

Miscibility Study on Blend of Thermotropic Liquid Crystalline Polymers and Polyester

Dae Soon Park, Seong Hun Kim

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

Received 14 January 2002; accepted 20 May 2002

ABSTRACT: The miscibility of thermotropic liquid crystalline polymers (TLCPs) and polyester blends was investigated with thermal and morphological analyses, as well as transesterification. TLCPs composed of 80 mol % *para*-hydroxybenzoate (PHB) and 20 mol % poly(ethylene terephthalate) (PET) or 60 mol % PHB and 40 mol % PET, and polyesters such as PET and poly(ethylene 2,6-naphthalate) (PEN) were melt blended in an internal mixer. DSC analyses were performed to investigate the thermal transition behavior and to obtain thermodynamic parameters. All the blends showed only a single glass-transition temperature, which means they are partially miscible in the molten state. The Flory–Huggins interaction parameter was calculated employing the Nishi–Wang approach, and negative values

were obtained except for the P(HB8-ET2)/PEN blends. Transesterification was investigated using $^1\text{H-NMR}$, and the change of chemical shift compared to pure PET or P(HB-ET)s was observed in the P(HB-ET)/PET blends. An intermediate chemical shift value (4.83 ppm) was observed in the P(HB6-ET4)/PEN blends, which indicates transesterification occurred. The fractured surface morphology of scanning electron micrographs showed that the interfaces between the LC droplets and matrix were not distinct. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1842–1851, 2003

Key words: thermotropic liquid crystalline polymer; melting point depression; interaction parameter; transesterification; miscibility

INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) have attracted considerable attention because of their advantageous properties such as high strength, high modulus, dimensional stability, and thermal stability. Apparently, the first full description of polymers exhibiting TLC behavior emerged in the mid-1970s when Jackson and Kuhfuss¹ reported the characteristic properties of copolyesters composed of *para*-hydroxybenzoic acid (PHB) and poly(ethylene terephthalate) (PET). After that, many studies were conducted, leading to extensive knowledge of the nature and properties of TLCPs.^{2–6}

In recent years, TLCP/thermoplastic blends have been intensively studied to reduce the cost of expensive TLCPs while maintaining many favorable properties.^{7–20} Because of their rigid-rod chemical structures, TLCPs exhibit low melt viscosity during melt processing. Thus, the addition of small amounts of TLCPs to other thermoplastics reduces their melt viscosity and thereby improves their processability. TLCPs also show high degrees of order in the melt under

the shear and elongational flow field, leading to deformation of LC domains within blends into fibrils having large aspect ratios; these fibrils can act as reinforcements in the *in situ* composites. However, thermodynamic incompatibility and poor adhesion between TLCPs and thermoplastics have limited the industrial applications of such TLCP/thermoplastic blends.

Miscibility can be influenced by various factors such as morphology, crystalline phase, intermolecular interaction, and reduction of surface tension. There have been several reports about miscibility in the blends of TLCPs and thermoplastics.^{13,14,21,29}

In 1975 Nishi and Wang³⁰ reported melting point depression in the blends of amorphous polymers and crystalline polymers using poly(vinylidene fluoride) and poly(methyl methacrylate) based on Scott's concept of thermodynamics in mixing and Flory–Huggins theory.^{31,32} Although a great deal of work has been done in this area, the research has been primarily limited to amorphous and semicrystalline polymer pairs.

Taking into account the great amount of work on TLCP blends, this is surprising. A limited effort has been directed toward the understanding of the thermodynamics of mixing of TLCPs and thermoplastics. In this study, blends of commercially available TLCPs and polyesters were used as the blends of materials to be investigated.

Correspondence to: S. H. Kim (kimsh@hanyang.ac.kr).

Contract grant sponsor: Center for Advanced Functional Polymers.

300°C and then held for 5 min followed by quenching to the desired temperature. Each sample was isothermally crystallized for 20 min.

For the $^1\text{H-NMR}$ analyses the samples were dissolved in a 7:3 volume fraction mixture of deuterated chloroform and deuterated trifluoroacetic acid. The $^1\text{H-NMR}$ spectra were recorded on a Varian Unity Inova FT-NMR apparatus operating at 300 MHz.

To observe the fracture surface of the samples, they were made into thin films using a hydraulic press

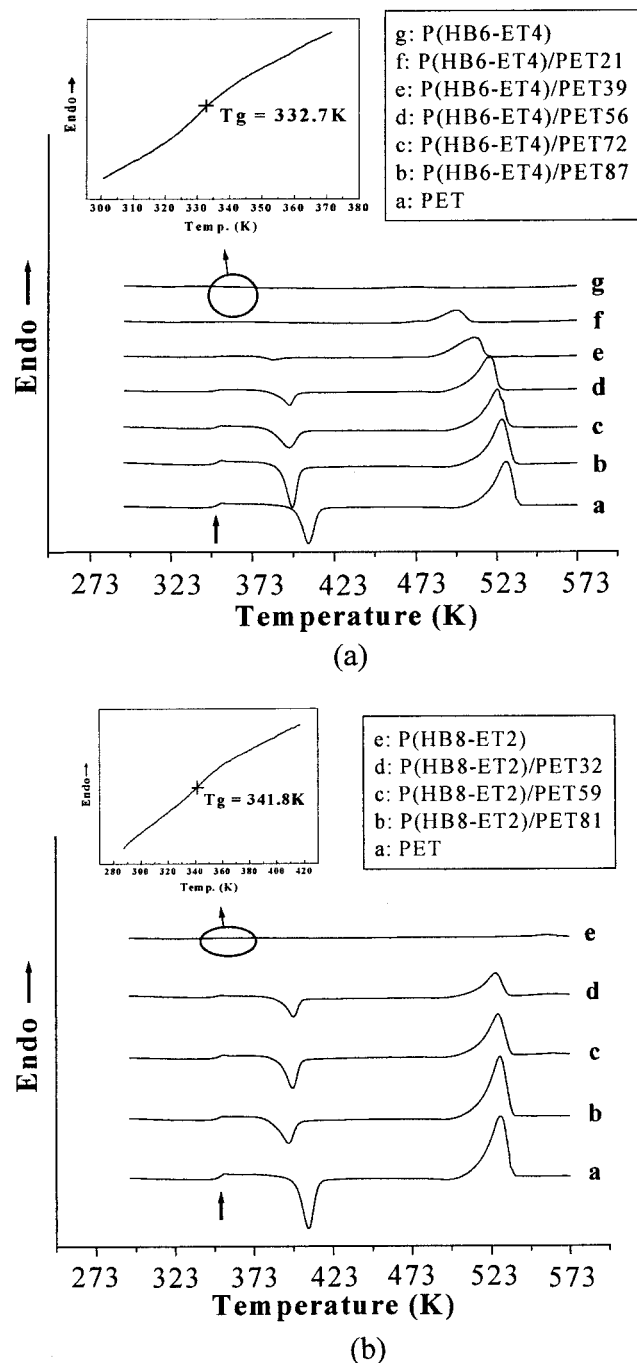


Figure 2 DSC thermograms of (a) P(HB6-ET4)/PET and (b) P(HB8-ET2)/PET blends at a heating rate of 10 K/min.

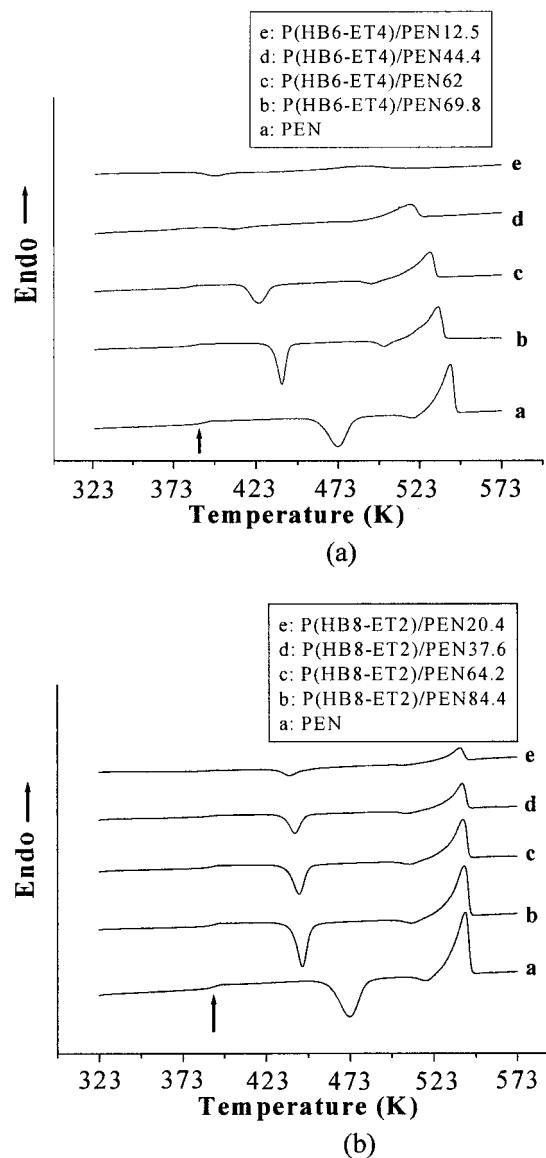


Figure 3 DSC thermograms of (a) P(HB6-ET4)/PEN and (b) P(HB8-ET2)/PEN blends at a heating rate of 10 K/min.

(Carver Press) and quenched in liquid nitrogen. Field emission scanning electron microscopy (FE-SEM) was employed with 10,000 power magnification.

RESULTS AND DISCUSSION

Thermal behavior and miscibility

DSC thermograms of all the blends are depicted in Figures 2 and 3 (second heating) and the relevant explanations are given in Tables II and III. The T_g of pure P(HB6-ET4) was 332.7 K and its change in heat capacity at constant temperature (ΔC_p) was 0.052 J/gK. Likewise, the T_g of pure P(HB8-ET2) was 341.8K and its ΔC_p value was 0.036 J/gK. These ΔC_p values are very small compared to those of PET and PEN. The reason for these small values is because of the

TABLE II
Thermal Characteristics of P(HB6-ET4)/PET and P(HB8-ET2)/PET Blends from DSC Measurement

Code	T_g (K)	ΔC_p (J/gK)	T_c (K)	ΔH_c (J/g)	T_m (K)	ΔH_f (J/g)
PET	352.2	0.336	407.4	25.2	528.9	46.3
P(HB6-ET4)/PET87	352.0	0.238	397.4	25.1	526.2	46.3
P(HB6-ET4)/PET72	351.4	0.178	395.4	17.1	523.4	39.8
P(HB6-ET4)/PET56	351.0	0.122	395.7	9.7	518.9	34.1
P(HB6-ET4)/PET39	351.2	0.041	385.5	2.4	508.9	24.8
P(HB6-ET4)/PET21	—	—	—	—	497.9	11.9
P(HB6-ET4)	332.7	0.052	—	—	468.7	0.7
P(HB8-ET2)/PET81	351.0	0.207	395.0	14.8	528.4	44.5
P(HB8-ET2)/PET59	351.4	0.219	397.7	15.6	527.4	30.3
P(HB8-ET2)/PET32	350.4	0.096	398.2	9.3	525.7	15.9
P(HB8-ET2)	341.8	0.036	—	—	559.5	0.1

near absence of an amorphous phase in P(HB6-ET4) and P(HB8-ET2). Although the T_g values of P(HB6-ET4) and P(HB8-ET2) are not distinct in Figures 2 and 3, all the blends showed only a single T_g over the entire range of compositions.²⁴ In Figure 2 and Table II the T_g of each blend shifted to a slightly lower temperature as the content of P(HB6-ET4) or P(HB8-ET2) increased, although it is not notable. This negligible shift is likely due to the small difference in T_g values of the two blend components.

In the case of P(HB-ET)/PEN blends, the T_g of each blend clearly shifts to lower temperatures with the increase in P(HB6-ET4) or P(HB8-ET2). In addition, P(HB6-ET4)/PEN showed a bigger drop in the T_g than P(HB8-ET2). This difference can be attributed to a larger PET portion in the P(HB6-ET4) (40 mol % PET) than in the P(HB8-ET2) (20 mol % PET). Generally, a single T_g and/or its shift in the blends represents miscibility or partial miscibility. In our experiment all the blends are thought to be partially miscible at this moment based on the discussion above, and further evidence is presented in the following sections. Many other reports on the miscible blends are found elsewhere, in which single a T_g and/or its shift to some extent has been reported.^{24,26,33–37}

In Tables II and III the ΔC_p values of all the blends decreased with the increase in the content of TLCPs.

This is in good agreement with the report of Jung et al.³⁷ who suggested that the reduction of ΔC_p resulted from the dissolution of a corresponding component in the conjugate phase and that is characteristic of partially miscible blends.

The dependence of the T_g on the blend composition can be predicted by the Fox equation³⁸ and the Gordon–Taylor equation.³⁹ However, the Fox equation was not applicable to predict the relationship between the T_g and blend composition in all the cases. The Fox equation is represented as follows:

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

where w_1 and w_2 are the weight fractions of TLCP and PET (or PEN), respectively. The glass-transition temperature of the blends is represented as T_{gb} . The symbols T_{g1} and T_{g2} are the glass-transition temperatures of TLCP and PET (or PEN), respectively.

The Gordon–Taylor equation was fit to predict the relationship between the T_g and composition only in case of the P(HB6-ET4)/PEN blends as shown in Figure 4. It is not yet revealed why the Gordon–Taylor equation does not fit the other cases, and further studies are needed. The Gordon–Taylor equation is presented as follows:

TABLE III
Thermal Characteristics of P(HB6-ET4)/PEN and P(HB8-ET2)/PEN Blends from DSC Measurement

Code	T_g (K)	ΔC_p (J/gK)	T_c (K)	ΔH_c (J/g)	T_m (K)	ΔH_f (J/g)
PEN	393.4	0.372	472.8	45.1	542.0	56.5
P(HB6-ET4)/PEN69.8	386.2	0.248	438.5	29.7	534.4	54.1
P(HB6-ET4)/PEN62.0	383.6	0.206	424.2	22.0	529.0	43.6
P(HB6-ET4)/PEN44.4	373.6	0.104	409.6	2.9	516.9	24.7
P(HB6-ET4)/PEN12.5	367.0	0.104	397.6	4.3	486.1	10.2
P(HB6-ET4)	332.7	0.052	—	—	468.7	0.7
P(HB8-ET2)/PEN84.4	392.8	0.229	444.6	30.0	541.2	51.5
P(HB8-ET2)/PEN64.2	390.6	0.174	442.6	21.8	540.4	40.2
P(HB8-ET2)/PEN37.6	389.8	0.074	440.2	13.7	540.1	25.1
P(HB8-ET2)/PEN20.4	388.2	0.028	437.3	5.3	538.6	12.2
P(HB8-ET2)	341.8	0.036	—	—	559.5	0.1

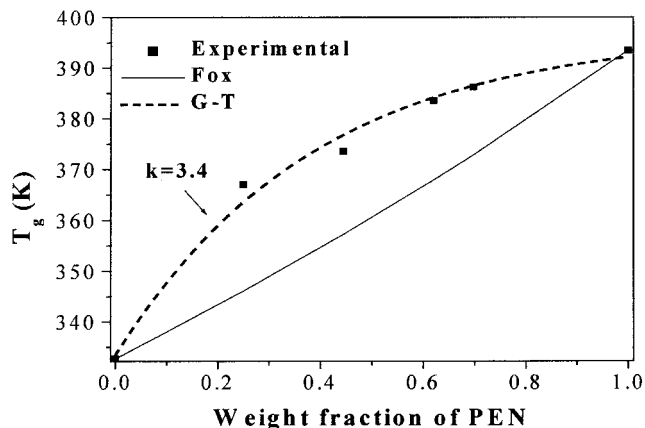


Figure 4 The composition dependence on the T_g predicted by the Fox equation and Gordon-Taylor equation in the P(HB6-ET4)/PEN blends.

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (2)$$

where w_i is the weight fraction of component i ; T_{gi} is the glass-transition temperature of component i ; and the numbers 1 and 2 represent P(HB6-ET4) and PEN, respectively. The symbol k is the empirical fitting parameter related to the strength of the interaction forces between the two components. It is known that a high k value is expected in the blends with restricted chain mobility as reported by Xing et al.³⁴ In this study, when k is about 3.4, the T_g is well matched with the experimental results.

Melting point depression

When certain blends are miscible, melting point depression may occur and it is a fundamental phenomenon in characterizing the corresponding blends. In general, thermodynamic considerations predict that the chemical potential decreases with the addition of miscible diluent. When one component is crystallizable, its decrease in chemical potential leads to a depression of the melting point. In most cases, melting point depression has been reported in amorphous polymer and crystalline polymer blends.^{30,34,40-42} Recently, however, there have been several reports about melting point depression in semicrystalline polymer pairs. Penning and Manley³³ reported the phenomenon in the solution blend of poly(vinylidene fluoride) and poly(1,4-butylene adipate). Wei and Tyan²⁶ also reported melting point depression in the solution blend of TLCP and PEN. This suggests that if the T_m of one blend component is significantly different than that of the other component, the component having a lower T_m plays a role of a diluent and decreases the melting temperature of the blends. In this work the P(HB6-ET4) has a lower T_m (468.7 K) with respect to

the pure PET (528.9 K) and PEN (542.0 K). However, P(HB8-ET2) has a higher T_m (559.5 K) compared with the pure PET and PEN. Therefore, a more favorable thermodynamic interaction between P(HB6-ET4) and PET (or PEN) was expected than between P(HB8-ET2) and PET (or PEN). Because our interest was focused on TLCs, the possible diluent effect of PET or PEN on P(HB6-ET4) and P(HB8-ET2) was not considered in this study.

Melting point depression is affected not only by thermodynamic factors but also by morphological effects such as crystal thickness and size.⁴³ To remove the morphological effects, the equilibrium melting temperature (T_m^0) was derived from the Hoffman-Weeks theory⁴⁴ represented as

$$T_m = \frac{T_c}{\gamma} + \left(1 - \frac{1}{\gamma}\right) \times T_m^0 \quad (3)$$

where T_c is the isothermal crystallization temperature, T_m^0 is the equilibrium melting temperature, and γ is the ratio of the initial to final lamellar thickness. The value of T_m^0 is obtained from intersecting the Hoffman-Weeks plot with the $T_m = T_c$ line. The results regarding P(HB6-ET4)/PET, P(HB8-ET2)/PET, and P(HB6-ET4)/PEN blends are shown in Figures 5(a,b) and 6(a). These figures show that melting point depression occurred with the addition of P(HB6-ET4) or P(HB8-ET2) to PET or PEN. As expected, P(HB6-ET4)/PET blends show greater melting point depression than P(HB8-ET2)/PET blends in Figure 5. Generally, when melting point depression takes place, crystals become imperfect and lamellar thickness is reduced.⁴⁵ In case of the P(HB8-ET2)/PEN blends in Figure 6(b), however, the T_m^0 remained almost constant or was a little depressed, if at all. This indicates that there might not be enough thermodynamic driving force necessary to cause melting point depression. Otherwise, it might be the reason that PEN and P(HB8-ET2) crystals were formed separately, because they were not affected by any crystallization temperature and composition.

The Flory-Huggins interaction parameter (χ_{12}), which represents miscibility of blends or mixtures, can be determined by using melting point depression. To determine the χ_{12} value, we made use of the Nishi-Wang approach,³⁰ which is expressed as

$$\frac{1}{T_m^0} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_2 V_1} \left[\frac{1n\phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1} \right) \times (1 - \phi_2) + \chi_{12} (1 - \phi_2)^2 \right] \quad (4)$$

where T_m^0 and T_m^0 are the equilibrium melting temperatures of the blends and PET (or PEN), respectively; ΔH_2 is the heat of fusion of 100% crystalline PET

(0.1176 kJ/g)⁴⁶ or PEN (25 kJ/g)⁴⁷; V_1 and V_2 are the molar volumes of the repeating unit of P(HB6-ET4) [or P(HB8-ET2)] and PET (or PEN), respectively; ϕ_1 and ϕ_2 are the volume fractions of P(HB6-ET4) [or P(HB8-ET2)] and PET (or PEN), respectively; and m_1 and m_2 are the degree of polymerization of P(HB6-ET4) [or P(HB8-ET2)] and PET (or PEN), respectively. When the molecular weight is large enough, it can be simplified to eq. (5).

$$\frac{1}{T_m^0} - \frac{1}{T_m} = - \frac{RV_2}{\Delta H_2 V_1} \chi_{12}(1 - \phi_2)^2 \quad (5)$$

Equation (5) is plotted in Figures 7 and 8. The plot for the P(HB6-ET4)/PET blends in Figure 7(a) has a line

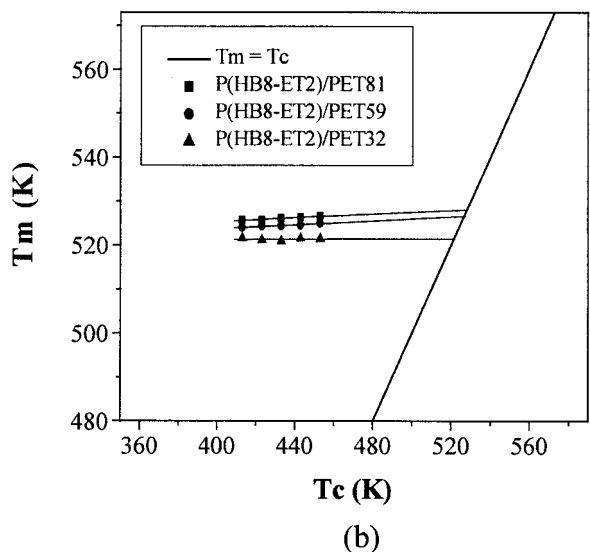
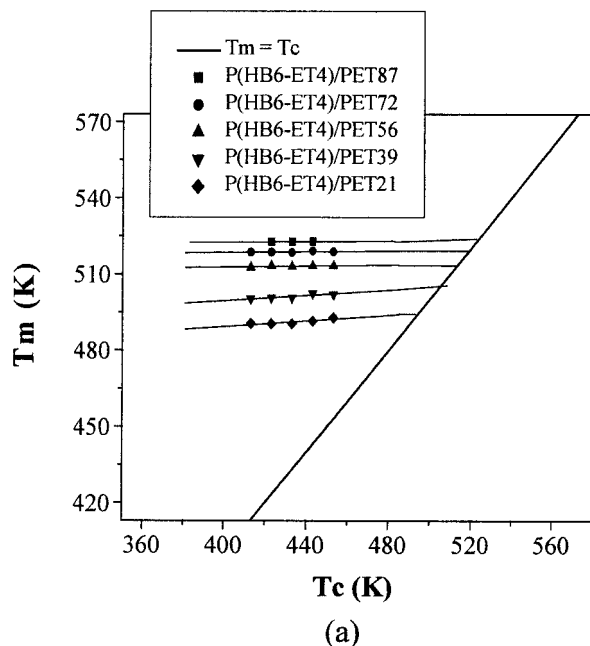


Figure 5 Hoffman-Weeks plots for (a) P(HB6-ET4)/PET and (b) P(HB8-ET2)/PET blends with various compositions.

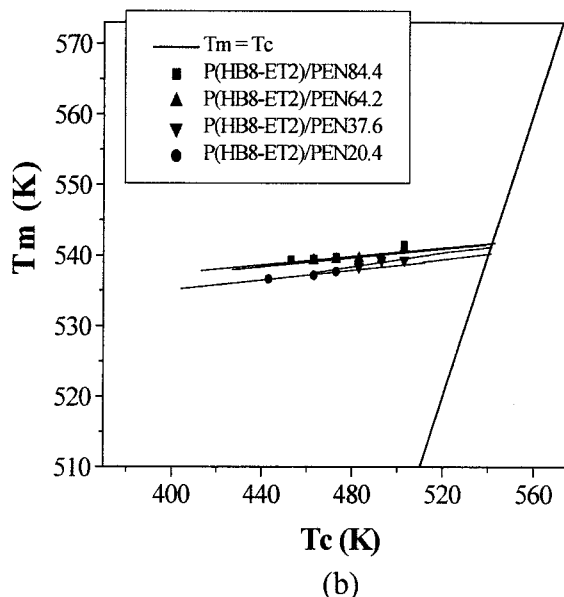
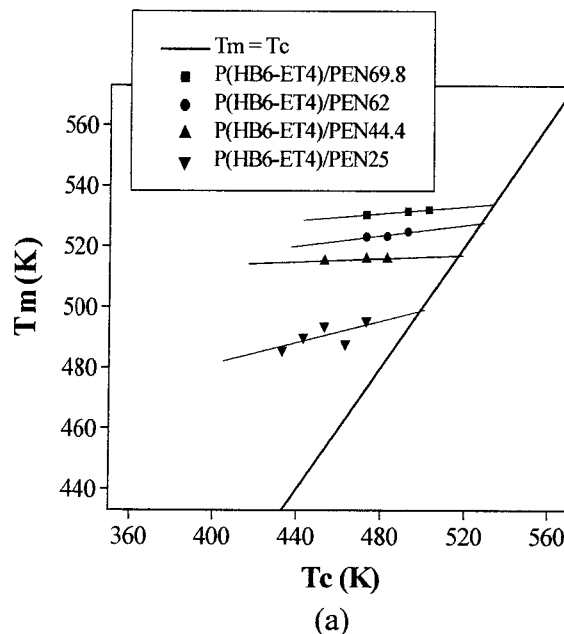


Figure 6 Hoffman-Weeks plots for (a) P(HB6-ET4)/PEN and (b) P(HB8-ET2)/PEN blends with various compositions.

passing through the experimental points where the χ_{12} value is calculated to -0.0196 . Likewise, the plots for the P(HB8-ET2)/PET blends in Figure 7(b) and the P(HB6-ET4)/PEN blends in Figure 8 have χ_{12} values of -0.0058 and -0.0003 , respectively. However, the χ_{12} value for P(HB8-ET2)/PEN was not achieved because of low melting point depression as shown in Figure 6(b). From the results above, P(HB6-ET4)/PET, P(HB8-ET2)/PET, and P(HB6-ET4)/PEN blends are thought to be partially miscible.^{24,40}

Transesterification and miscibility

In polyester blends, it is well established that various reactions may take place such as hydrolysis, alcohol-

ysis, and transesterification. Among these reactions, transesterification takes place the most frequently and dominantly because commercial thermoplastic polyesters have very high molecular weight and their end effect for chains can be neglected. Generally, the miscibility of the polyester blends is correlated with transesterification. Consequently, $^1\text{H-NMR}$ analyses were performed to investigate the structural differences in the blends with respect to the pure components.

There are two possible transesterification reactions in the P(HB-ET)/PET blends. One is between HB segments and pure PET; the other is between ET segments and pure PET. As depicted in Figure 9, the chemical shifts (δ) for the ethylene unit in the P(HB6-ET4)/PET blends fell within the range of 4.78 ppm for pure PET and 4.80 ppm for pure P(HB6-ET4) with δ of 4.79 ppm on average. In addition, the chemical shifts for the terephthalate unit in the blends moved down-

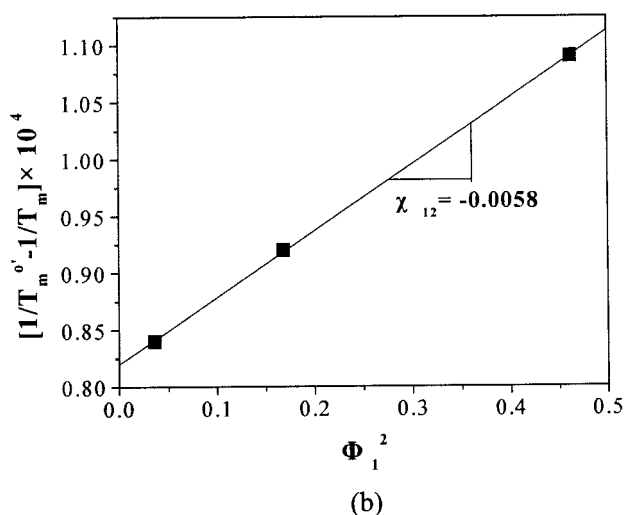
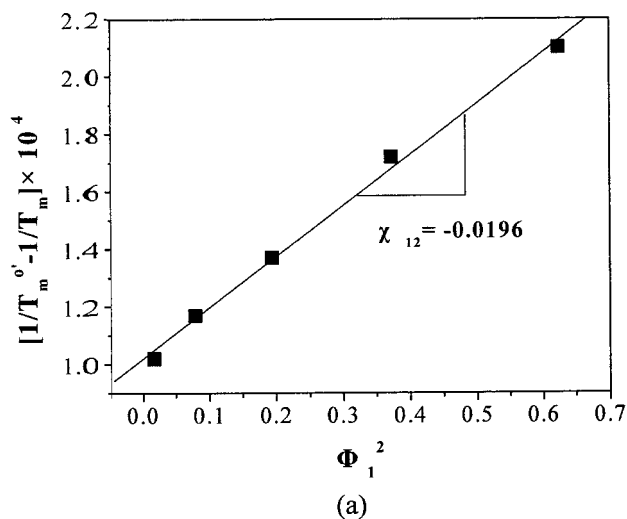


Figure 7 The Flory–Huggins interaction parameter (χ_{12}) employing melting point depression calculated from the Nishi–Wang approach for (a) P(HB6-ET4)/PET and (b) P(HB8-ET2)/PET blends.

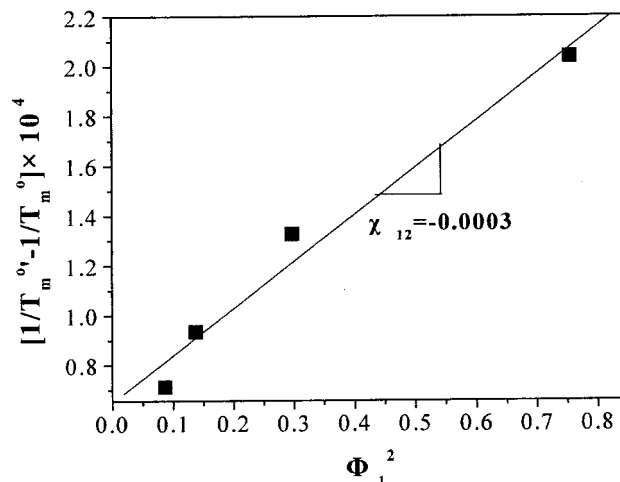


Figure 8 The Flory–Huggins interaction parameter (χ_{12}) employing melting point depression calculated from the Nishi–Wang approach for P(HB6-ET4)/PEN blends.

field with respect to pure PET with an average value of 8.13 ppm. However, no specific chemical shift was observed for HB segments and pure PET. In the P(HB8-ET2)/PET blends, the change of chemical shifts is the same as that of the P(HB6-ET4)/PET blends with the average values of 4.79 and 8.13 ppm as mentioned. Thus, it is concluded that transesterification occurred among esters in pure PET and P(HB6-ET4) or P(HB8-ET2). In this sense, P(HB6-ET4)/PET and P(HB8-ET2)/PET blends are thought to be partially miscible, which is in accordance with the results of the thermal analyses.

The transesterification study of P(HB6-ET4)/PEN is shown Figure 10. Provided that transesterification did not occur between HB segments in P(HB-ET)s and esters in PEN, the main transesterification would be between the ET segments in P(HB6-ET4) and the esters in pure PEN. As shown in Figure 10, new peaks at the ethylene unit were observed in the P(HB6-ET4)/PEN blends between 4.79 ppm for P(HB6-ET4) and 4.89 ppm for PEN with the δ of 4.83 ppm on average. This is the same as the transesterification between the pure PET and PEN. The δ values are in good agreement with the results reported by others.^{11,48–50} However, no new peak was generated for the P(HB8-ET2)/PEN blends, which was due to a very small content of ET segments in P(HB8-ET2) because transesterification seemed to not take place between the HB segment and PEN as noted. This indicates that the miscibility, if any, is limited to a great extent.

Morphology

To investigate the morphologies, FE-SEM images of the cryogenically fractured samples were obtained. In the P(HB6-ET4)/PET blends, LC droplets were dispersed in the matrix. As the content of P(HB6-ET4)

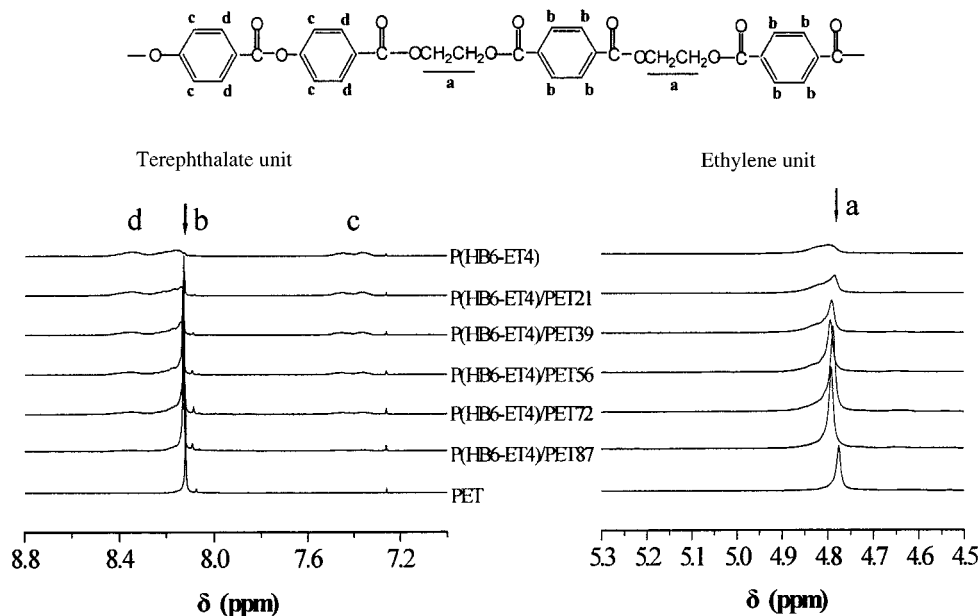


Figure 9 The $^1\text{H-NMR}$ spectra in the P(HB6-ET4)/PET blends.

increased, the size of the droplets increased and phase inversion occurred from the PET-rich to P(HB6-ET4)-rich phase. Droplet formation seems to be caused by both the internal mixer itself and the difference in the torque values between P(HB6-ET4) and PET. Simple shear flow seemed to be induced dominantly in the internal mixer and elongational flow was more or less limited. As a result, mainly LC droplets were formed and fibrils were not well developed. In Table IV the

total torque value of PET is 9.71 Nm and that of pure P(HB6-ET4) is 0.26 Nm, which is a very low value stemming from its LC phase. Obviously, the torque value is closely related to the melt viscosity. Because of the large difference in the torque value or melt viscosity, droplet formation was inevitable.

A cross-sectional view of an FE-SEM image for P(HB6-ET4)/PET56 is depicted in Figure 11 as an example with 10,000 \times magnification. The interface be-

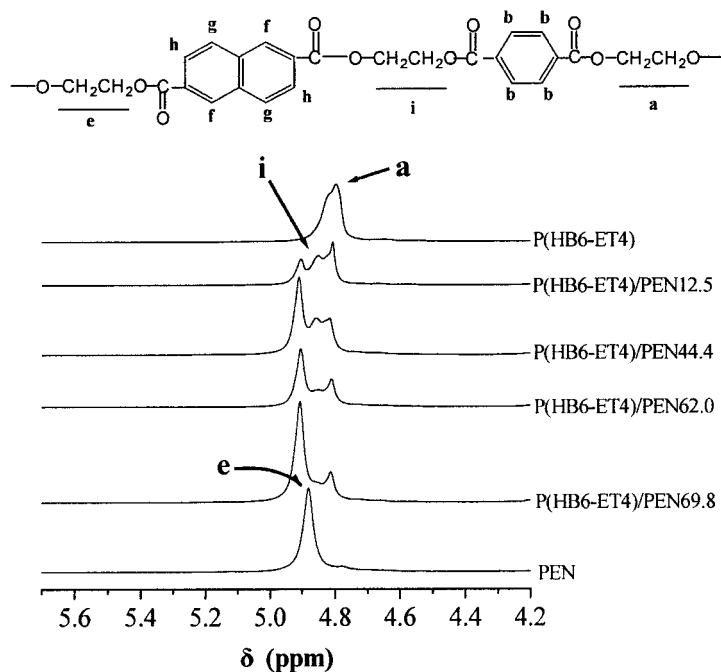


Figure 10 The $^1\text{H-NMR}$ spectra in the P(HB6-ET4)/PEN blends.

TABLE IV
Torque Values for Pure Materials During Mixing

	PET	PEN	P(HB6-ET4)	P(HB8-ET2)
TQ (Nm)	0.53	1.27	0.05	0.74
TTQ (Nm × time)	9.71	9.35	0.26	5.46

TQ; Final torque value in 5 min; TTQ; total torque value for 5 min during the mixing.

tween the droplets and matrix was not distinct (Fig. 11). The same trend of morphology was evident in P(HB8-ET2)/PET blends.

Likewise, cross-sectional views of cryogenically fractured samples for P(HB6-ET4)/PEN blends were examined. The morphologies were similar to those of P(HB6-ET4)/PET blends with dispersed droplets that were attributed to the reasons mentioned above. Therefore, irrespective of the miscibility, droplet formation was natural. To closely observe the interface between the droplets and matrix, the FE-SEM image magnified 10,000× is represented in Figure 12.

On the basis of the results above, it seems that P(HB6-ET4)/PET, P(HB8-ET2)/PET, and P(HB6-ET4)/PEN blends are partially miscible. Nevertheless, from the microscopic point of view, it is difficult to ascertain the degree of miscibility of the blends from the morphologies because even the P(HB8-ET2)/PEN blends have a similar ones. As mentioned, however, the melting point depression result for P(HB8-ET2)/PEN was not satisfactory. Others observed similar morphologies for the partially miscible blends between TLCPs and engineering polymers.^{27–29,51}

CONCLUSION

To investigate the miscibility in P(HB6-ET4)/PET, P(HB8-ET2)/PET, P(HB6-ET4)/PEN, and P(HB8-

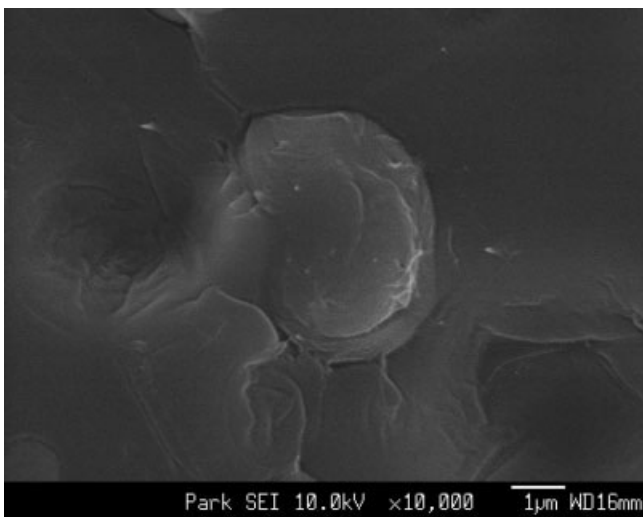


Figure 11 A cross-sectional view of the fractured surface of the FE-SEM micrograph of P(HB6-ET4)/PET56 (original magnification ×10,000).

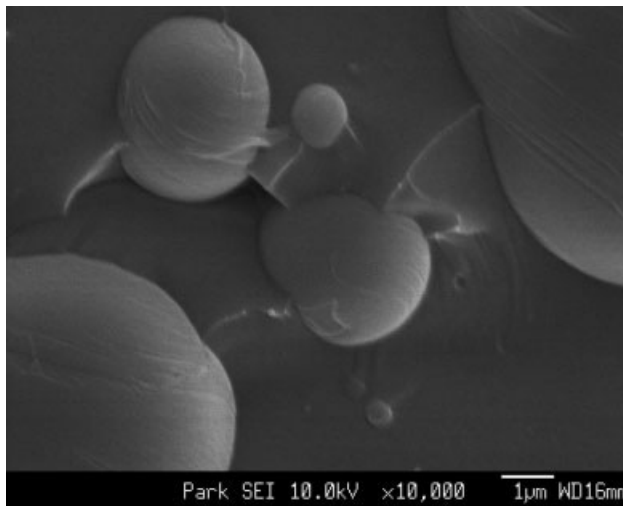


Figure 12 A cross-sectional view of the fractured surface of the FE-SEM micrograph of P(HB6-ET4)/PEN44.4 (original magnification ×10,000).

ET2)/PEN blends, DSC analyses were performed. The DSC results demonstrated that all the blends showed only a single T_g and its shift to some degree.

Equilibrium melting point depression was observed in all the blends except for the P(HB8-ET2)/PEN blends. The Flory–Huggins interaction parameter was calculated by applying the Nishi–Wang equation. The values were -0.0196 , -0.0058 , and -0.0003 for the P(HB6-ET4)/PET, P(HB8-ET2)/PET, and P(HB6-ET4)/PEN blends, respectively, which implies that those blends are partially miscible.

Transesterification was investigated from the $^1\text{H-NMR}$ study. In the P(HB6-ET4)/PET and P(HB8-ET2)/PET blends, δ of 4.78 ppm on average for the ethylene unit and 8.13 ppm for the terephthalate unit was observed. For the P(HB6-ET4)/PEN blends, a new chemical shift at 4.83 ppm was found between the chemical shifts of PET segments in P(HB6-ET4) and pure PEN.

The SEM morphologies showed that interfaces between the droplets and matrix were not apparent.

The authors acknowledge the support for this research by the Center for Advanced Functional Polymers.

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