

Structures and Physical Properties of Poly(ethylene 2,6-naphthalate) / Liquid Crystalline Polymer Blends

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ABSTRACT: Poly(ethylene 2,6-naphthalate) (PEN) and liquid crystalline polymer (LCP) blend fibers were prepared by reactive extrusion. Structures and physical properties of PEN/LCP blends were investigated with respect to blend ratio and transesterification reaction. Orientation, modulus, and thermal expansion coefficient of the PEN/LCP blend fibers were improved by increasing the draw ratio. Interfacial adhesion between PEN and LCP phases was enhanced when the blends were processed with dibutyltindilaurate (DBTDL) as reactive catalyst to promote transesterification. Optimum amount of the reaction catalyst turned out to be about 500 ppm in 75/25 PEN/LCP blend systems. Enhanced compatibility between two immiscible polymers resulted in decrease of dissipation energy in interfacial region. Thus $\tan \delta$ value decreased. As a result of transesterification, density and reduction of thermal expansion coefficients of PEN/LCP blends increased by closer chain packing and higher interactions.

KEY WORDS Reactive Extrusion / Modulus / Thermal Expansion Coefficient / Orientation / Structure / Physical Properties /

Reinforcement of thermoplastics by blending thermotropic liquid crystalline polymers (LCPs) has been attempted.^{1–12} There are two major advantages of blending LCPs into engineering thermoplastics. First, blends with LCPs exhibit outstanding physical properties such as strength, modulus, thermal stability, dimensional stability, low dielectric constant, low coefficients of thermal expansion, and low moisture pick-up, etc.^{13–16} Secondly, LCPs in blends that possess rigid molecular structures in the main chain enhance high order under shear and/or tensile deformation process. LCPs easily deform during fiber spinning process and microfibrils come into existence during processing. These microfibrils in the blends behave as reinforcing elements because LCP exhibit higher strength and higher modulus compared with matrix polymers.^{13,14} Consequently a LCP blend is a sort of *in situ* composite. In a LCP blend system it is very important to control morphology and molecular orientation since they determine physical properties of the blends.^{17,18} Fibrillation of LCPs in thermoplastic melts under stress is influenced by miscibility between LCP and thermoplastics, LCP concentration, melt viscosity ratio of LCP against matrix polymer, and processing parameters such as processing temperature, flow mode, and shear rate.

Several methods to determine the morphology and orientation of thermoplastic LCP blends are reported. Blackwell *et al.* reported X-Ray diffraction experiment results where structures of drawn fibers of aromatic copolyesters based on *p*-hydroxybenzoic acid and 2,6-hydroxybenzoic acid are consistent with those made of

extended chains with completely random monomer sequence.^{19,20} Uzman *et al.* studied the orientation of side chain LCP blends with polycarbonate (PC) or poly(methyl methacrylate) (PMMA) *via* optical microscopy and scanning electron microscopy (SEM), X-Ray diffraction, and interfacial tension measurement.²¹ They found that, even in fiber-drawing, LCP droplets do not orient in the PC matrix, but in the PMMA matrix. The characteristic behavior of the blends is thus related to interfacial adhesion, phase separation, and distribution of the LCP in the blends.

Interfacial adhesion and compatibility enhancement in an *in situ* composite system are crucial for the improvement of physical properties of composite. Various methods have been developed to enhance interfacial adhesion and compatibility: introducing long flexible spacers^{22,23} or functional groups,^{24,25} reactive extrusion,^{29,30} block copolymerization,^{26–28} addition of a component having functional groups such as maleic anhydride group,³¹ and incorporation of a LCP miscible with matrix polymer, etc. Reactive extrusion may be one of the most effective method for the preparation of *in situ* composites. We investigated the effects of additives and compatibilizers on the physical properties of immiscible *in situ* composite systems.^{32–34} Our recent interests are expanded to application of *in situ* composites based on polyester fiber or polyester film. Polyester fibers with low thermal expansion coefficients are essential for application of automobile tire cord that requires high modulus and low shrinkage properties. Temperature of tires increases by heat build-up, when wearing and fric-

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tion occur during driving.^{35–38} It is thus important to reduce the thermal expansion coefficient of fibers in order to minimize thermal stress in the rubber-fiber composite system. Thermal expansion properties of oriented PEN/LCP fibers have not yet been examined in detail. The PEN/LCP blend system investigated in this study is of particular interest, because it was found to display good dimensional stability and mechanical properties from room temperature to the application temperature for automobile tire cord. This blend can be prepared by transesterification between ester^{33,39} or other chemical reactions.^{29,30} Previous paper reported that compatibility between poly(ethylene 2,6-naphthalate) (PEN) and LCP is improved when dibutyltin dilaurate (DBTDL) is used as transesterification catalyst.³⁴

This study investigates the structures and physical properties of immiscible ternary PEN/LCP/DBTDL blend fibers prepared by reactive extrusion. Molecular orientation of the blend fibers and roles of the reactive catalyst were related with mechanical properties, density, thermal expansion coefficient, etc.

EXPERIMENTAL

Materials

LCP used as a reinforcement agent was supplied from Unitica Co. under the trade name of LC 5000. LCP is a copolyester of 80 mol% *p*-hydroxybenzoic acid (PHB) and 20 mol% poly(ethylene terephthalate) (PET). PEN used as matrix polymer was kindly supplied from Mitsubishi Co. PEN has a melting temperature of 270°C and inherent viscosity of 0.61 dL g⁻¹ in phenol/tetrachloroethane 60/40 mixture by weight at a concentration of 0.25 dL g⁻¹ at 25°C. DBTDL purchased from Aldrich Chemical Co. was used as reactive catalyst for immiscible PEN and LCP blend.

Preparation of Blend Fibers

PEN and LC 5000 pellets were dried in a forced convection oven at 120°C for 24 h before compounding. LCP content of PEN/LCP blends was varied as 1.5, 3, 5, 10, and 25 wt%, respectively. The ratio of DBTDL to total weight of resins was 500 and 1000 ppm.

The formulated components were compounded using a Brabender twin-screw extruder at 290°C and at 30 rpm, while the hopper was purged with nitrogen gas. Spinning experiments were carried out using a Rosand Capillary rheometer (model RH 7-2). Capillary radius and length were 1 mm and 16 mm, respectively. The strand leaving the die exit was directly quenched in air and drawn with a take-up machine. Draw ratio of the blend fibers was controlled by take-up speed in the melt spinning. Draw ratio of the fibers was determined by dividing the capillary diameter (*D*) by the diameter of as-spun fiber (*D*₀) [*D*/*D*₀].

Measurements of Physical Properties

Thermal properties were investigated by Du Pont Thermal Analyzer Differential Scanning Calorimeter (DSC) 2100. Heating and cooling rates were 10°C min⁻¹.

Dynamic mechanical analysis (DMA) of the PEN/LCP blends was carried out with Dynamic Mechanical Thermal Analyzer MK III (Rheometric Scientific Co, UK) in

bending mode. Rectangular-shaped samples for DMA measurements were prepared using a minimax molder model CS-183 MMX (CSI Co.) at 290°C. Measurement was performed at the heating rate of 5°C min⁻¹ in the temperature range of 50°C and 200°C at the frequency of 1 Hz.

Thermal expansion coefficients of the samples were measured by Du Pont made thermomechanical analyzer (TMA) model 2190 in the temperature from 30°C to 150°C with a heating rate of 5°C min⁻¹ by applying fiber-tensile method.

Density of the PEN/LCP blend fibers was measured by a density gradient column made from liquids of carbon tetrachloride and heptane, of densities of 0.608 and 1.680 g cc⁻¹, respectively. The column was calibrated using a set of beads of known density at 25°C. Density of PEN/LCP blends was taken from average value of at least three samples.

Tensile test was performed at room temperature with an Instron universal tensile tester model 4201. Gauge length and crosshead speed were 30 mm and 5 mm min⁻¹, respectively.

Wide angle X-Ray diffraction (WAXD) experiments at room temperature were carried out using a MAC Science (SRA M 18 XHF) diffractometer with a copper X-Ray source, at 40 KV and 200 mA. The scanning angle (2θ) was 5–40°, and scanning rate 5° min⁻¹ with a step increment of 0.02°.

RESULTS AND DISCUSSION

Thermal Behaviors

Thermal study was performed using DSC for the PEN/LCP blend fibers with draw ratios of 10 and 20. Table I shows the heat of fusion and heat of crystallization of PEN/LCP blend fibers and these values are normalized with respect to LCP content. Heat of fusion of the blends shows a maximum at around 10 wt% of LCP irrespective of draw ratio and decreases with increasing LCP content. Crystallinity, *X*_c was calculated from the simple relationship, *X*_c = *H*_m/*H*_m⁰, where *H*_m⁰ is the heat of fusion calculated for 100% crystalline PEN (= 190 J g⁻¹) and *H*_m is the heat of fusion of crystalline PEN.⁴⁰ It should be noted that the crystallinity calculated in this way is an apparent value.⁴¹ Crystallinity of the blend showed a maximum at 10 wt% of LCP and then decreased at higher LCP content, due to the increase in the mobility of PEN matrix in the blend system, sometimes reported for other crystalline/amorphous blend systems.⁴⁰

At a draw ratio of 20, PEN shows a cold crystallization temperature (*T*_c) peak at 198.8°C and a cold crystallization enthalpy of 35.10 J g⁻¹. Crystallization enthalpy was normalized by PEN. *T*_c shifts downward to 175.0°C when 5 wt% LCP is added, and crystallization enthalpy is reduced to 31.32 J g⁻¹. *T*_c shift occurred more for the blend with 10 wt% LCP. At this content of LCP, transition of *T*_c has a similar tendency with heat of fusion and crystallinity.

Crystallization behavior of the PEN/LCP blends is related to the fact that LCPs can play a role of nucleating agents as reported for other blend systems.⁴² As previously described,^{13,14} LCP microfibrils produced during fi-

Table I. Thermal Properties of PEN/LCP Blend Fibers

PEN/LCP	Draw ratio	T_{cc}	ΔH_{cc}	ΔH_{cc}^*	T_m	ΔH_m	ΔH_m^*	X_c
		°C	J g ⁻¹	J g ⁻¹	°C	J g ⁻¹	J g ⁻¹	
100/0	10	196.5	39.1	39.1	267	40.2	40.2	21.1
	20	198.8	35.1	35.1	267	39.0	39.0	20.5
95/5	10	176.3	30.1	31.7	267	41.7	43.9	23.1
	20	175.0	29.7	31.3	266	39.0	41.0	21.6
90/10	10	174.7	28.5	31.6	266	42.1	46.8	24.6
	20	174.5	27.5	30.5	266	42.2	46.9	24.2
75/25	10	171.8	23.2	30.9	266	32.2	42.9	22.6
	20	174.1	22.2	29.6	266	31.5	42.0	22.1

T_g : Glass transition temperature. T_{cc} : Cold crystallization temperature. ΔH_{cc} : Heat of cold crystallization of the blends. ΔH_{cc}^* : Heat of cold crystallization based on the mass of PEN in the blends. T_m : Melting temperature. ΔH_m : Heat of fusion of the blends. ΔH_m^* : Heat of fusion based on the mass of PEN in the blends. X_c : Crystallinity.

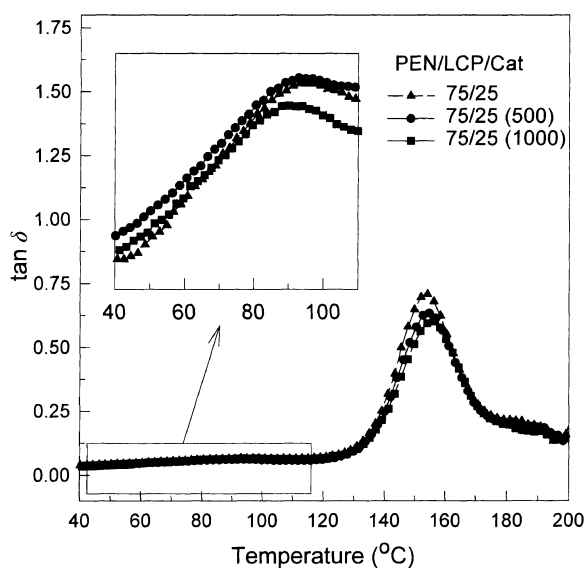


Figure 1. $\tan \delta$ curves of 75/25 PEN/LCP blends as function of catalyst content.

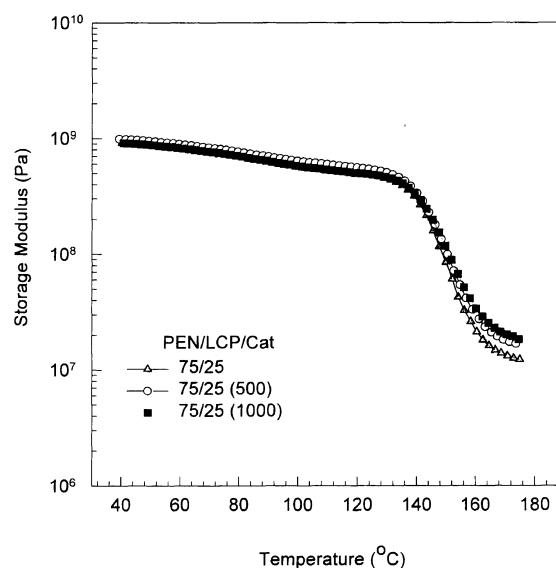


Figure 2. Storage modulus (E') of 75/25 PEN/LCP blend as function of catalyst content.

ber spinning possess large surface areas, thus the oriented crystalline LCP fibrils are effectively stimulated to grow crystalline spherulites of PEN matrix polymer.

Dynamic Mechanical Behaviors

Compatibility and phase separation properties of polymer blends can be inferred from analysis of thermomechanical behavior. To investigate phase transition of PEN/LCP blends, DMA was performed at 40°C to 200°C. Figure 1 shows $\tan \delta$ curves near glass transition temperature (T_g) of 75/25 PEN/LCP blend as a function of DBTDL catalyst content. The two peaks of $\tan \delta$ in this figure correspond to the characteristics of two immiscible phase systems.^{40,43} Peaks appearing at around 99°C and 154°C correspond to T_g of LCP and PEN rich phases, respectively.⁴² The values of $\tan \delta$ decrease with increasing catalyst content. This implies that transesterification between PEN and LCP occurs more by the addition of reaction catalyst. Enhancement of compatibility between two immiscible PEN/LCP blends by transesterification results in decrease of energy dissipation in interfacial region, and $\tan \delta$ value thus decreases.

Figure 2 shows storage modulus of 75/25 PEN/LCP blend as function of catalyst contents. 75/25 PEN/LCP blend containing 500 ppm reaction catalyst DBTDL

showed higher storage modulus than the blends containing 0 or 1000 ppm catalyst. The extent of increase is, however, relatively small. The increase of storage modulus may be related to enhanced interfacial adhesion between two immiscible polymers.

Thermomechanical Behaviors

Dimensional stability of PEN/LCP blend fibers was determined from linear thermal expansion coefficients. Figure 3 shows the effects of draw ratio on the thermal expansion coefficients of PEN/LCP blend fibers at various LCP content. Thermal expansion coefficients of PEN/LCP blend fibers are affected significantly by the draw ratio, which has close relationships to the orientation of micro fibrils in PEN/LCP blend fibers. Rigid fibrils of LCP in the PEN/LCP blends easily orient under tensile or shear deformation. In addition, thermal expansion coefficients of the PEN/LCP blend fibers decreased with increasing LCP content. The thermal expansion coefficient of LCP is relatively low compared with other organic materials. In some cases, oriented LCP fibers or films often show negative thermal expansion coefficients. So in this PEN/LCP blend system, the thermal expansion coefficient of a blend fiber decreased with increasing LCP content. Reduction of thermal ex-

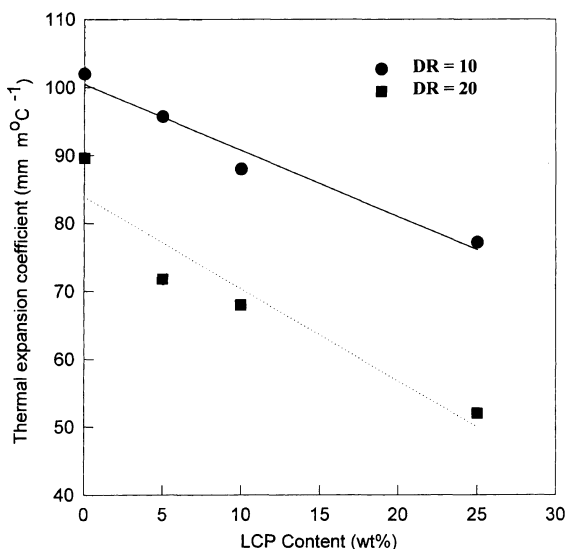


Figure 3. Effects of the draw ratio on the thermal expansion coefficient of PEN/LCP blend fibers at various LCP content.

Table II. Tensile modulus of PEN/LCP Blend Fibers

PEN/LCP	Tensile modulus (kg, mm^{-2})	
	Draw ratio = 10	Draw ratio = 20
100/0	238	250
98.5/1.5	248	285
97/3	256	298
95/5	260	299
90/10	275	358
75/25	311	441

pansion coefficient by the addition of LCP is related to decrease in noncrystalline part of LCP phase. Similar results were reported by Hong *et al.* for biaxially oriented liquid crystalline polyester films.⁴⁴

Table II summarizes the tensile modulus of PEN/LCP blend fibers at various LCP content. As previously described, tensile modulus increases with LCP content. This is related to the improved orientation of matrix polymer by oriented LCP molecules. LCPs with rigid molecules orient easily in the melt state by an external field. LCP blends processed in the liquid crystalline state exhibit excellent mechanical properties in the direction of orientation. PEN/LCP blend systems can be regarded as *in situ* composites, since LCP microfibrils in the blends behave like reinforcing agents. Enhanced mechanical properties are thus obtained by incorporation of LCP in the blend system.

In Figure 4 modulus of the PEN/LCP blend fibers at draw ratios of 10 and 20 is plotted against thermal expansion coefficients. Interestingly, PEN/LCP blend fibers with low thermal expansion coefficients show high modulus in this figure. Highly crystalline and well oriented samples normally show greater tensile modulus. A low thermal expansion coefficient is expected from the samples with this rigid structure. The degree of orientation and modulus increases with the draw ratio, and hence the thermal expansion coefficient decreases.^{43,44}

Figure 5 shows the effects of DBTDL transesterification catalyst on the thermal expansion coefficient for 75/25 PEN/LCP blend fibers at draw ratios of 10 and 20.

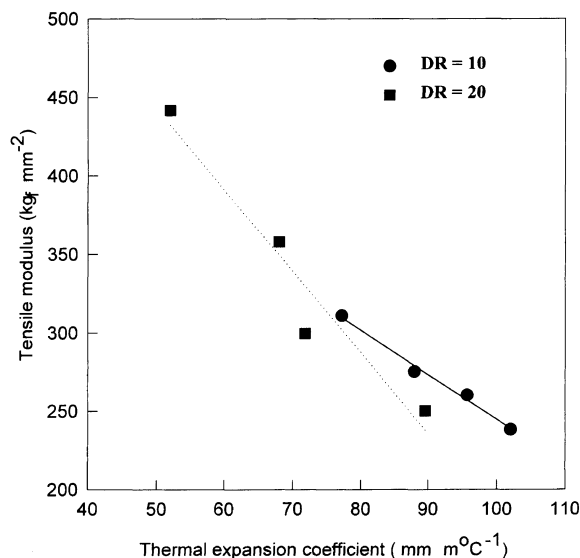


Figure 4. Relationships between tensile modulus and thermal expansion coefficients of PEN/LCP blend fibers at draw ratios of 10 and 20.

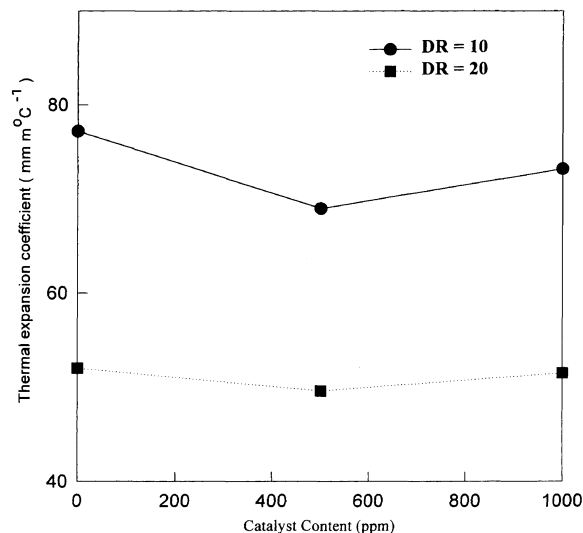


Figure 5. Effects of catalyst content on the thermal expansion coefficient of 75/25 PEN/LCP blend fibers at draw ratios of 10 and 20.

Addition of DBTDL in the blends slightly decreased thermal expansion coefficient of the blends at the particular content of 500 ppm. The optimum amount of DBTDL is about 500 ppm, as seen from thermal expansion coefficient behavior. It was found by morphological study in our previous paper that interfacial adhesion between PEN and LCP phases and melt strength are enhanced by the addition of DBTDL.³⁴ PEN molecules reacted with LCP by the transesterification catalyst DBTDL show lower thermal expansion coefficient since PEN molecules reacted with LCP easily orient on stretching. This suggests that improved interfacial adhesion in an immiscible polymer blend system containing LCP by reactive extrusion with very short residence time. It is essential to control the amount of reactive catalyst. When transesterification between PEN and LCP occurs too much by the addition of excess catalyst, no good adhesion is obtained as in the case of 1000 ppm

catalyst content in Figure 5. Use of excess catalyst may give rise to reduction of molecular weight, which deteriorates the physical properties of PEN/LCP blends.³⁹

Molecular Orientation

Figure 6 shows wide angle X-Ray diffraction patterns of PEN/LCP blend fibers as a function of LCP content. There are two distinct diffraction peaks at 19.6° and 21.6° in this Figure. The first reflection appearing at around 19.6° corresponds to the 110 reflection of LCP phase. The second reflection appearing at around 21.6° originates from the mesophase of PEN.⁴⁵ As the amount of LCP in the PEN/LCP blends increases, the intensity of the 110 reflection appearing at 19.6° increases. The mesophase was first reported by Jakeways *et al.* from quenched melt spun fibers, which has one dimensional order along the fiber direction.⁴⁵ The mesophase is quite stable not to change the intensity of reflection when fibers are annealed at 180°C for 30 min. Reflection of the

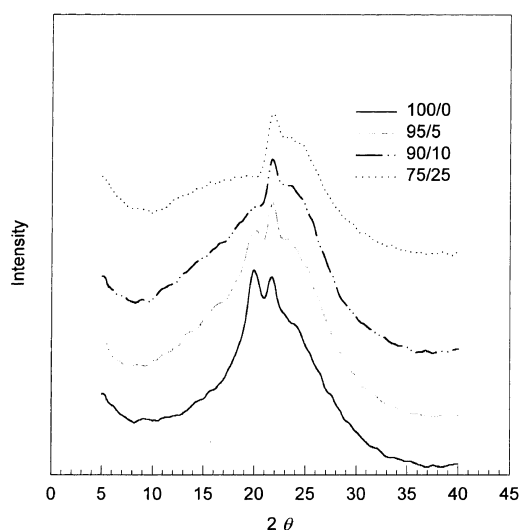


Figure 6. Wide angle X-Ray diffraction (WAXD) patterns of PEN/LCP blend fibers as function of LCP content at a draw ratio of 20.

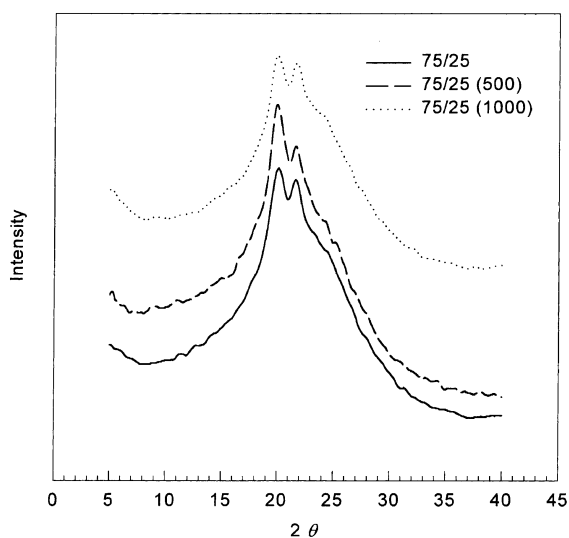


Figure 7. Wide angle X-Ray diffraction (WAXD) patterns of 75/25 PEN/LCP blend fibers as function of catalyst content.

mesophase that might show the average distance of molecules changes easily to the crystalline reflection after crystals are grown by heat treatment. PEN has two crystal modifications, and the crystal system changes depending on annealing temperature.^{46,47}

X-Ray diffractometer scans of 75/25 PEN/LCP blend fibers containing the reactive catalyst of DBTDL at the concentration of 0, 500, and 1000 ppm are shown in Figure 7. Crystallite size is evaluated by the broadness of reflection. The peak of the blend fiber with 500 ppm catalyst is a little narrow compared with other samples. This means that blend fibers processed with 500 ppm catalyst may have higher crystallinity and the crystallite size of the reacted blend is larger than that of the unreacted blend system, due to enhanced ordering resulting from the dense chain packing by reactive extrusion with addition of reactive catalyst. This is consistent with density measurements, as shown in Figures 8 and 9. The blend fiber processed with 1000 ppm catalyst is

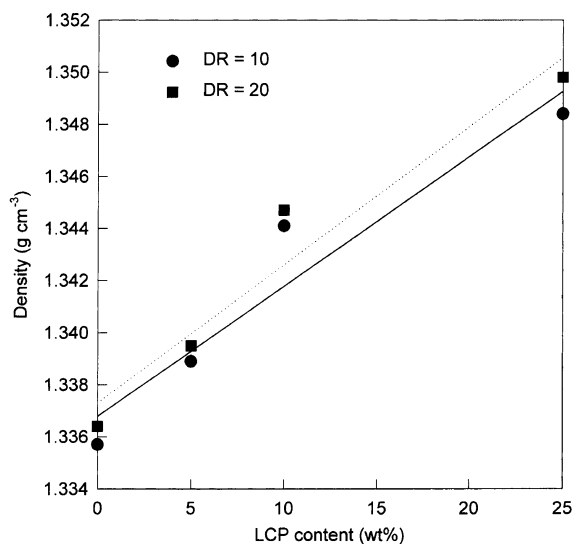


Figure 8. Variation of density of PEN/LCP blend fibers at various LCP content at draw ratios of 10 and 20.

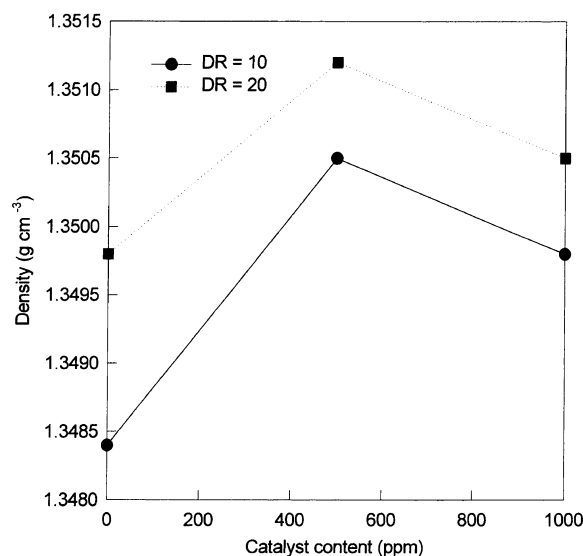


Figure 9. Variation of density for 75/25 PEN/LCP blend fibers at various catalyst content at draw ratios of 10 and 20.

broad compared with other samples. Transesterification might occur excessively by a large amount of catalyst, which gives adverse effect to the sample. Large crystals can not be grown from molecules containing large amount of defects by excess transesterification. These results demonstrate that use of an appropriate amount of transesterification catalyst is essential for better orientation and higher crystallinity in this blend system. The physical properties of PEN/LCP blends such as crystallization enthalpy, crystallinity, modulus, $\tan \delta$, and thermal expansion coefficients are consistent with the results of the X-Ray diffraction experiment.

Density Analysis

Figure 8 shows variation of density of PEN/LCP blend fibers at draw ratios of 10 and 20 as a function of LCP content. The density of PEN/LCP blend fibers as well as modulus of the blends is influenced significantly by the draw ratio and LCP content. The tendency of density variation is the same as that of crystallinity as shown in Table I, because the two parameters are directly related to each other.

Transesterification may change the density of the PEN/LCP blend fibers. Figure 9 shows variation of density for 75/25 PEN/LCP blend fibers at various catalyst content at draw ratios of 10 and 20. By addition of DBTDL the density of 75/25 PEN/LCP blend fibers slightly increased at a content of 500 ppm. Transesterification enhances interfacial adhesion between PEN and LCP phases and increases closer dense chain packing and higher interactions. Density measurements were coincident with thermomechanical measurements and X-Ray diffraction study.

CONCLUSIONS

PEN was blended with LCP and melt spun fibers of the blends were prepared. Interfacial adhesion in the PEN/LCP blend system was improved by introducing transesterification reaction. A reactive catalyst DBTDL effectively promotes transesterification, which was added in the compounding step before fiber spinning. The optimum amount of catalyst was 500 ppm in the PEN/LCP blend system. When the reactive catalyst was used excessively, amorphous region increased and physical properties of the blends deteriorated. X-Ray diffraction study of the melt spun fibers showed that PEN exhibits a mesophase rather than crystalline structure. This is in accordance with the study of Jakeways.⁴⁵ We understand that the PEN/LCP system is a sort of *in situ* composite. Introducing LCP domains into PEN matrix polymer improves modulus, thermal expansion coefficient, and density.

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