix.

Because the compatibility between LCP and PET has a significant influence on the blend morphology and the mechanical properties, *in situ* compatibilization was studied by addition of multifunctional epoxy monomers.<sup>26,27</sup> During blending, LCP, PET, and epoxy monomer form the epoxy–*co*-PET–*co*-LCP copolymer, which acts as compatibilizer. This process enhances the LCP fibrillation and results in a substantial improvement to the tensile strength and Young's modulus.

Given that PEN has only recently been developed, only a few studies of the LCP/PEN blends have been carried out.<sup>25,28,29</sup> Kim et al. studied the mechanical, morphological, rheological, and thermal properties of LCP (Vectra A950)/PEN blends. The tensile strength and flexural modulus exhibit a synergistic behavior and their values were higher than those predicted by the rule of mixtures. Furthermore, the tensile strength and

modulus of a 70 wt % LCP blend were above those of pure LCP.

Ternary blends of a PHB80–PET/PEN/PET were studied by Kim et al.<sup>25</sup> Their results showed that the morphology and the mechanical properties depended strongly on the PHB content in the blends. The LCP is irregularly dispersed as spherical domains below PHB content of 20 wt %, but it is ellipsoidal and fibrous when PHB content is in the range of 30 to 40 wt %.

In this study, binary blends of a PHB80–PET copolyester and PEN were prepared by melt blending. Attention is focused on the effects of LCP content on the miscibility between LCP and PEN; the crystallization of PEN; and the influence on the mechanical, morphological, and thermal properties of the blends.

## EXPERIMENTAL

### Materials

The LCP used is Rodrun LC-5000 produced by Unitika (Osaka, Japan). It is a copolyester of PET and hydroxybenzoic acid (HBA) with a mole ratio of HBA : PET of 80 : 20. The nematic transition temperature is 280°C. PEN used is a homopolymer from Eastman Chemical Company (Rochester, NY) and possesses a viscosity of 200 Pa/s at a shear rate of 100 s<sup>-1</sup>.

### Blend Preparation

The LCP and PEN pellets were dried in a vacuum oven at 120°C for 8 h prior to blending. The blends of different LCP contents were dry mixed at room temperature and then melt blended in a Haake twin-screw extruder. The temperatures of the heating zones from hopper to die were set to 280, 290, 295, 290, and 260°C, respectively. The screw speed was 20 rpm. Melt extrudate was quenched in a water bath at room temperature and subsequently pelletized. The blend pellets were dried under vacuum and then injection molded with a Manumold 77/30 injection molding machine into dumbbell-shaped tensile bars in accordance with the ASTM standard. The barrel temperatures were 270, 285, and 230°C from the hopper to nozzle. Unless otherwise stated, the pure PEN and LCP samples were processed in the extruder under the same conditions as the blends, to maintain a thermal history similar to that of the blends.

## Mechanical Properties

Tensile properties were determined by using an Instron 4204 tester (Instron Corp, Canton, MA) at 25°C with a cross-head speed of 5 mm/min. The gauge length was 50 mm. The test bars were dumb-bell-shaped with a width and thickness of the narrow section of 10 and 3.5 mm, respectively, according to the ASTM standard. A total of 10 test samples were tested for each blend composition to achieve a standard deviation of less than 10%.

## Scanning Electron Microscopy (SEM)

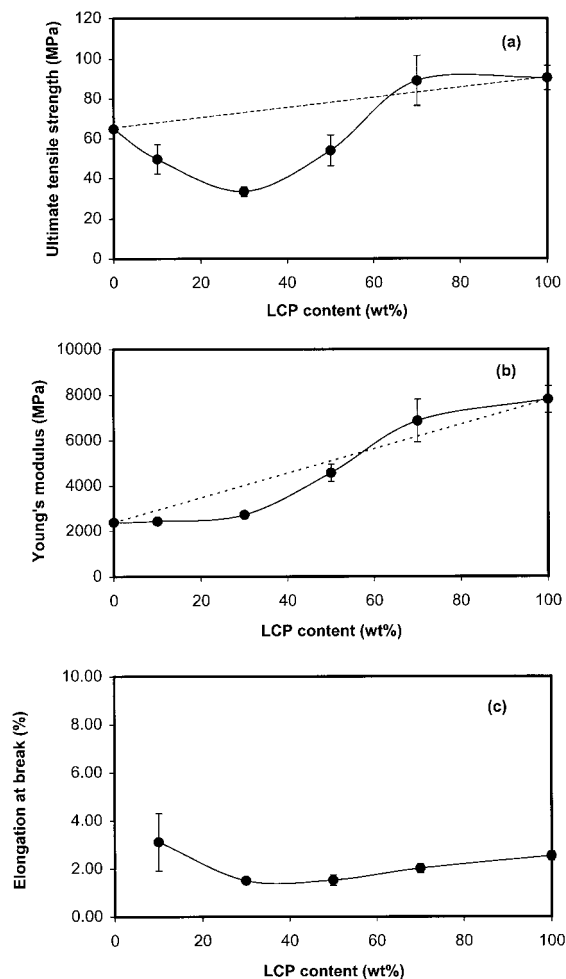
The morphology of the fractured surfaces of all the blends was observed with a JEOL JSM-5600LV scanning electron microscope (JEOL, Peabody, MA). The specimen surface was coated with a thin layer of gold prior to SEM observation. For better evaluation of the LCP dispersed particles and their distribution, the tensile bar was fractured in liquid nitrogen in the longitudinal direction.

## DSC Analysis

The DSC-7 (Perkin Elmer Cetus, Norwalk, CT) was used to determine the glass-transition temperature, cold crystallization and crystallization temperatures, melting temperature, heat of fusion, and crystallization. A 4- to 5-mg sample was taken from the dried pellets and heated at 40°C/min from 40 to 280°C, maintained at 280°C for 2 min, then cooled from 280 to 40°C at 40°C/min. This heat treatment was to ensure that each sample was subjected to the same thermal history. The heat-treated samples were finally scanned from 40 to 280°C and cooled to 40°C at 10°C/min. The data from the last heating and cooling scans were used to determine the transition temperatures and enthalpy. During the DSC testing, the furnace was maintained under nitrogen environment to prevent polymer degradation.

## DMA

The dynamic mechanical analysis of the injection-molded specimens was conducted with a DMA-2980 analyzer (TA Instruments, New Castle, DE). A rectangular sample (length, 60 mm; thickness, 3.5 mm; width, 10 mm) was cut from the narrow part of the dumbbell-shaped tensile bar. A dual cantilever clamp was used and a frequency of 1 Hz and an oscillation amplitude of 20  $\mu\text{m}$  were applied to the samples. The measurements were



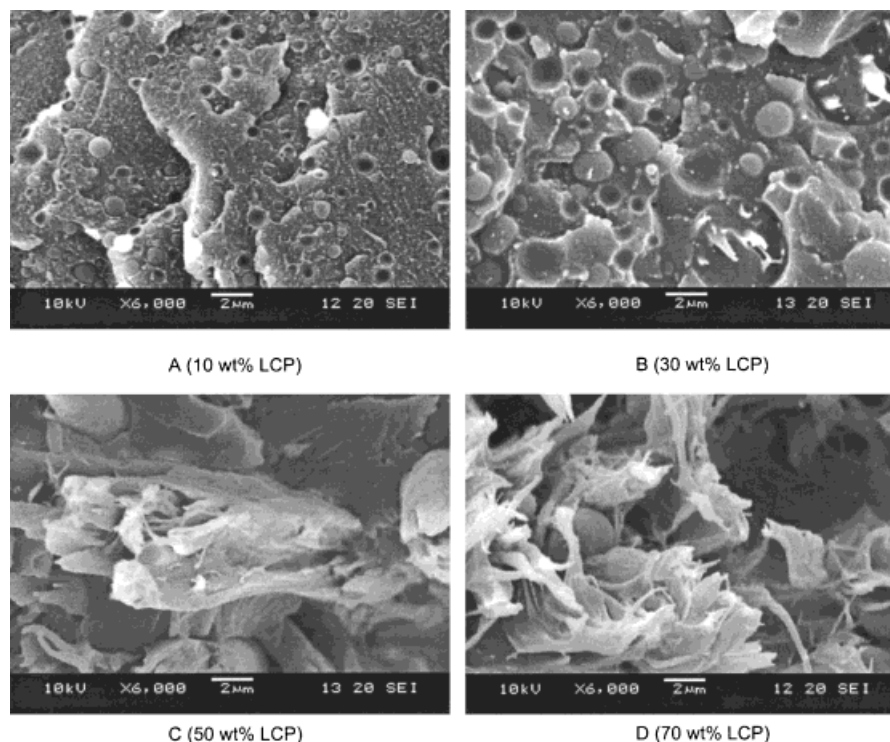
**Figure 1** Mechanical properties as a function of LCP content: (a) ultimate tensile strength, (b) Young's modulus, and (c) elongation at break. The dotted lines in (a) and (b) are theoretical values calculated from the rule of mixtures.

performed in the temperature range of 40 to 200°C with a heating rate of 2°C/min. The  $\tan \delta$  peak temperature was taken as  $T_g$ .

## RESULTS AND DISCUSSION

### Mechanical Properties

Figure 1(a)–(c) show the mechanical properties of LCP/PEN blends. Figure 1(a) shows the tensile strength as a function of LCP content. The tensile strength decreases with LCP content up to 30 wt %; thereafter it increases with LCP content. At 70 wt % of LCP, the tensile strength is higher than the predicted value with the rule of mixtures. This means the blend exhibits a synergistic effect.



**Figure 2** SEM micrographs of LCP/PEN blends in the core region. Samples were tensile fractured from the injection-molded bars. LCP contents in (A) through (D) are 10, 30, 50, and 70 wt %, respectively.

Figure 1(b) shows the Young's modulus as a function of LCP content. It remains unchanged up to 30 wt % of LCP; thereafter it increases with further addition of LCP. At 70 wt % LCP, a synergism is displayed, similar to that observed for the tensile strength.

Figure 1(c) shows the elongation at break versus the LCP content. It decreases drastically with the addition of 10 wt % LCP and thereafter remains unchanged up to 30 wt % LCP and then slightly increases with further increase of the LCP content. This suggests that the addition of LCP causes the blend to be stiff and brittle. In fact, PEN is tough and has an elongation at break of about 200%.

The increases in the tensile strength, modulus, and elongation at break after addition of 30 wt % LCP suggest a better interfacial adhesion. Further discussion in conjunction with SEM, DSC, and DMA data will be presented later.

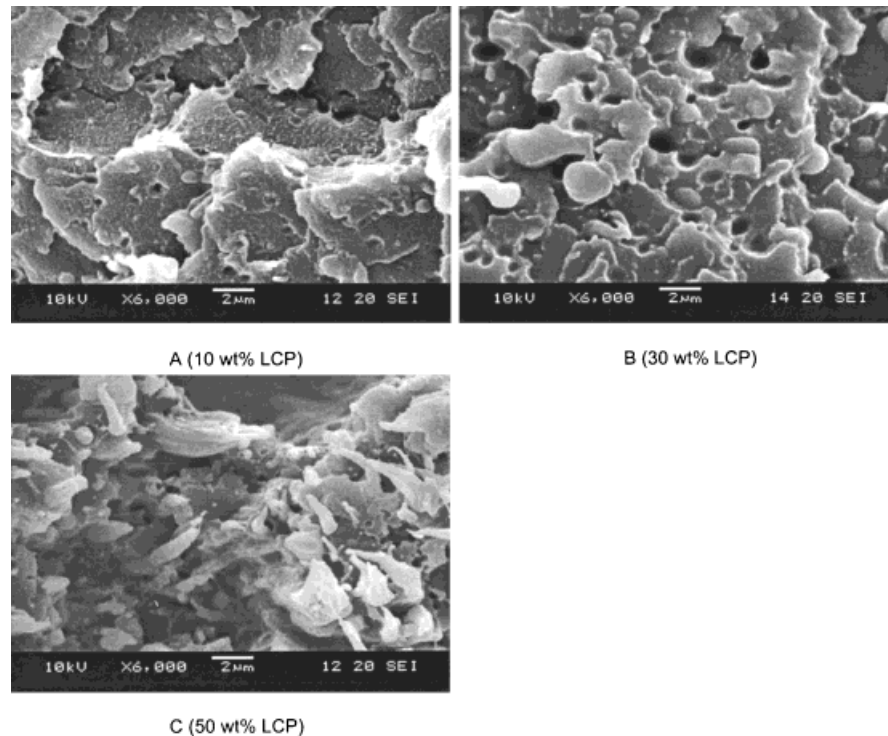
In general, the mechanical properties of the LCP/engineering plastic blends depend on many factors such as LCP fibrillation capacity, interfacial properties of the component phases, and the processing conditions. The synergism at 70 wt %

blends is consistent with the results of Kim et al.<sup>29</sup> on blends of Vectra A950/PEN. But in their study, the tensile strength and Young's modulus were higher than the theoretical values predicted by the rule of mixtures for the LCP contents ranging from 10 to 70 wt %. However, our results are below the rule of mixtures for LCP content lower than 70 wt %. The difference may arise from the LCP used. Note that Vectra A950 is a copolyester of 73 mol % of hydroxybenzoic acid (HBA) and 27 mol % of 2,6-hydroxy naphthoic acid (HNA). However, LC-5000 is a copolyester of 80 mol % HBA and 20 mol % of PET. The backbone of the former polymer contains 100% of aromatic hydrocarbon chains, whereas the latter polymer possesses 20 mol % of the flexible PET spacer. Thus molecules of the former are much more rigid than those of the latter. The mechanical properties of the pure Vectra A950 are much better than those of Rodrun LC-5000.

### Morphology

Blend morphology directly governs the mechanical properties. Morphology contains the informa-





**Figure 3** SEM micrographs of LCP/PEN blends in the skin region. Samples were tensile fractured from the injection-molded bars. LCP contents in (A) through (C) are 10, 30, and 50 wt %, respectively.

tion on the shape, size, and distribution of the dispersed phase and the interfacial adhesion. In this study, both the tensile fractured and the cryogenically fractured surfaces were investigated with SEM.

SEM micrographs, summarized in Figures 2 and 3, show the morphology of tensile fractured surfaces in the core and skin regions. The morphology depends on the LCP composition. For all LCP compositions, a typical skin/core structure existed and the LCP dispersion is less oriented in the core than in the skin.

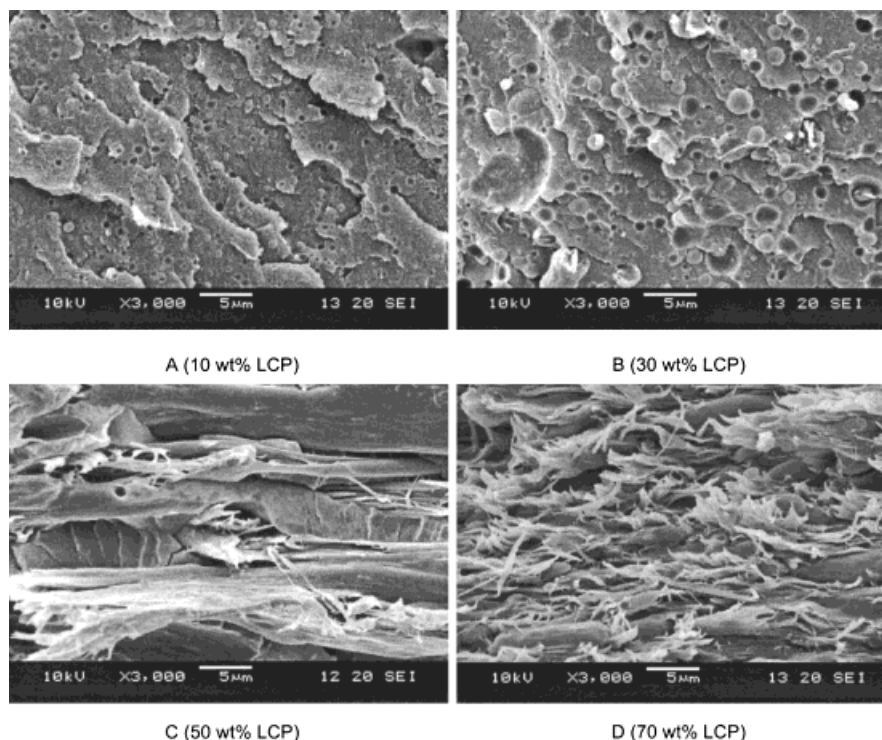
At lower LCP content, the LCP is the dispersed phase and PEN is the continuous phase. However, a co-continuous and finally a LCP continuous structure is formed with further increase in the LCP content. In the blends containing 10 and 30 wt % LCP [Fig. 2(A) and (B)], the fractured surface is smooth. However, the fractured surfaces are rough and fibrous for the blends containing more than 50 wt % LCP. In the skin region, many pulled-out LCP fibrils can be observed for the 50 wt % LCP blend. For the blend of 70 wt % LCP, large amounts of LCP fibrils are observed in the core region. However, a SEM observation in the cross section of the skin was not possible

because the tensile fractured surface was so rough that the core was pulled out from the skin.

To investigate the morphology of blends without deformation, the narrow part of the tensile bars was cryogenically fractured in the flow direction. The SEM micrographs of the cryogenically fractured surfaces (Figs. 4 and 5) confirm the skin/core morphology observed in the tensile fractured surfaces. Furthermore, the LCP phase is more oriented in the skin than in the core region for all LCP content blends.

The LCP dispersed phase in the core region is spherical for 10 and 30 wt % blends, whereas it becomes ellipsoidal and fibrous and is oriented in the flow direction in the skin region. The LCP particle is much larger in the 30 wt % blends than in the 10 wt % LCP blends. The average particle areas, calculated by the Imagepro software, are 0.4 and 1.5  $\mu\text{m}^2$  for 10 and 30 wt % LCP blends, respectively. This is attributed to the coalescence of LCP droplets, which increases with the particle collision probability and the probability is proportional to the volume fraction of the dispersed phase during the dispersing process.<sup>30,31</sup>

By further increasing the LCP content, a co-continuous lamellar structure is formed. At 70 wt



**Figure 4** SEM micrographs of LCP/PEN blends in the core region. Samples were obtained by injection molding and cryogenically fractured in the flow direction. LCP contents in (A) through (D) are 10, 30, 50, and 70 wt %, respectively.

% LCP, the LCP phase becomes a continuous phase and is highly oriented in both core and skin regions. However, the LCP orientation is better in the skin than in the core region.

### Thermal Properties

Figure 6(a) and (b) show the thermograms of the LCP/PEN blends during heating and cooling scans at 10°C/min. As shown in Figure 6(a), the  $T_g$  transition of the PEN component is ~120°C for pure PEN, 10 and 30 wt % LCP blends. The heat flow increment at  $T_g$  becomes smaller with increasing LCP content. The heat capacity increments  $\Delta C_p$  at the  $T_g$  are 0.456, 0.176, and 0.044 J g<sup>-1</sup> °C<sup>-1</sup> for pure PEN and 10 and 30 wt % LCP blends, respectively. But when the LCP content reaches 50 wt %, it is difficult to determine the  $T_g$ . At 70 wt % LCP, the heat flow increment is not detectable, hence the  $T_g$  cannot be determined. The decrease in heat flow (or  $\Delta C_p$ ) increment at  $T_g$  with increasing LCP content is attributed to the smaller fraction of amorphous PEN in the blends, given that the  $T_g$  of semicrystalline polymers is a characteristic of the amorphous region. Hence,  $\Delta C_p$  is proportional to the PEN fraction in the

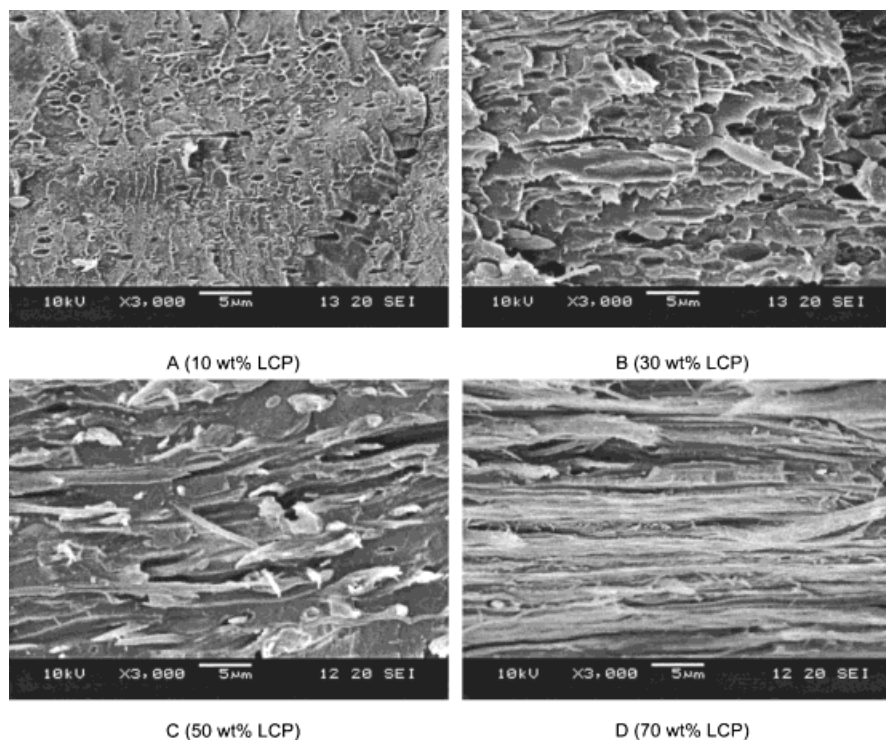
blend and the ratio of amorphous PEN, which is determined by the initial crystallinity of PEN ( $C_i$ ) before the heating ramp at 10°C/min. The  $C_i$  values are between about 3 and 20%, respectively, for the pure PEN and the LCP/PEN blends.  $C_i$  can be calculated from the heating scan using the following equation:

$$C_i = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \times 100\% \quad (1)$$

where  $\Delta H_m$  and  $\Delta H_{cc}$  are the heats of fusion and cold crystallization, respectively, in J/g PEN;  $\Delta H_m^0$  is the heat of fusion calculated for 100% crystalline PEN and has the value of 190 J/g.<sup>29</sup>  $C_i$  values for different LCP blends are listed in Table I.

Because the  $T_g$  of the PEN component in the blends is independent of LCP content for the lower LCP content blends, PEN and LCP are immiscible. The smooth fractured surfaces in the SEM micrographs in Figures 4(a) and (b) and 5(a) and (b) suggest that the PEN and LCP are immiscible.

Figure 6(a) shows the presence of cold crystallization peak for pure PEN and the absence of



**Figure 5** SEM micrographs of LCP/PEN blends in the skin region. Samples were obtained by injection molding and cryogenically fractured in the flow direction. LCP contents in (A) through (D) are 10, 30, 50, and 70 wt %, respectively.

cold crystallization for LCP blends. This is attributed to the fact that the crystallization is much faster for the PEN in the presence of LCP than in the pure PEN during the heat-treatment step. Figure 7 shows the thermograms during the heat treatment prior to the test run. When heating and cooling the blends at 40°C/min, cold crystallization and crystallization occur for all the LCP/PEN blends. However, neither cold crystallization nor crystallization took place for pure PEN. This means the crystallization and cold crystallization rates are higher in the presence of LCP.

The melting temperature of the PEN component increases initially with addition of 10 wt % LCP then decreases slightly with LCP content upon further addition of LCP. The initial increase in the  $T_m$  is considered to be the result of the more perfect PEN crystals formed in the presence of LCP, because the melting exotherm peak is narrower than that in the pure PEN. The  $T_m$  span for the 10 wt % blend is 11.7°C, whereas it is 14.4°C for pure PEN. The  $T_m$  depression after addition of 30 wt % of LCP can be partially attributed to the solvent effect of LCP addition. The  $T_m$  depression of a semicrystalline polymer in the presence of an amorphous polymer is analogous to the  $T_m$  de-

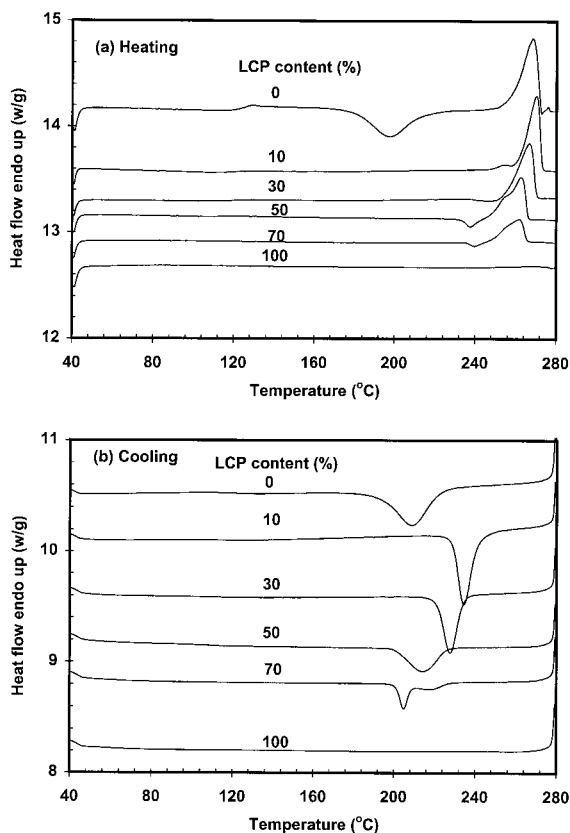
pression in the presence of a low molecular solvent as described by the following equation<sup>32,33</sup>:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R\nu_{2u}\chi_{12}}{\Delta H\nu_{1u}}(1 - \phi_2)^2 \quad (2)$$

where  $T_m^0$  is the melting temperature of the pure semicrystalline polymer;  $\nu_{1u}$  and  $\nu_{2u}$  are the molar volumes for crystalline and amorphous polymers, respectively;  $\chi_{12}$  is the interaction parameter;  $\phi_2$  is the volume fraction of the crystalline polymer;  $R$  is the gas constant; and  $\Delta H$  is the heat of fusion per mole of crystalline repeating units.

The important point is the role played by  $\chi_{12}$ ; in eq. (2), the  $T_m$  depression is specified by the heat of mixing rather than entropy of mixing. This equation states that the melting point depressions can be realized only if  $\chi_{12}$  is negative, which implies that the two polymers are miscible.

The depression of  $T_m$  was reported by Gabellini and Bretas<sup>34</sup> on the blends of poly(*p*-phenylene sulfide)/HX4000 (LCP of copolyester of terephthalic acid, phenylhydroquinone, and hydroquinone from Dupont, Wilmington, DE). The  $T_m$  depression was attributed to two reasons: (1) low



**Figure 6** Thermograms of LCP/PEN blends during (a) heating and (b) cooling scans at 10°C/min. Prior to the testing, samples were heated from 40 to 280°C at 40°C/min, maintained at 280°C for 2 min, and then cooled to 40°C at 40°C/min.

weight LCP molecules, rejected during the LCP crystallization and diffusing into the PPS melt, become entrapped intraspherulitically during the PPS crystallization and less-perfect PPS crystals are produced; (2) less-perfect PPS transcrystallites are formed on the LCP fibril surfaces.

However, the melting temperature–LCP content relationship may vary from one blend pair to another. In a study by Kim et al.,<sup>29</sup> the  $T_m$  of PEN in Vectra A950/PEN blends was found to be independent of the LCP content. In their study, the  $T_g$  of PEN is independent of the LCP content, suggesting that the PEN/Vectra-type LCP is not compatible. This result confirms that  $T_m$  depression can occur only in the miscible semicrystalline/amorphous polymer blends and is attributed to the solvent effect of the latter.<sup>32,33</sup> We suggest that a transesterification reaction between the PET moiety in the LCP molecules and the PEN occurs at high temperature. This *in situ* reaction produces a copolymer of LCP–PET, which acts as

a compatibilizer for the immiscible LCP/PEN polymer pair. In other words, LCP and PEN become partially miscible after the transesterification reaction in the melt-blending step. Because the transesterification rate depends on the concentrations of the repeating unit of PET and PEN, the concentration of LCP–PEN copolymer is thus a function of LCP content. The  $T_m$  depression is more significant with increasing LCP concentration in the blend.

Transesterification has been widely studied in the polyester/LCP blend systems. PET and copolyester LCP (PHB–PET) proved to be miscible or partially miscible because of the transesterification reaction between PHB–PET and PET under the conditions of high blending temperature,<sup>35</sup> prolonged mixing time,<sup>36</sup> or in the presence of catalyst.<sup>37</sup> It was demonstrated that there is almost no miscibility between PET and PHB–PET copolyester before transesterification. By annealing at 300 or 325°C, the melting temperature of PET decreased from about 249 to 207°C as a result of the transesterification reaction.<sup>38</sup> A separate study on the transesterification in the PEN/LCP blend in the presence of catalyst is in progress.

The crystallization temperature  $T_c$  is higher in the PEN/LCP blends up to 50 wt % LCP than in the pure PEN [Fig. 6(b)]. This indicates that LCP acts as a nucleating agent for PEN crystallization, although at 70 wt % LCP the  $T_m$  of PEN is lower than that of the pure PEN. This implies that large amounts of LCP phase hinder the crystallization resulting from steric hindrance effects. The nucleating effects of LCP for semicrystalline polymers were reported previously.<sup>29,39–41</sup>

Figure 8 shows the curves of storage modulus and the  $\tan \delta$  versus temperature for the blends of LCP and PEN at different compositions. The samples were taken from the narrow part of the injection-molded tensile bars. They were immediately kept in a desiccator after injection molding to prevent the influence of moisture on the thermal mechanical properties. For all the blends, the storage modulus exhibits an abrupt decrease at about 120 to 130°C, corresponding to the  $T_g$  of the PEN component. It then increases with temperature attributed to the crystallization of PEN. The onset temperature corresponding to the decrease in the storage modulus in the presence of LCP is related to the nucleating effect of the LCP on PEN crystallization. The storage modulus in the plateau region (below  $T_g$ ) increases with LCP content. Furthermore, we notice that the storage



**Table I Thermal Properties of LC5000/PEN Blends<sup>a</sup>**

Property <sup>b</sup>	LCP (wt %)				
	0	10	30	50	70
$T_g$ (°C)	121.3	119.6	120.5	116.4	
$T_{cc}$ (onset) (°C)	181.4				
$T_{cc}$ (peak) (°C)	197.3				
$\Delta H_{cc}$ per gram of blend (J/g)	34.4	0	0	0	0
$\Delta H_{cc}$ per gram of PEN (J/g)	34.4	0	0	0	0
$T_m$ (onset) (°C)	257.9	261.7	255.5	252.4	248.4
$T_m$ (peak) (°C)	268.4	270.2	266.7	262.6	261.6
$T_m$ (end) (°C)	272.3	272.9	270.2	266.1	265.6
$T_m$ span (°C)	14.4	11.7	14.7	13.7	17.2
$\Delta H_m$ per gram of blend (J/g)	40.3	32	28.6	22.5	12.8
$\Delta H_m$ per gram of PEN (J/g)	40.3	35.6	40.9	45.0	42.7
$C_i$ (%)	3.1	18.7	21.5	23.7	22.5
$T_c$ (onset) (°C)	222.9	241.4	234.3	226.0	209.0
$T_c$ (peak) (°C)	208.6	234.6	228.0	214.6	205.0
$T_c$ (end) (°C)	192.4	228.9	221.2	201.1	201.0
$\Delta H_c$ (J/g)	39.6	34.7	27.1	20.1	12.4
$\Delta H_c$ per gram of PEN (J/g)	39.6	38.6	38.7	40.2	41.3

<sup>a</sup> Samples were subjected to heat scan from 40 to 280°C at 10°C/min, maintained at 280°C for 2 min, then cooled to 40°C at 10°C/min.

<sup>b</sup>  $T_g$ , glass-transition temperature;  $T_{cc}$ , cold crystallization temperature;  $\Delta H_{cc}$ , heat of cold crystallization;  $T_m$ , melting temperature;  $\Delta H_m$ , heat of fusion;  $C_i$ , initial crystallinity;  $T_c$ , crystallization temperature;  $\Delta H_c$ , heat of crystallization.

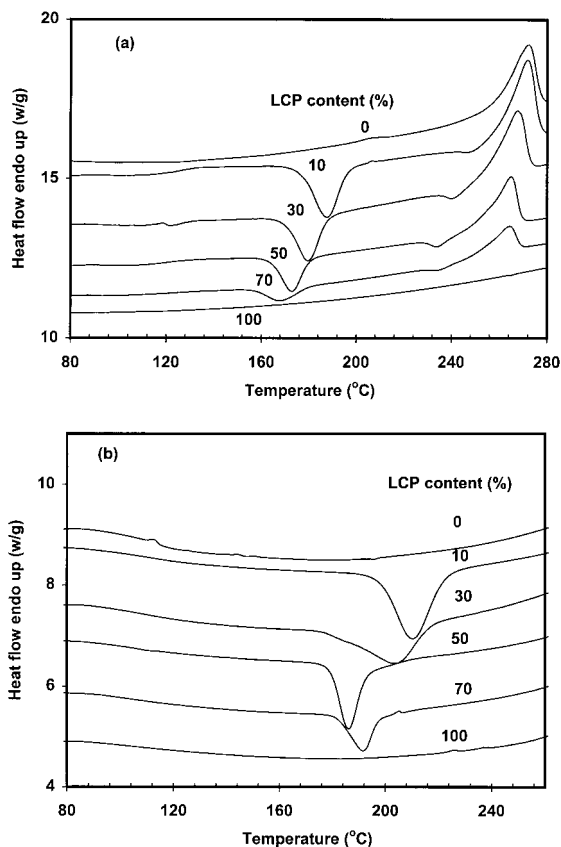
modulus below  $T_g$  for 70 wt % LCP blends is greater than that of the pure LCP. This indicates a significant blend synergism between LCP and PEN. Table II summarizes the  $T_g$  and the onset crystallization of PEN obtained from Figure 8. From the  $\tan \delta$  versus temperature curves, the peak temperature is taken as  $T_g$ . The peak  $\tan \delta$  decreases with the LCP content because of the addition of the rigid LCP molecules. The  $T_g$  of LCP is 80°C, with a peak  $\tan \delta$  of 0.067, whereas that of pure PEN is 1.84. For all blend compositions studied, the  $T_g$  of the LCP component is not detectable because of the insignificant loss tangent values of LCP component compared to that of PEN. From Figure 8(b) and Table II, we note that the  $T_g$  does not depend on the LCP content for blends of less than 30 wt % LCP. However,  $T_g$  decreases after 30 wt % LCP, suggesting that LCP and PEN phases are partially miscible.

Figure 9 compares the  $T_g$  of PEN obtained by DMA and the calculated values according to different models. The Fox equation<sup>42</sup> holds for a miscible blend pair:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (3)$$

where  $T_g$ ,  $T_{g1}$ , and  $T_{g2}$  are the  $T_g$ 's of the blend, component 1, and component 2, respectively;  $w_1$  and  $w_2$  are the weight fractions of components 1 and 2, respectively. However,  $T_g$ 's of the component polymer are independent of the composition for immiscible blends. Figure 9 indicates that, below 30 wt % LCP, LCP and PEN are immiscible but that above this LCP content, they are partially miscible. This accounts for the small  $T_m$  depression for 30 wt % LCP blends and more significant  $T_m$  depression and mechanical enhancement for the blends with higher LCP content.

Combining the results of DSC, DMA, and SEM, the interfacial property–morphology and mechanical property relationship in the LCP/PEN blends can be better understood. The decrease in the tensile strength for the blends at lower LCP content is attributed to the immiscibility and the poor interfacial adhesion between the phases. Therefore, tensile stress cannot be effectively transferred from the PEN matrix to the LCP phase. The modulus remains unchanged, however, because the modulus is defined as the derivative between the stress and the strain in the elastic region (at small strains). The increase in

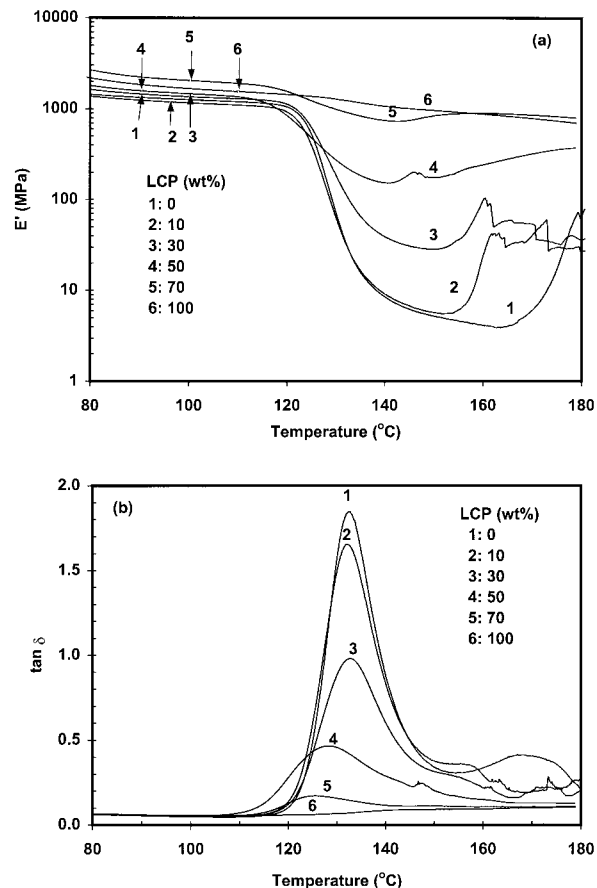


**Figure 7** DSC thermograms of LCP/PEN blends during the heat treatment: (a) heating from 40 to 280°C at 40°C/min, (b) cooling from 280 to 40°C at 40°C/min. The curves were shifted in the heat flow direction for better display.

the tensile strength and the modulus at higher LCP content is attributed to the improvement of the interfacial adhesion and better stress transfer from the matrix to the dispersed phase resulting from the transesterification reaction between LCP and PEN during melt blending and processing.

## CONCLUSIONS

Binary blends of a copolyester LCP PHB80–PET and PEN were melt blended and injection molded. The mechanical properties were studied as a function of LCP content. Both the ultimate tensile strength and Young's modulus exhibit higher values than those obtained by the rule of mixtures at 70 wt % LCP blends. However, the tensile strength decreases with LCP content and Young's modulus remains unchanged at lower LCP con-



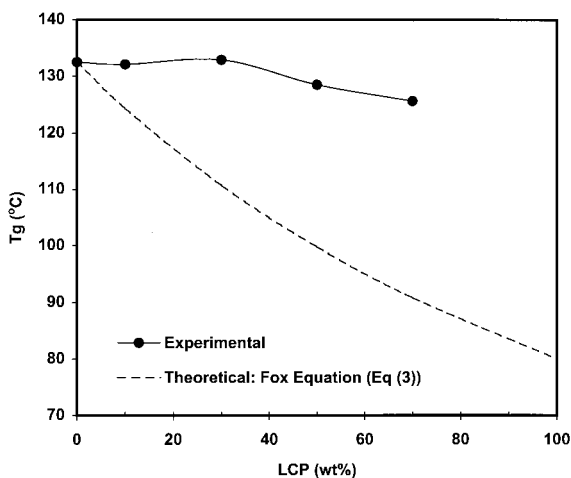
**Figure 8** Storage modulus  $E'$  (a) and loss tangent  $\tan \delta$  (b) versus temperature for the blends of LCP/PEN with various compositions, at a heating rate of 2°C/min and 1 Hz.

tent (10–30 wt %). SEM observation reveals a skin/core morphology in the tensile bars where the LCP phase is better oriented in the skin than in the core region. At lower LCP content, the LCP dispersed phase is spherical in the core and ellip-

**Table II**  $T_g$  and Peak  $\tan \delta$  of PEN Component in the Blends of LCP/PEN

	LCP (wt %)					
	0	10	30	50	70	100
$T_g$ (°C)	132.5	132.1	132.9	128.5	125.6	80 <sup>a</sup>
Onset	165.0	154.2	151.4	141.7	144.5	
$T_c$ (°C)						
Peak $\tan \delta$	1.84	1.64	0.98	0.46	0.17	0.067 <sup>a</sup>

<sup>a</sup> Data for  $T_g$  and  $\tan \delta$  of LCP component.



**Figure 9** Comparison between  $T_g$ 's of experimental data and calculated data in the case of miscible and immiscible blend pairs.

soidal in the skin and is oriented in the flow direction.

DSC study reveals that the crystallization rate is enhanced by the presence of LCP up to 50 wt %, where the LCP acts as a nucleating agent for PEN crystallization. The melting temperature decreases with LCP content, probably as a result of the less-perfect crystals formed in the presence of heterogeneous LCP nucleating centers and the increasing miscibility between LCP and PEN.

Both  $T_g$  and mechanical property–morphology correlation indicate the LCP and PEN are immiscible at lower LCP content (up to 30 wt % LCP), whereas they are partially miscible at higher LCP content because of the transesterification reaction between PEN and PET moiety in the LCP molecules. Hence, the mechanical properties of the blends are poor at lower LCP content. LCP fibril formation in the blend pair is also difficult. Therefore it is necessary to improve the interfacial adhesion and facilitate the LCP fibril formation to enhance the mechanical properties of PEN at lower LCP concentrations.

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