Studies on the Ternary Blends of Liquid Crystalline Polymer and Polyesters

Seong Hun Kim* and Seong Wook Kang

Department of Fiber & Polymer Engineering, Center for Advanced Functional Polymers,
Hanyang University, Seoul 133-791, Korea

Abstract: Thermotropic liquid crystalline polymer made up of poly(*p*-hydroxybenzoate) (PHB)-poly(ethylene terephthalate) (PET) 8/2 copolyester, poly(ethylene 2,6-naphthalate) (PEN) and PET were mechanically blended to pursue the liquid crystalline phase of ternary blends. Complex viscosities of blends decreased with increasing temperature and PHB content. DSC thermal analysis indicated that glass transition temperature (*Tg*) and melting temperature (*Tm*) of blends increased with increasing PHB content. Both tensile strength and initial modulus increased with raising PHB content and take-up speed of monofilaments. In the WAXS diagram, only PEN crystal reflection at $2\Theta = 15.5°$ appeared but PET crystal reflection was not shown in all compositions. The degree of transesterification and randomness of blends increased with blending time but sequential length of both PEN and PET segment decreased.

Keywords: Liquid crystal polymer, Fiber spinning, Mechanical property, Polyethylene naphthalate

Introduction

Blends of thermotropic liquid crystalline polymers (TLCPs) and engineering plastics have been studied extensively in recent years[1-5]. Their major advantage is the possibility of the inclusion of a rigid rod polymer in an isotropic matrix for forming *in situ* composites. In general, LCP rigid rod nature and the LC order often result in favorable properties such as low melt viscosity, low die swell, excellent mechanical properties in the flow direction, low thermal expansion coefficient, good solvent resistance, and high barrier properties[6-16]. However, exclusive use of LCP causes problems such as high degree of anisotropy in molded parts and relatively high production cost compared to the commodity polymers. Therefore, blending of LCP with polymers can be effective means for improving properties of target products and reducing cost. TLCPs are very useful additives to thermoplastic materials because their addition may lead to low melt viscosity of blended articles, which may be important where the thermoplastic material is highly viscous. Melt viscosity of LCP is lower than that of the matrix, and some degrees of elongational flow will appear. The minor composition of LCP may produce fibrils and reduce melt viscosity of blends. There will also be slight increment in moduli of blends owing to the reinforcing effect of fibrils. However, in general, when a rigid rod polymer and a flexible polymer are simply mixed together, the blended polymer becomes immiscible, which is not favorable in terms of thermodynamics. Reactive extrusion may provide a useful way to improve physical properties, and miscibility between LCP and thermoplastic polymer.

In the following thermodynamics of polymer blends, the homogeneity of polymer blends is known to depend on the compatibility or the molecular interaction between two polymers. The degree of interaction between two polymers is best described by the free energy of mixing, ΔG, which contains enthalpy (ΔH) and entropy (ΔS) contributions. When a blend is to show a single phase, the necessary condition ought to be $\Delta G < 0$. Since the entropy terms are usually small, the enthalpy terms dominate the free energy of mixing in polymer blends. Introduction of interacting groups by chemical modification of a polymer or by copolymerization can result in negative contribution to the enthalpy for the mixture. The enthalpy for the mixture of LCP with engineering plastics is usually positive. Consequently, phase separation of the LCP blend occurs during processing where high stress and temperature exist.

In recent years, much interest in thermotropic liquid crystalline copolyesters has grown[17]. Binary copolyesters of poly(*p*-hydroxybenzoate) (PHB)/poly(ethylene terephthalate) (PET), PHB/poly(ethylene 2,6-naphthalate) (PEN), and ternary copolyester of PHB/PEN/PET that are able to form TLCP melts have been synthesized and studied by many researchers[18-21]. Those investigations reveal the followings: first, ternary copolyesters containing 30 mol% PHB are partially LC, and those containing over 50 mol% PHB are completely LC. Second, in the copolyesters containing up to 50 mol% PHB, both PET and PEN crystals are formed. Third, ternary copolyester of PHB/PEN/PET (30/35/35) is in LC phase up to 160°C where it gradually starts to become isotropic, and is completely isotropic at 290°C.

In this research, commercially available PHB/PET copolyester LCP, PEN, and PET are melt blended to pursue LC phase of blended articles. Critical PHB composition necessary to show LC behavior in ternary blends is investigated, and miscibility and thermal behavior are studied by thermal analysis. PHB content in the ternary blend is controlled by regulating the amount of PHB/PET copolyester because PHB homopolymer with high molecular weight finds no melting temperature at 482~538°C, where it

decomposes rapidly[22]. In addition, relationship between mechanical property and morphology of ternary blends of different PHB contents is observed by SEM using melt spun monofilament. Furthermore, as transesterification reaction occurs during melt blending, degree of transesterification with various compositions and melt blending time is investigated by probabilistic analysis of NMR spectrum. Transesterification reaction can be readily facilitated with the following possibilities. It can open a new method to miscible blend and preparation of copolymer with high degree of randomness, and lead to more uniform polymer by minimizing molecular fluctuations in the melt during processing. Exchange reaction in the polymer blends depends strongly on their initial compatibility and blending conditions. These include temperature, preparation method, melt viscosity ratio, and presence of catalysts as well as inhibitors. As transesterification reaction continues, the blends are first converted into block copolymers and, finally, become random copolymers. When the blends are in the form of random copolymers, benefit of adding LCP to the matrix polymer will be lost. To have some transesterification reaction between the liquid crystalline copolyester and the matrix polymers without losing the liquid crystalline characteristics becomes an important research objective.

Experimental

Materials

Thermotropic liquid crystalline polymer used in this research was a copolyester, which was synthesized with the composition of 80 mol% PHB and 20 mol% PET in Unitika Co., Japan. The trade name of LCP is Rodrun 5000, hereafter poly(HB/ET) (8/2) LCP. The PEN with an intrinsic viscosity of 0.51 dl/g was supplied by courtesy of Kolon Co. in Korea. The PET with an intrinsic viscosity of 0.64 dl/g was prepared by courtesy of Samyang Co. in Korea. Both PEN and PET were used as matrix for preparing a reinforcing LCP composite, and they were expected to increase compatibility of blends by transesterification reaction among ester groups in each polymer. The pellets of TLCP, PEN, and PET were dried in the oven at 120°C for 24 hrs to minimize moisture effects before they are used.

Preparation of the Blends

The materials with various compositions were blended at 285°C using Haake Rheomix 600 at 60 rpm for 5 min, then blends were extracted and ground to powder for thermal measurements and film preparation. Homopolymers of PEN, PET, and LCP were handled in the same way to let them ensure similar melt and thermal histories. PHB/PEN/PET blends were prepared to allow investigation of miscibility as well as LC phase behavior in ternary blends whose composition is as follows; 0/0/100, 0/100/0, 10/45/45, 20/40/40, 30/35/35, 40/30/30, 50/25/25, 60/20/20, 70/15/15,

Table 1. Processing conditions for monofilament spinning

Composition of PHB/PEN/PET (mol%)	Heating zone temperature (°C)	Screw rotation speed (rpm)	Take-up speed (m/min)
10/45/45	260, 280, 295, 290	20, 30	500, 1000
20/40/40	260, 280, 295, 290	20, 30	500, 1000
30/35/35	260, 280, 295, 290	20, 30	500, 1000
40/30/30	260, 280, 295, 290	20, 30	500, 1000

and 80/0/20, respectively, by weight fraction. In addition, samples for the NMR experiments were blended at 285°C with various blending times from 5 to 20 min.

Melt blending to make pellets was carried out in a Brabender twin-screw extruder at 290°C under constant rotating speed of 22 rpm. PHB content in the ternary blends were diversified from 10 mol% to 40 mol%, and each PEN and PET component was used exactly the same mol%. To exclude possible degradation of the macro-molecular chains by hydrolysis, the extruded pellets were dried in the oven at 120°C for at least 24 hrs before processing.

Melt spinning was done using a Haake Rheomex 252 single-screw extruder equipped with a 1.0 mm capillary die (L/D 30). The monofilament is air cooled, and the detailed processing conditions of Haake for monofilament spinning are listed in Table 1.

Characterization

Rheological properties of PHB/PEN/PET blends were investigated by Advanced Rheometric Expansion system (ARES) under a nitrogen atmosphere. The gap between 25 mm diameter parallel plates was at least 1 mm, and applied strain was 10%. Frequency and temperature sweep test were performed. Thermal analysis of blends was carried out with Perkin-Elmer DSC-7. The samples were preheated to 260, 280 or 300°C at the rate of 200°C/min, and held for 2 min then cooled to 0°C at the rate of 200°C/min. The DSC measurements of blends after preheating were performed from 40 to 300°C at the scanning rate of 10°C/min. Tensile tests of monofilament of blends were performed using an UTM 10E (United Calibration Co.) equipped with fiber grips at a room temperature. Cross-head speed of 20 mm/min, gauge length of 20 mm, and load cell of 10 N were used. Morphologies of fracture surface and LCP fibrils of monofilament were observed using a SX-30E SEM (Topcon Co.). LCP fibrils of monofilament were obtained by dissolving matrix polymers in 2-chlorophenol at 55°C. In addition, LC phase behavior of blends was investigated using Polarized Optical Microscope equipped with hot stage. Wide-angle X-ray diffraction (WAXD) experiments for crystallization behavior were conducted using a Rigaku Denki X-ray generator with a 12 kW rotating anode. The samples were prepared in a hot press at 290°C and immediately thrown into water to obtain the quenched films. The quenched films were annealed in the oven at 160 or

220°C for 30 min for crystallization. X-ray crystallinity determination of the films was carried out by subtraction of the background, which corresponds to the WAXD patterns of the amorphous region obtained from the quenched films. ^{1}H-NMR measurements were performed at 23°C using Jeol 300 MHz FT-NMR spectrometer. The samples for the NMR experiments were prepared by dissolving the blends in deuterated trifluoroacetic acid (TFA-d) and then solution was filtered through glass syringe equipped with filter holder.

Results and Discussion

Rheology

Rheological properties of ternary blends are shown in Figures 1 and 2. Complex viscosities of blends decreased

with increasing temperature and PHB content, and for those of blends containing more than 40 mol% PHB content, it decreased abruptly at 290°C due to the characteristics of nematic transition of thermotropic liquid crystalline polymer. Slope of log G' versus log G" can be used to decide homogenity of the blend system. If the slope value is approaching to 2, and it means that the blend system is homogeneous blend. Slope of log G' versus log G" plot for this system, the slope value increased from 0.82 to 1.41 with increasing PHB content. Therefore, the blends containing more than 40 mol% PHB content show approximately homogeneous phase compared with the blends containing less than 30 mol% PHB content.

Thermal analysis

DSC thermograms of PHB/PEN/PET blends are shown in

Figure 1. Complex viscosity change with increasing temperature and PHB contents (ω: 10 rad/s, strain: 25%).
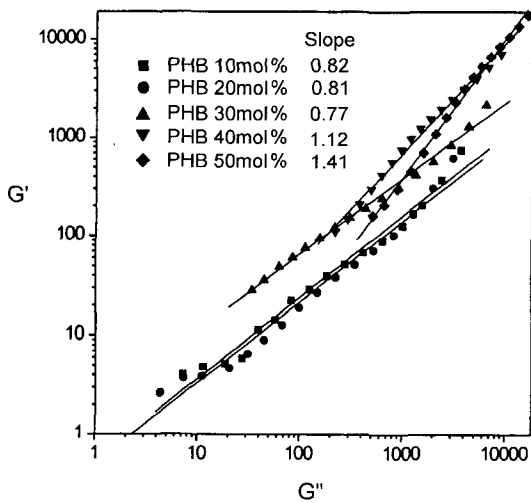
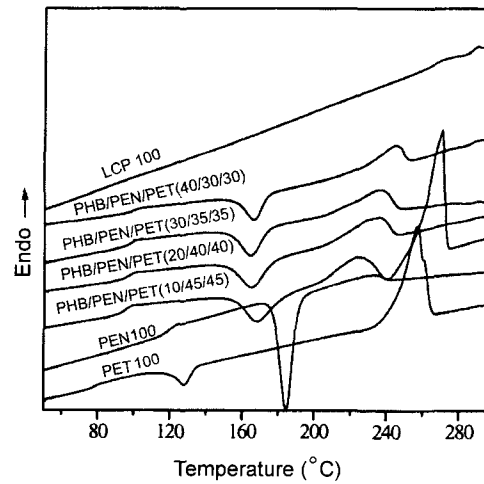**Figure 2.** Log G' vs log G" plot of PHB/PEN/PET blends at 290°C.

Figure 3. DSC thermograms of PHB/PEN/PET blends; heated to 280°C at the rate of 200°C/min and held for 2 min then cooled to 0°C; 2 nd heating rate of 10°C/min (mol%).
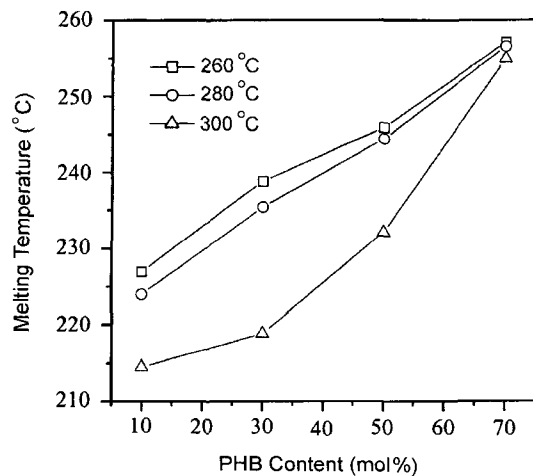

Figure 4. Effect of preheating temperatures and blend compositions on the melting temperatures for the PHB/PEN/PET blends.

Figure 3. All blends have single *Tg*, and it increases slightly with increasing PHB content. Moreover, melting temperatures of blends increased with increasing PHB content. The effect of preheating temperature on the melting temperature of blends is shown in Figure 4. The blends are preheated at 260, 280, and 300°C for 2 min, respectively. At 260°C only

Figure 5. Tensile strength, initial modulus and % Elongation of PHB/PEN/PET as-spun and annealed monofilaments (annealed at 160°C for 30 min).

the PET melts; at 280°C the PEN and PET portion melt ; at 300°C the system is in a completely isotropic state. As the preheating temperatures increased, melting temperatures decreased. PEN and PET crystal formation disturbed by adding of PHB liquid crystal polymer as well as transesterification reaction between PEN-PET, PHB-PEN, and PHB-PET.
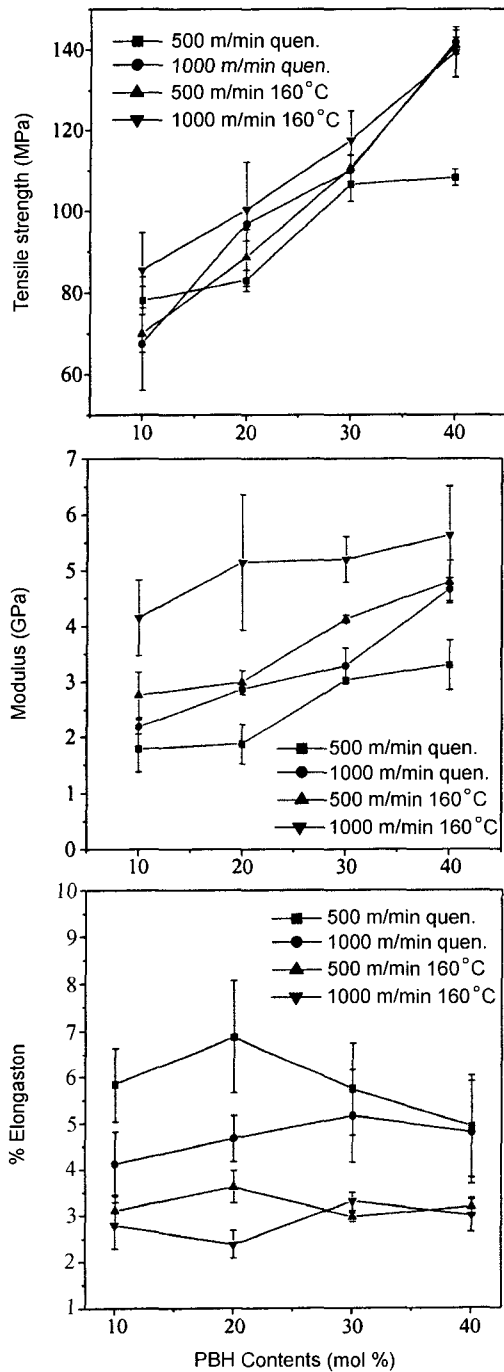
Mechanical properties

Mechanical properties of melt spun monofilaments are greatly affected by composition of blends and melt spinning condition as shown in Figure 5. Both tensile strength and initial modulus increased with enhancing PHB content and take-up speed for all compositions. Especially, when take-up speed is 500 m/min, initial modulus of monofilament increased greatly at 30 mol% PHB content. As take-up speed increased to 1000 m/min, initial modulus of monofilament increased greatly at 40 mol% PHB content. Those results are attributed to the formation of co-continuous LCP fibril structures that consist of long fibrils in the matrix polymers, which are confirmed by the morphological analysis below.

The effect of annealing temperature on the initial modulus is also presented in Figure 5. Moduli of annealed monofilaments at 160°C for 30 min are higher than those of normal monofilaments because matrix polymers are recrystallized at low PHB content and LCP molecules in domain are reoriented at high PHB content.

Morphology

Results of SEM micrographs of fractured surface and LCP fibrils of monofilaments are presented in Figures 6, 7, 8, and 9. At less than 20 mol% PHB content, micrographs of monofilaments that are wound up with the speed of 500 m/min show irregular cross-sectional area and shortly broken LCP fibrils (Figure 9). At more than 30 mol% PHB content, micrographs of monofilaments that are wound up with 500 m/min rate show fine and long LCP fibrils. At less than 30 mol% PHB content, micrographs of monofilaments with the winding speed of 1000 m/min show various diameters and mixture of short and long LCP fibrils. At 40 mol% PHB content, micrographs of monofilaments having 1000 m/min of winding rate show very fine and long LCP fibrils. Composite composed of fine and long LCP fibrils in the matrix polymers improves mechanical properties of monofilaments. Polarized optical photographs of blends are shown in Figure 10. The blend of 30 wt% PHB content shows partial liquid crystal phase and the blend of 40 wt% PHB content is considered to show liquid crystal phase.

Crystallization behavior

Information on the crystallization behavior is obtained by means of WAXS measurements. The quenched film can be considered to be amorphous. However, the crystallized film shows crystal reflections. The crystal reflections (2Θ) of
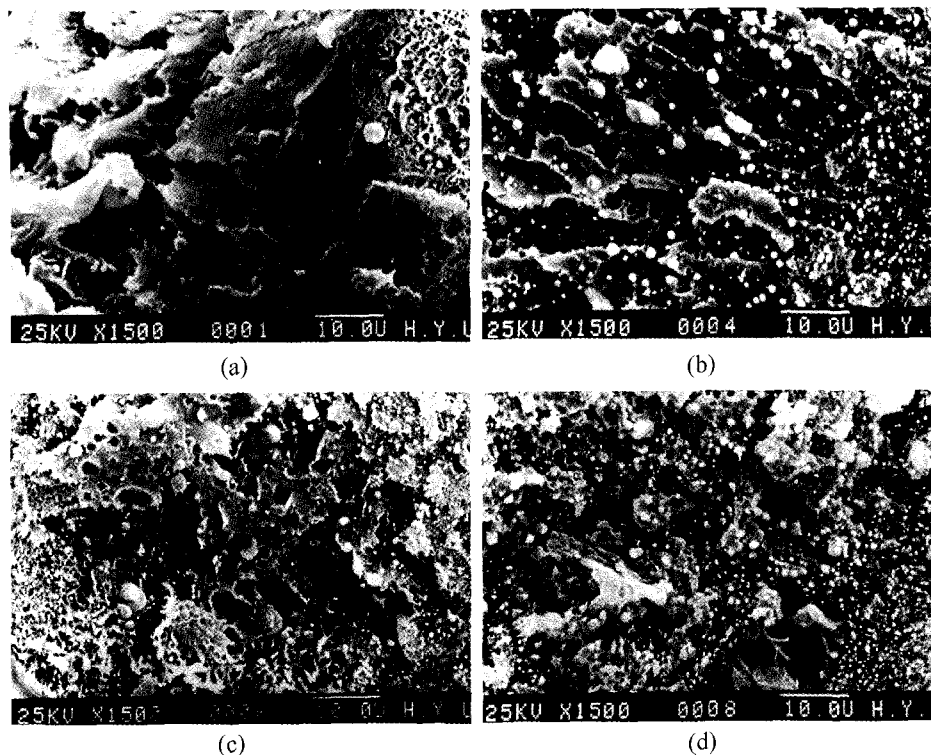
Figure 6. SEM micrographs of fracture surface of PHB/PEN/PET fibers (take up speed: 500 m/min): (a) 10/45/45; X1500, (b) 20/40/40; X1500, (c) 30/35/35; X1500, (d) 40/30/30; X1500.
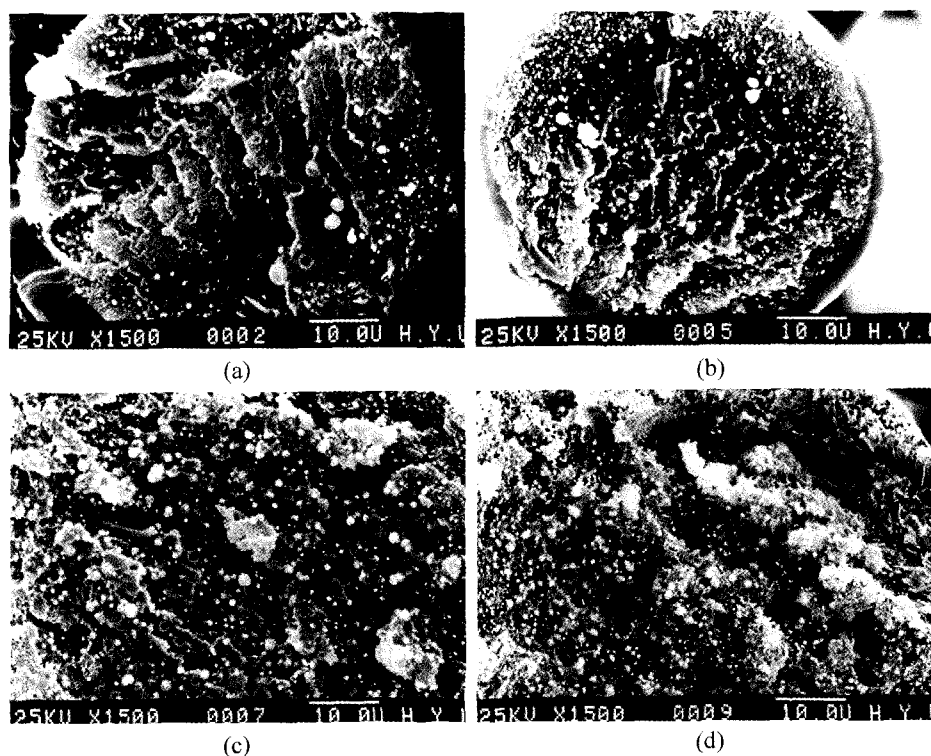

Figure 7. SEM micrographs of fracture surface of PHB/PEN/PET fibers (take up speed: 1000 m/min): (a) 10/45/45; X1500, (b) 20/40/40; X1500, (c) 30/35/35; X1500, (d) 40/30/30; X1500.
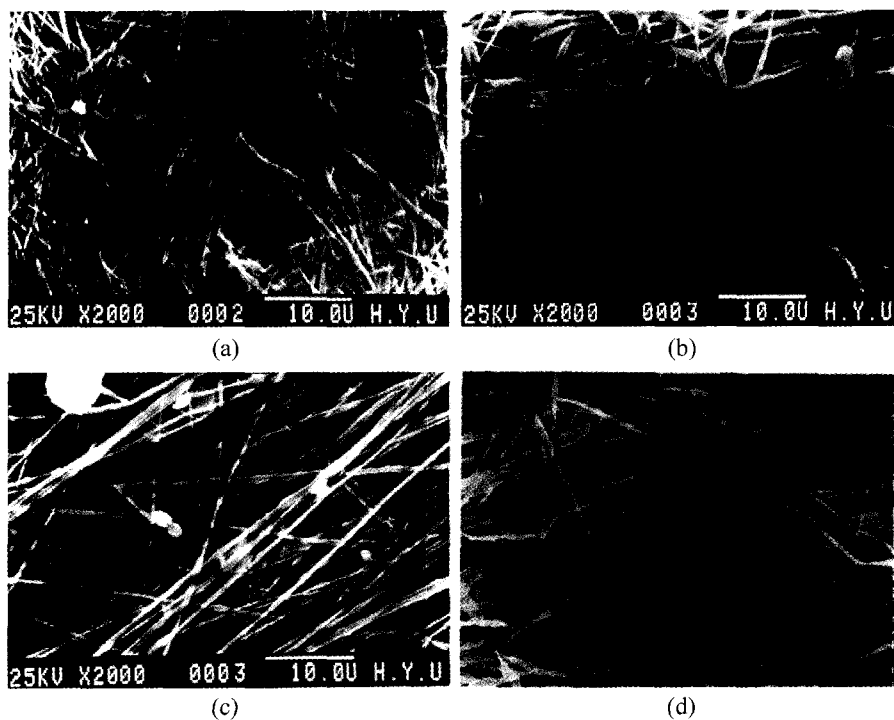
Figure 8. SEM micrographs of LCP fibrils prepared by dissolving PEN/PET in 2-chlorophenol at 55°C for 2 hours: (a) 10/45/45; winding speed 500 m/min; X2000, (b) 20/40/40; winding speed 500 m/min; X2000, (c) 30/35/35; winding speed 500 m/min; X2000, (d) 40/30/30; winding speed 500 m/min; X2000.
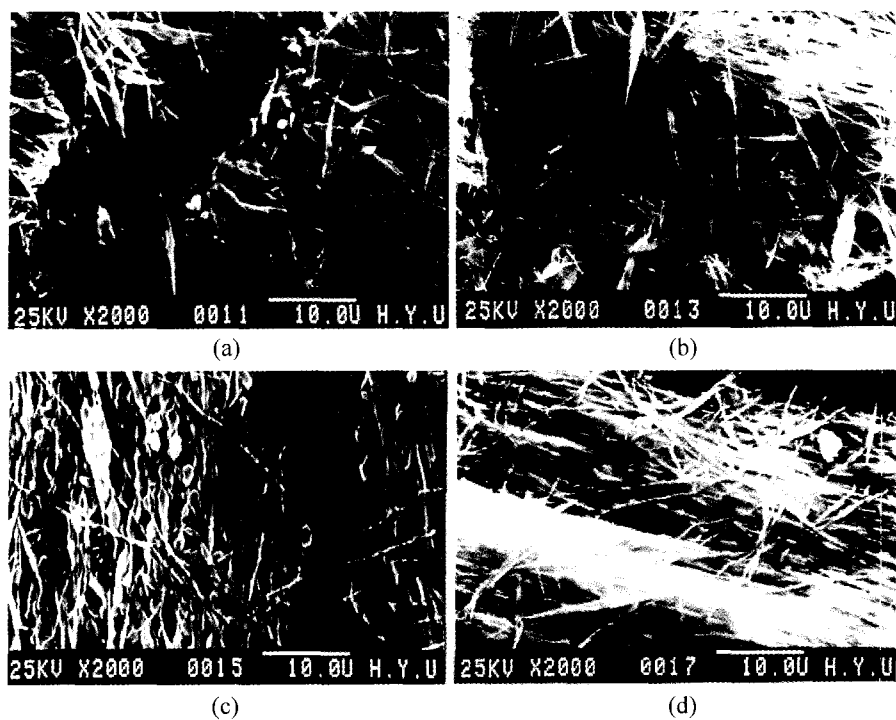

Figure 9. SEM micrographs of LCP fibrils prepared by dissolving PEN/PET in 2-chlorophenol at 55°C for 2 hours: (a) 10/45/45; winding speed 1000 m/min; X2000, (b) 20/40/40; winding speed 1000 m/min; X2000, (c) 30/35/35; winding speed 1000 m/min; X2000, (d) 40/30/30; winding speed 1000 m/min; X2000.
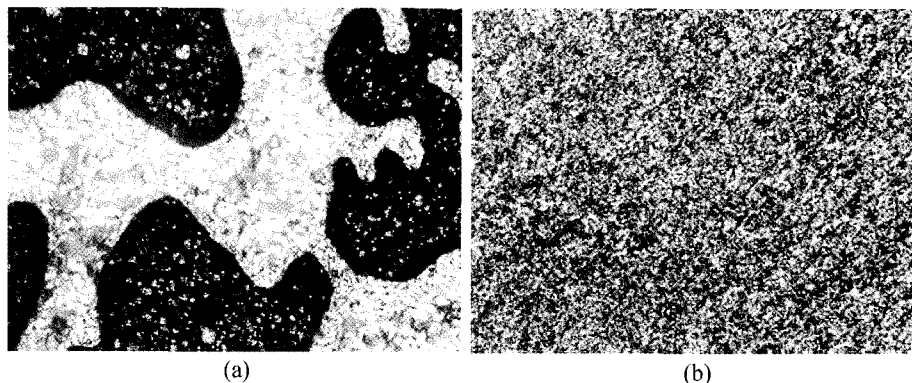
(a)   (b)

Figure 10. Polarized optical photographs of PHB/PEN/PET blends;   ×400 (a) 20/40/40, (b) 40/30/30 (mol%).

Table 2. The characteristic diffraction angles (2Θ) of LCP, PEN, and PET components

LCP	PEN	PET
	15.5°	18.2°
20.1°	23.4°	22.7°
	26.8°	26.4°

LCP, PEN, and PET components are presented in Table 2. Unfortunately, however, the crystal reflections of PEN and PET lie quite close together. Therefore, at 2Θ = 15.5°, PEN is best characterized because its (010) reflection is distinctive to that of PET. PET is best characterized by the (010) reflection at 2Θ = 18.2° where no reflection of PEN appears. The diffraction diagrams of ternary blends with various crystallization temperatures are shown in Figure 11. In the diagrams obtained from crystallized films, only PEN crystal reflection at 2Θ = 15.5° appears but PET crystal reflection is not shown in all compositions. Crystallinity of blends calculated by deconvolution is shown in Figure 12. Crystallinity of blends that are isothermally crystallized from 140°C to 260°C has its maximum at 220°C and increases slightly with increasing PHB content.
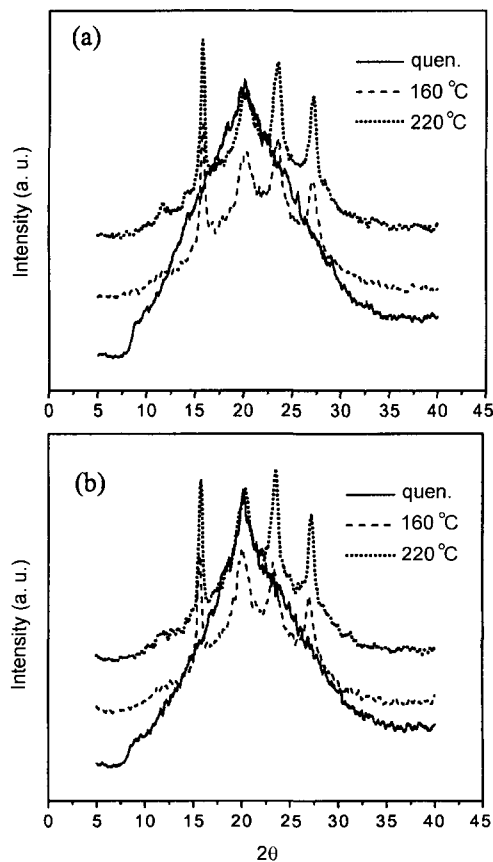
Transesterification reaction

Transesterification investigated by probabilistic analysis of NMR results shows that the exchange reaction between PEN

Figure 11. X-ray diffraction patterns of ternary blends with various annealing temperature for 30 min: (a) 30/35/35, (b) 40/30/30 (mol%).
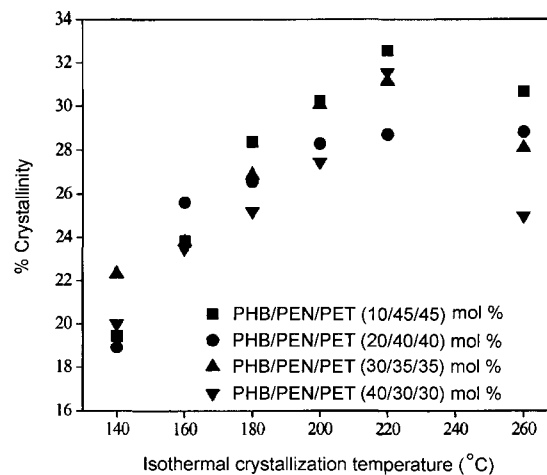

Figure 12. Crystallinity of PHB/PEN/PET ternary blends annealed for 30 min as a function of isothermal crystalline temperature; characterized by WAXD.

and PET occurs during the blending. NMR data for the blends containing PHB component cannot be obtained because poly(HB/ET) (8/2) LCP component is not dissolved in TFA-d. Therefore, NMR spectra are only obtained for the soluble PEN and PET component. The degree of transesterification in the blends can be determined from the area ethylene units occupy in the NMR spectrum. The peak for PET appears at 5.11 ppm, and 5.30 ppm for PEN. A new peak appears at 5.25 ppm. This is attributed to the ethylene units, which exist between terephthalic and naphthalic groups in the polymer backbone. The peaks of spectrum are shown in Figure 13. According to the theory of probabilistic analysis[23], the block length of naphthalate unit (L_{nPEN}) and
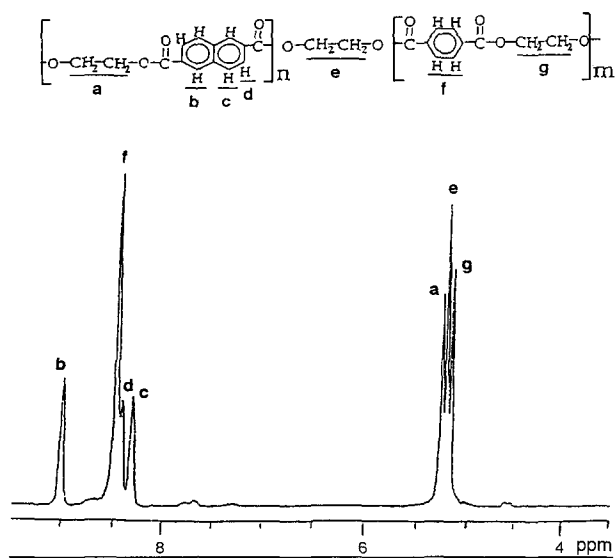

Figure 13. ^{1}H-NMR sectrum at 300 MHz with the assignments of absorptions for the PHB/PEN/PET blends dissolved in D-trifluoroacetic acid.

terephthalate unit (L_{nPET}) as well as the probability (P_{NT} and P_{TN}) of finding N (or T) unit next to T (or N) unit can be calculated from the integrated intensities of resonance peaks (f_{NEN}, f_{NET} and f_{TET}).

$$P_{NT} = \frac{f_{NET}}{(f_{NET} + 2f_{NEN})} = \frac{1}{L_{nPEN}}$$

$$P_{TN} = \frac{f_{TEN}}{(f_{TEN} + 2f_{TET})} = \frac{1}{L_{nPET}} \qquad (1)$$

The degree of randomness (B) can be defined as the summation of two probabilities ($P_{NT} + P_{TN}$). For the random copolymers, B=1; for the alternative copolymers, B=2; for the block copolymers or physical blends, B is close to zero.

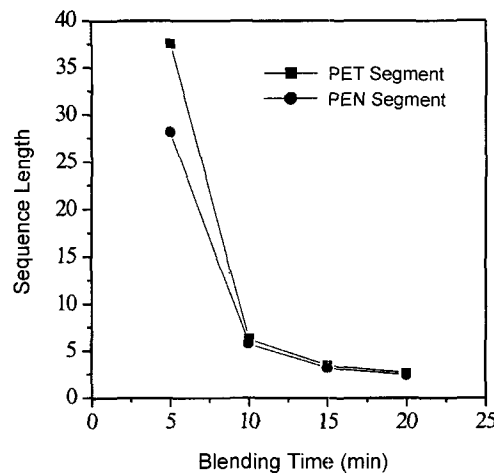Table 3 gives the various parameters of blends as a function of blending time. The degree of randomness is

Figure 14. Effect of blending time as a function of sequencde length of PET and PEN segments for the PHB/PEN/PET (39/26/35) blend.

Table 3. Content of hetero sequence (f_{TEN}), sequence length of PET segment (L_{nPET}) and PEN segment (L_{nPEN}), and degree of randomness (B) of PHB-PEN-PET blends

Composition of PHB/PEN/PET (mol%)	Blending time (min)	f_{TEN}	L_{nPET}	L_{nPEN}	B
13/38/49	5	0.015	80.00	53.48	0.031
	10	0.128	9.07	6.52	0.264
	15	0.209	5.63	3.95	0.431
	20	0.336	3.43	2.53	0.688
34/25/41	5	0.030	37.59	28.17	0.062
	10	0.165	6.33	5.79	0.331
	15	0.299	3.47	3.20	0.600
	20	0.399	2.66	2.42	0.789
52/16/32	5	0.010	90.91	106.38	0.020
	10	0.158	4.85	7.84	0.334
	15	0.298	2.69	4.02	0.621
	20	0.396	2.11	2.94	0.815

significantly influenced by blending time but negligibly influenced by blend composition. It can be seen that the degree of transesterification increases with blending time. The effect of blending time on the sequential length of PEN and PET segments is shown in Figure 14. The sequential lengths of PEN and PET segments decreased clearly at initial blending time but slightly decreased at more than 10 min. This is closely concerned with the change of chemical structure and, especially, intermolecular chain reaction known as transesterification reaction.

Conclusions

Thermal analysis, mechanical properties, morphology, crystallization behavior, and transesterification reaction of PHB/PEN/PET ternary blends were investigated with changing PHB content. For the rheological properties, complex viscosities of blends decreased with increasing temperature and PHB content. Blends containing more than 40 mol% PHB content were approximately homogeneous phase compared to the blends containing less than 30 mol% PHB content.

According to the thermal analysis, glass transition temperatures and melting temperatures of blends increased with increasing PHB content. Moreover, melting temperatures of preheated samples decreased with increasing preheating temperatures. It was well understood that the length of homo segment in the polymer chain decreased, and crystal formation was disturbed by the irregular structure in the blends with the progress of transesterification reaction.

For the mechanical property and morphology of monofilament, both tensile strength and initial modulus increased with higher PHB content and take-up speed from 500 m/min. to 1000 m/min. for all the compositions. It was supposed that the monofilament consists of fine and long LCP fibrils in the matrix polymers improved mechanical property of monofilaments. In the polarized optical photographs, the blend of 30 wt% PHB content showed partial liquid crystal phase and the blend of 40 wt% PHB content was considered to show liquid crystal phase.

In the WAXS diagrams obtained from crystallized films, only PEN crystal reflection at $2\Theta = 15.5°$ appeared but PET crystal reflection was not shown in all compositions. Crystallinity of blends calculated by deconvolution had its maximum at 220°C and increased slightly with increasing PHB content.

For the transesterification reaction, degree of transesterification and randomness of blends increased with blending

time. However, the sequential lengths of PET segment and PEN segment decreased.

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