Effect of Composition and Molecular Structure on the LC Phase of PHB–PEN–PET Ternary Blend

SEONG HUN KIM,[1] SEONG WOOK KANG,[1] JAE KEE PARK,[2] YUN HEUM PARK[3]

[1] Department of Textile Engineering, College of Engineering, Hanyang University, Seoul 133-791, Korea

[2] Textile and Cleaner Production R & D Center Korea Institute of Industrial Technology, Suwon 440-746, Korea

[3] Department of Textile Engineering, Sungkyunkwan University, Suwon 440-746, Korea

ABSTRACT: Poly(*p*-hydroxybenzoic acid) (PHB)–poly(ethylene terephthalate) (PET) 8/2 thermotropic liquid crystalline copolyester, poly(ethylene 2,6-naphthalate) (PEN), and PET were mechanically blended to pursue the liquid crystalline (LC) phase of ternary blends. The torque values of blends with increasing PHB content abruptly decreased above 40 wt % of PHB content because the melt viscosity of ternary blends dropped. Glass transition temperature and melting temperature of blends increased with increasing PHB content. The tensile strength and initial modulus of blends were low at 10 and 20 wt % PHB. However, the blends containing above 30 wt % PHB were improved with increasing PHB content due to the formation of fibrous structure. The blend of 20 wt % PHB formed irregularly dispersed spherical domains, and the blends of 30–40 wt % PHB showed LCP ellipsoidal domains and fibrils. In the polarized optical photographs, the blends of 40 wt % PHB showed *pseudo* LC phases. The degree of transesterification and randomness of blends were increased with blending time. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1065–1073, 1998

Key words: liquid crystalline polymer; poly(*p*-hydroxybenzoic acid); poly(ethylene 2,6-naphthalate); poly(ethylene terephthalate); reactive extrusion

INTRODUCTION

Poly(ethylene 2,6-naphthalate) (PEN) has been known since 1948, when its synthesis was first reported by ICI Co.[1] In spite of its long history, application of PEN is limited as compared with poly(ethylene terephthalate) (PET) because the PEN monomer is expensive and PEN exhibits relatively high melt viscosity that is not easy for fiber spinning and injection molding.[2] However, PEN is a high-performance polyester that exhibits superior physical and chemical properties to those of PET. The naphthalene moiety in PEN provides stiffness to the polymer backbone, leading to the improved thermal resistance, excellent mechanical properties, and outstanding gas barrier characteristics.[3–6] Therefore, blending of PEN with thermotropic liquid crystalline polymers (TLCPs) represents an interesting system for application and fundamental studies for the properties of LCP–polymer blends.[7–11] Blending of polymers can be an effective means for improving properties of components. However, in general, when a rigid rod polymer and a flexible polymer are simply mixed together, the blended polymers can form an immiscible blend. Reactive extrusion may provide a useful way to improve physical properties and miscibility between TLCP and thermoplastic polymers.

In recent years, interest in thermoplastic liquid crystalline (TLC) copolyesters has been grown.[12] Binary copolyesters of poly(p-hydroxybenzoic acid) (PHB)–PET, PHB–PEN, and a ternary copolyester of PHB–PEN–PET that form TLCP melts have been synthesized and studied by many researchers.[13–16] Crystallization behaviors and the thermal transition temperature, including the LC phase transition temperature, have been reported. These investigations reveal the following.

1. Ternary copolyesters containing 30 mol % PHB are partially LC, and those containing over 50 mol % PHB are completely LC.[13]
2. In the copolyesters containing up to 50 mol % PHB, both PET and PEN crystals are formed. In those containing 80–90 mol % PHB, only crystals of PHB are observed.[14]
3. A ternary copolyester of PHB–PEN–PET (30/35/35) is in a LC phase up to 160°C, where it starts to become gradually isotropic, and it is completely isotropic at 290°C.[15]
4. For PET–PEN copolymers, no LC phase is formed.[13]

In this research, commercially available PHB–PET copolyester LCP, PEN, and PET are mechanically blended to pursue LC phase of blended articles. The critical composition of PHB in the PEN and PET to show LC ternary blended articles are investigated, and miscibility and thermal behavior are studied by thermal analysis. The PHB content in the ternary blend is controlled by the amount of PHB–PET copolyester because PHB homopolyester of high-molecular weight finds no melting temperature at 482–538°C, where the polymer decomposes rapidly.[17] In addition, the relationship between mechanical property and morphology of ternary blends with different PHB contents are observed by scanning electron microscopy (SEM) micrograph of tensile bar after tensile testing. Furthermore, transesterification reactions occur during melt blending, and the degree of transesterification with various compositions and melt blending time is investigated by statistical analysis of a nuclear magnetic resonance (NMR) spectrum.

EXPERIMENTAL

Materials

TLCP used in this research was a TLC copolyester, Rodrun 5000 (Unitika Co., Japan), supposed to be prepared from 80 mol % PHB and 20 mol % PET; 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. The pellets of TLCP, PEN, and PET were dried *in vacuo* at 120°C for 24 h to minimize moisture effects before use.

Ternary Blends Preparation

The blends were made by melt blending in a Haake Rheomix 600 at 285°C for 5 min with different compositions, and the roller blade speed was fixed at 60 rpm. Blending composition of PHB–PEN–PET blends in weight ratios were 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, and 80/0/20; they are listed in Table I. In addition, the samples for the NMR experiments were blended at 285°C for the various blending times from 5 to 20 min.

Characterization

Rheological property of PHB–PEN–PET blends was investigated by rheomix torque value during melt blending at 285°C under constant rotating speed of 60 rpm. Thermal behavior of blends was conducted in a 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. The DSC measurements of blends after preheating were performed from 40 to 300°C at the scanning rate of 10°C/min. Tensile testing and impact strength testing specimens were prepared using Minimax Molder model CS-183 MMX (CSI Co.) at 290°C. Tensile tests were performed using UTM 10E (United Calibration Co.) according to the ASTM-D638 method. The crosshead speed was 10 mm/min, and the used gauge length
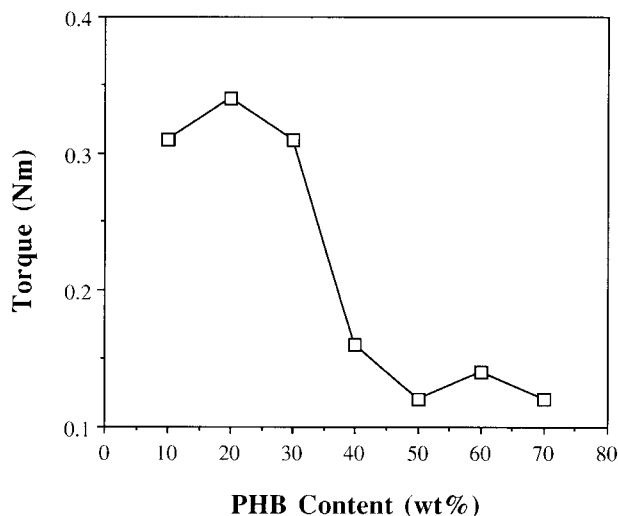
Table I   Composition of PHB–PEN–PET Blends

PHB–PEN–PET (wt %)	PHB–PEN–PET (mol %)	LCP–PEN–PET (wt %)
10/45/45	13/38/49	12.5/45/42.5
20/40/40	24/30/46	25/40/35
30/35/35	34/25/41	37.5/35/27.5
40/30/30	44/20/36	50/30/20
50/25/25	52/16/32	62.5/25/12.5
60/20/20	59/12/29	75/20/5
70/15/15	63/9/28	85/15/0

Figure 1   Torque value as a function of PHB content for PHB–PEN–PET blends measured at 285°C (60 rpm).

Figure 3   Melting temperature and melting enthalpy as a function of PEN content for the PEN–PET blends.

was 25.4 mm. Unnotched Izod impact strength test was performed by Universal Impact Tester No. 255 following ASTM-D256. Morphology of fracture surface for the narrow section of tensile bar prepared by injection molding were observed at parallel and perpendicular to the injection flow direction using a SX-30E SEM (Topcon Co.). The LC phase of blends were investigated by a polarized optical microscope. The samples for the NMR experiments were prepared by dissolving the blends in deuterated trifluoroacetic acid (TFA-d).
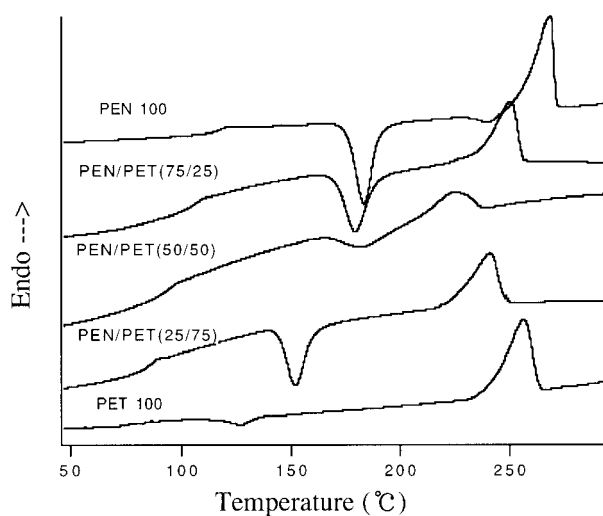
^{1}H-NMR measurements were performed at 23°C on a Jeol 300 MHz Fourier transform (FT)–NMR spectrometer.

RESULTS AND DISCUSSION

Rheology

Torque value versus PHB content for the PHB–PEN–PET blends is shown in Figure 1. Pure PEN (0.65 Nm) needs the highest torque versus pure

Figure 2   DSC scans of PEN–PET blends that were heated to 300°C at the rate of 200°C/min and held for 2 min, then cooled to 0°C (heating rate of 10°C/min).
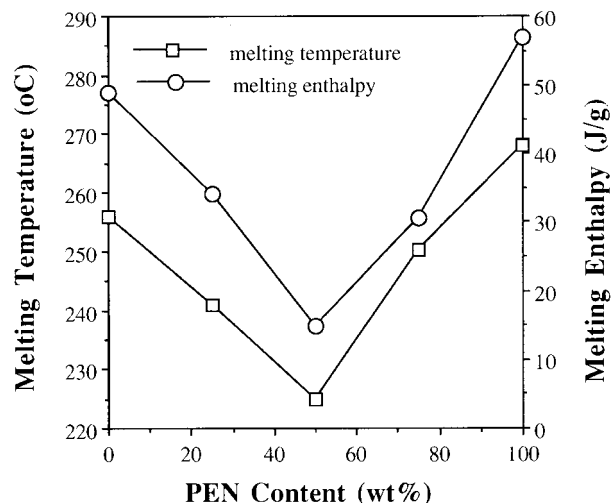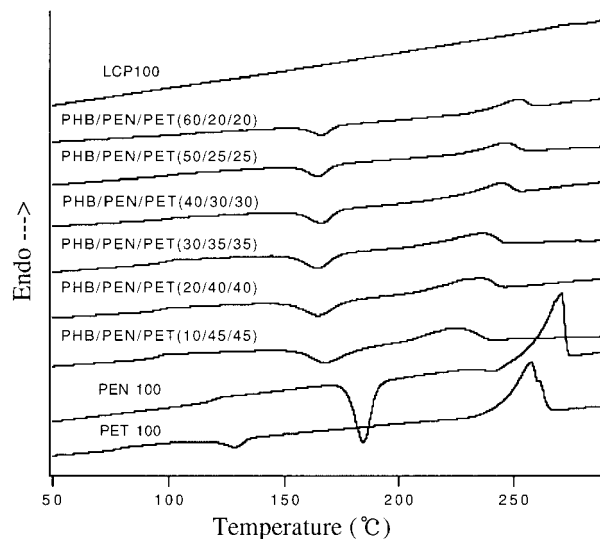

Figure 4   DSC scans of PHB–PEN–PET blends that were heated to 280°C at the rate of 200°C/min and held for 2 min, then cooled to 0°C (heating rate of 10°C/min).
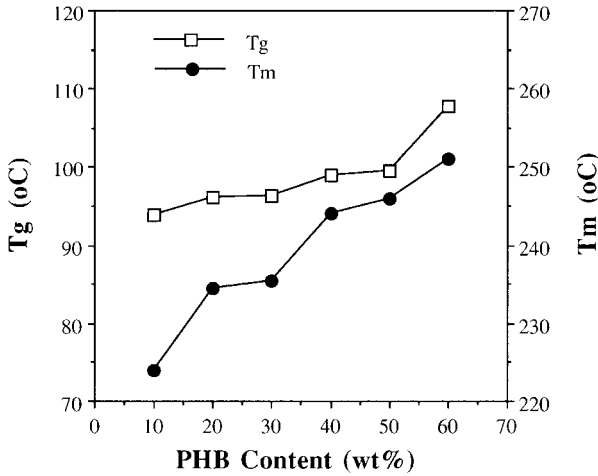
Figure 5 Glass transition temperature and melting temperature as a function of PHB content for the PHB–PEN–PET blends.

PET (0.38 Nm) and all blends due to its high melt viscosity. Torque values of blends show similar levels below 30 wt % PHB content. Torque values are greatly decreased with increasing PHB content over 40 wt % PHB; we propose that the high content of PHB provides *pseudo* LC phase to the ternary blend, as is confirmed by the morphology study below.

Thermal Behavior

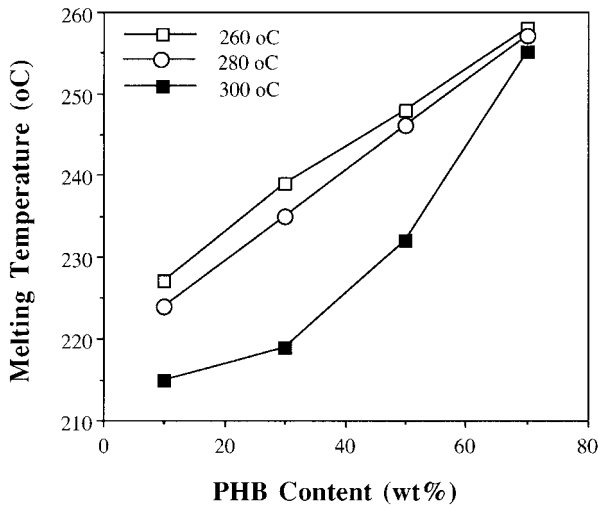Differential scanning calorimetry (DSC) measurements of PEN–PET blends on several compo-

Table II Tensile Strength and Modulus of PHB–PEN–PET Blends, Which Were Molded at 290°C

PHB–PEN–PET (wt %)	Tensile Strength (MPa)	Modulus (GPa)
0/0/100	23.9	0.68
0/100/0	21.1	0.79
10/45/45	16.8	0.35
20/40/40	13.7	0.20
30/35/35	26.9	2.11
40/30/30	30.8	2.41
50/25/25	54.7	2.82
60/20/20	68.6	3.10
70/15/15	75.9	3.19
80/0/20	90.3	3.21

sitions prepared by melt blending are shown in Figures 2 and 3. In the dependence of melting behaviors on the composition, melting temperature (T_m) and melting enthalpy (ΔH_m) appear its lowest value at a PEN–PET (50/50) composition. This behavior indicates that at the 50/50 composition, the achievable crystallinity is the smallest or the crystalline structure formation is the least perfect. DSC thermograms of PHB–PEN–PET blends are shown in Figure 4, and glass transition temperature (T_g) and T_m of blends are shown in Figure 5. All blends have one T_g, and T_g of blends is slightly increased with increasing PHB content. Moreover, melting temperature of blends are increased with increasing PHB content. The
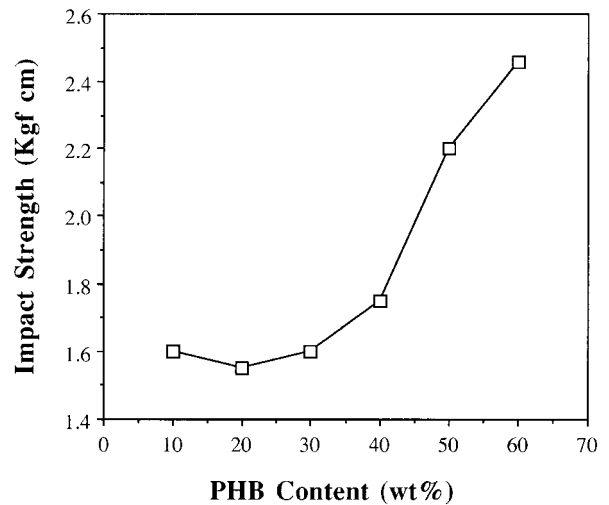

Figure 6 Effect of preheating temperatures and blend compositions on the melting temperatures for the PHB–PEN–PET blends.

Figure 7 Impact strength as a function of PHB content for the PHB–PEN–PET blends (injection-molded at 290°C).

effect of preheating temperature on the melting temperature of blends is represented in Figure 6. The blends are preheated at 260, 280 or 300°C for 2 min, respectively. At 260°C, only the PET should melt; at 280°C, the PEN and PET portion should melt; at 300°C, the system should be in a completely isotropic state. As the preheating temperature increases, melting temperatures are decreased. We believe that the length of homo segment in the polymer chain decreases, and the crystal formation is disturbed by the irregularity of structure with the progress of transesterification reaction. In other words, more randomization of segments occurs.

Mechanical Properties

The dependence of mechanical properties of PHB–PEN–PET blends on PHB content are estimated by tensile and impact test. Mechanical properties of blends are greatly affected by the PHB content, as shown in Table II and Figure 7. At the blends of 10 and 20 wt % PHB, tensile strength and initial modulus are relatively low compared to pure PET and PEN because spherical LCP domains irregularly disperse in PEN and PET matrix polymer. However, tensile strength and initial modulus of blends containing above 30 wt % PHB are improved with increasing PHB content due to the formation of fibrils and LC-rich phase in the blend. Therefore, the major factor in increasing mechanical properties of blends is the formation of LCP fibrilar structure, depending on the processing condition and the blending composition. Impact strength of PHB–PEN–PET blends is slightly increased with increasing PHB content because PEN and LCP are very tough materials.

Morphology

SEM micrographs of narrow section of tensile bar after tensile testing are represented in Figure 8. The SEM taking the location of the tensile bar is parallel or perpendicular to flow direction at near skin portion. In the blends of 20 wt % PHB [Fig. 8 (a) and (b)], the micrographs of parallel and perpendicular to flow direction clearly show the formation of circular LCP domains, and these form irregularly dispersed spherical domains with a diameter of 0.4–12.6 μm in the matrix polymers. The micrographs of 30 and 40 wt % PHB [Fig. 8 (c)–(f)] show the LCP ellipsoidal domains and fibrils, and the fibrils are increased with increasing PHB content. It is expected that the mechan-

ical property of blends is improved by the LCP fibrils. The micrographs of 50 wt % PHB [Fig. 8 (g) and (h)] show that PEN- and PET-rich phase is converted to a LC-rich phase. Therefore, the effect of PHB content on the morphology of blends is found that the fibrils form above 30 wt % PHB content, and the LC-rich phase occurs above 50 wt % PHB content. However, spherical LCP domains irregularly disperse in the PEN and PET phase below 20 wt % PHB content. Polarized optical photographs of blends are shown in Figure 9. The results observed from 30 wt % PHB reveal that a partially LC phase shows in the blended polymers. However, the blend of 40 wt % PHB shows *pseudo* LC phase. It is a similar result that the synthesized copolyesters by Chen and Zachmann[13] containing 30–40 mol % PHB form a LC phase.

Transesterification Reaction

Transesterification is investigated by statistical analysis of NMR results to follow the exchange reaction occurring during melt blending. NMR for the blends containing PHB component is not taken because poly(HB–ET) (8/2) LCP component does not dissolve in TFA-d. Therefore, NMR spectrums are obtained for the soluble PEN and PET components. The extent of transesterification in the blends can be determined from the NMR spectrum in the region corresponding to the ethylene unit. The peak for PET appears at 5.11 ppm, and the peak for PEN appears at 5.30 ppm. A new peak appears at 5.25 ppm. It is due to the ethylene units, which exist between terephthalic and naphthalic groups in the polymer backbone. The peaks of spectrum are shown in Figure 10. According to the theory of statistical analysis,[18] the block length of naphthalate unit (Ln_{PEN}) and terephthalate unit (Ln_{PET}), as well as the probability (P_{NT} and P_{TN}) of finding a N (or T) unit next to a T (or N) unit, can be calculated from the integrated intensities of resonance peaks (f_{NEN}, f_{NET} and f_{TET}).

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

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

The degree of randomness (B) can be defined as the summation of 2 probabilities ($P_{NT} + P_{TN}$).

(a) PHB/PEN/PET (20/40/40),
parallel to flow

(b) PHB/PEN/PET (20/40/40),
perpendicular to flow

(c) PHB/PEN/PET (30/35/35),
parallel to flow

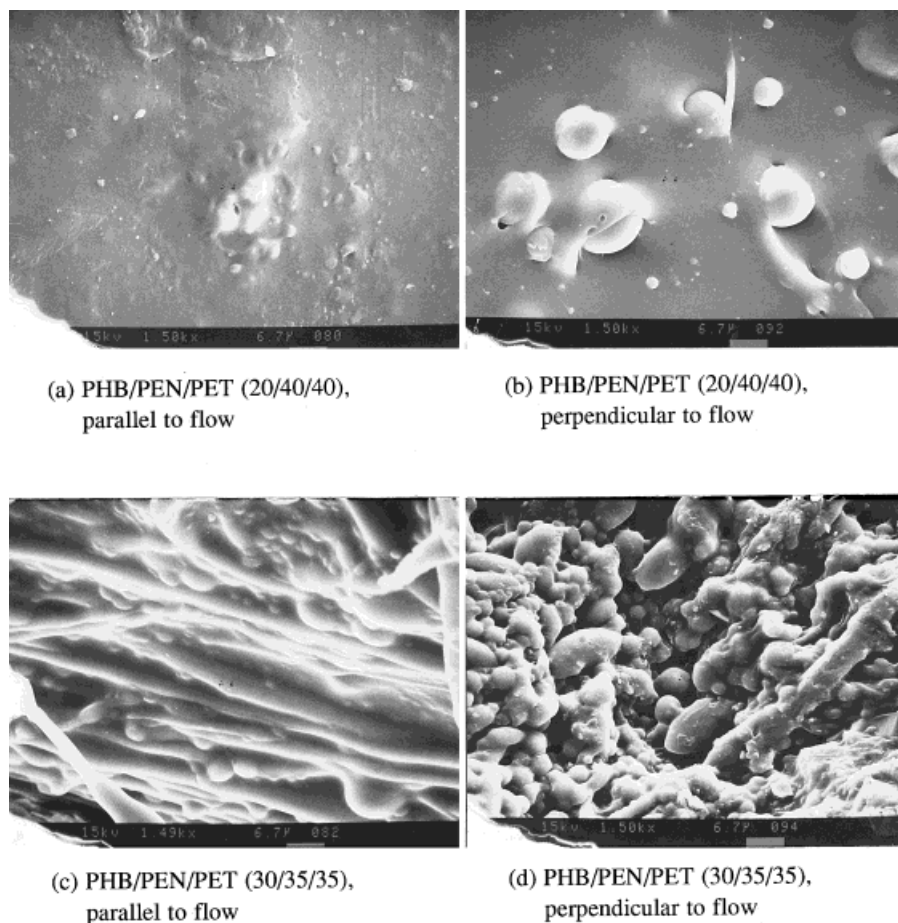(d) PHB/PEN/PET (30/35/35),
perpendicular to flow

Figure 8   SEM micrographs of PHB–PEN–PET blends molded at 290°C in a Minimax molder (narrow section of tensile bar).

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 III gives the various parameters of blends as a function of blending time. The degree of randomness is 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 block length of blends decrease with increasing blending time.

CONCLUSIONS

The rheology, thermal behavior, mechanical properties, morphology, and transesterification reaction of PHB–PEN–PET blends have been studied as a function of PHB content. The torque values of blends with increasing PHB were abruptly de-

creased above 40 wt % PHB because the melt viscosity of ternary blends dropped.

According to the thermal analysis, the melting temperature and enthalpy of PEN–PET blends showed its lowest value at a 50/50 composition. This suggested that crystalline was the smallest or that the crystalline structure formation was imperfect. For the PHB–PEN–PET blends, glass transition and melting temperature were increased with increasing PHB content. Moreover, the melting temperature of preheated samples was decreased with an increasing preheating temperature. The length of homo segment in the polymer chain decreased, and crystal formation was disturbed by the irregularity of structure with the progress of transesterification reaction.

In tensile testing, tensile strength and initial modulus of the blends were low at 10 and 20 wt % PHB. However, the blends containing above 30 wt
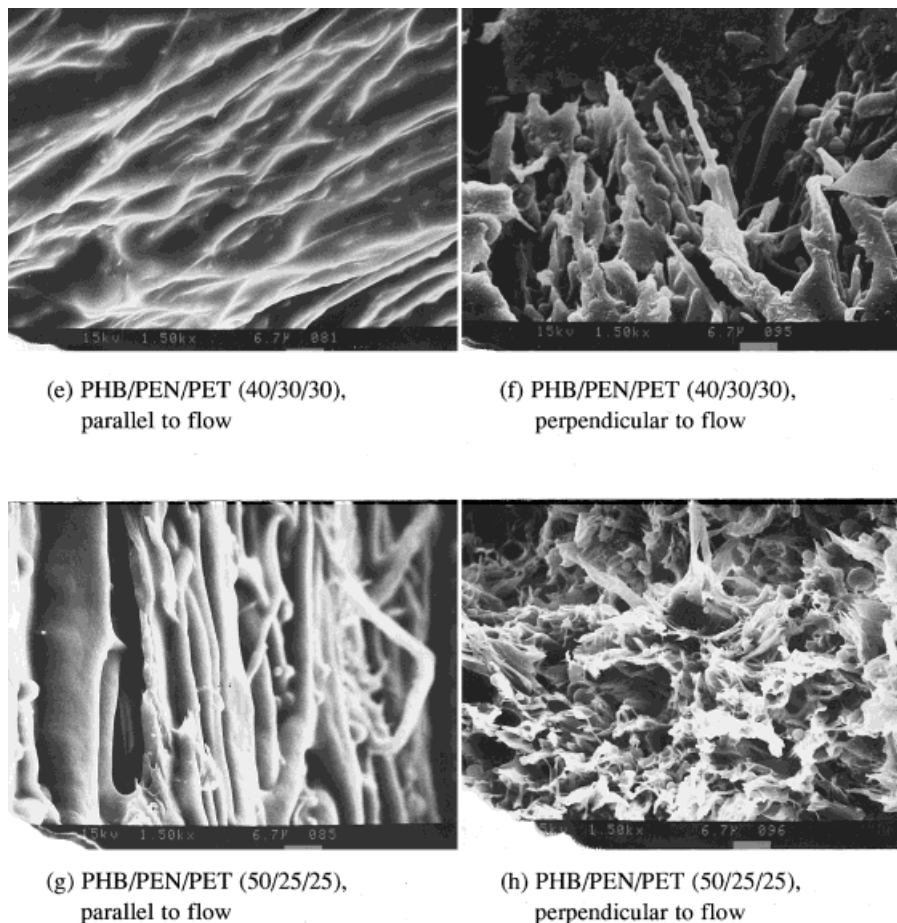
(e) PHB/PEN/PET (40/30/30),
parallel to flow

(f) PHB/PEN/PET (40/30/30),
perpendicular to flow

(g) PHB/PEN/PET (50/25/25),
parallel to flow

(h) PHB/PEN/PET (50/25/25),
perpendicular to flow

**Figure 8**   (*Continued from the previous page*)

Table III   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 Heated at 285°C for 5–20 min

| 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	0.393	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

% PHB were improved with increasing PHB content due to the formation of fibrous structure.

According to the morphology, the blend of 20 wt % PHB formed irregularly dispersed spherical domains with a diameter of 0.4–12.6 μm in the matrix polymers, and were observed LCP ellipsoidal domains and fibrils in the blends of 30–40 wt % PHB. Fibrils were increased with increasing PHB content. It was expected that the mechanical properties of blends were improved by the LCP fibrils. In addition, for the polarized optical photographs of, blends a partially LC phase at 30 wt % were observed, and the blend of 40 wt % PHB showed a *pseudo* LC phase.

For the transesterification reaction, the degree of transesterification and randomness of blends increased with blending time. However, the sequence length of PET segment and PEN segment decreased.
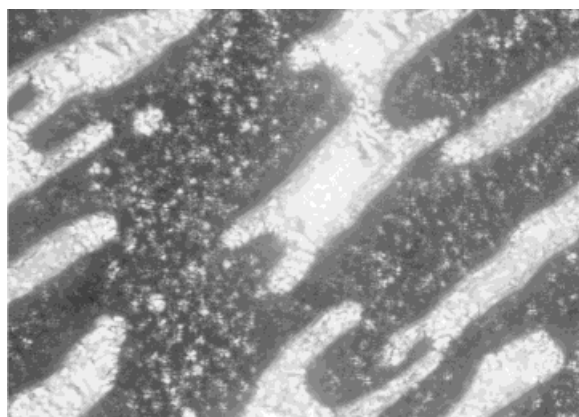
(a) PHB/PEN/PET (30/35/35)
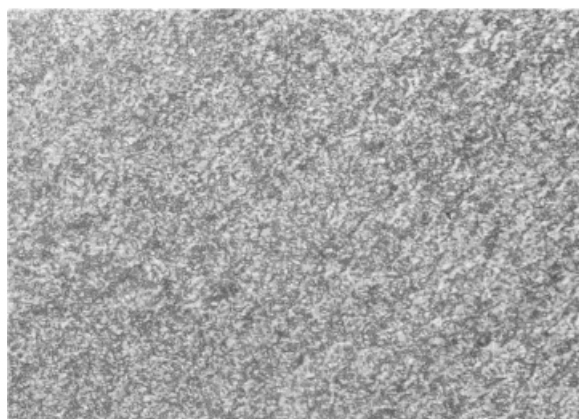
(b) PHB/PEN/PET (40/30/30)

Figure 9 Polarized optical photographs of PHB–PEN–PET blends ×400.
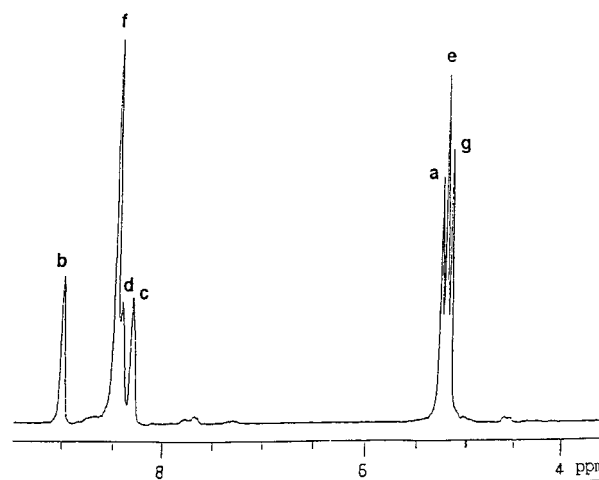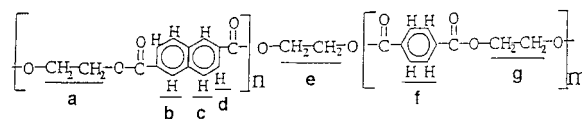

Figure 10 ^{1}H-NMR spectrum at 300 MHz with the assignments of the absorptions for PHB–PEN–PET blends dissolved in deuterated trifluoroacetic acid.

Therefore, the critical composition of PHB in the matrix polymers that shows a *pseudo* LC phase is 40 wt %, and fibril formation to improve mechanical properties was observed above 30 wt % PHB.

From these results, ternary blends of PHB–PEN–PET may provide ease of processing from the *pseudo* LC and higher mechanical properties than that of PEN–PET copolymer systems. Mechanically blended PHB–PEN–PET also shown LC above 40 wt % of PHB content, which is a similar result to the synthesized ternary copolyester system prepared by Chen and Zachmann.[13]

REFERENCES

1. J. G. Cook, H. P. W. Hugill, and A. R. Lowe, Brit. Pat. 604073 (1948).
2. Y. Ulcer and M. Cakmak, *Polymer,* **35,** 5651 (1994).
3. S. Buchner, D. Wiswe, and H. G. Zachmann, *Polymer,* **30,** 480 (1989).

4. M. Cakmak, Y. D. Wang, and M. Simhambhatla, *Polym. Eng. Sci.,* **30,** 721 (1990).

5. M. Ito, K. Honda, and T. Kanamoto, *J. Appl. Polym. Sci.,* **46,** 1013 (1992).

6. J. Jager, J. A. Juijn, C. J. M. Van Den Heuvel, and R. A. Huijts, *J. Appl. Polym. Sci.,* **57,** 1429 (1995).

7. W. C. Lee and A. T. Dibenedetto, *Polymer,* **34,** 684 (1993).

8. H. C. Chin, K. C. Chiou, and F. C. Chang, *J. Appl. Polym. Sci.,* **60,** 2503 (1996).

9. M. Singer, G. P. Simon, R. Varley, and M. R. Nobile, *Polym. Eng. Sci.,* **36,** 1038 (1996).

10. K. H. Wei, W. J. Hwang, and H. L. Tyan, *Polymer,* **37,** 2087 (1996).

11. K. Yoshikai, K. Nakayama, and M. Kyotani, *J. Appl. Polym. Sci.,* **62,** 1331 (1996).

12. S. H. Kim, S. W. Park, and E. S. Gil, *J. Appl. Polym. Sci.,* **67,** 1383 (1998).

13. D. Chen and H. G. Zachmann, *Polymer,* **32,** 1612 (1991).

14. F. J. Balta-Calleja, C. Santa-Cruz, D. Chen, and H. G. Zachmann, *Polymer,* **32,** 2252 (1991).

15. S. Spies and H. G. Zachmann, *Polymer,* **35,** 3816 (1994).

16. O. Ahumada, T. A. Ezquerra, A. Nogales, F. J. Balta-Calleja, and H. G. Zachmann, *Macromolecules,* **29,** 5003 (1996).

17. J. Economy, B. E. Nowak, and S. G. Cottis, *SAMPE J.,* **6,** 21 (1970).

18. R. Yamadera and M. Murano, *J. Appl. Polym. Sci.,* **5,** 2259 (1967).