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## Determination of interactions between aryl polyesters and poly(ether imide) via glass transition temperatures of separated phases in immiscible blends

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**Abstract** Phase behavior in domains of immiscible blends of poly(pentamethylene terephthalate)/poly(ether imide) (PPT/PEI) and poly(hexamethylene terephthalate)/poly(ether imide) (PHT/PEI) were investigated using differential scanning calorimetry (DSC). The measured glass transition temperature ( $T_g$ ) reveals that aryl polyesters dissolve more in the PEI-rich phase than the PEI does in the aryl polyester-rich phase, for both PPT/PEI and PHT/PEI systems. Additionally, optical microscopy supports the conclusion that PPT (or PHT) dissolves more in the PEI-rich phase than PEI does in the PPT-rich (or PHT-rich) phase in the aryl polyester/PEI blends. Furthermore, the Flory–Huggins interaction parameters ( $\chi_{12}$ ) for the PPT/PEI and the

PHT/PEI blends were calculated to be 0.12 and 0.17, respectively. For the blend systems comprising of PEI and homologous aryl polyesters, the value of  $\chi_{12}$  exhibits a trend of variation with respect to structure of aryl polyesters. For the PPT/PEI and PHT/PEI blends, investigated in this study, value of the polymer–polymer interaction parameter ( $\chi_{12}$ ) between the aryl polyester and the PEI was found to be positive, which increases with the number of methylene moieties in the repeating unit of the aryl polyester, ultimately resulting in phase separation observed.

**Keywords** Immiscible · Glass transition temperature · Aryl polyester · Flory–Huggins interaction parameter

### Introduction

Polymer blends, which comprise of various polymers with different characteristics, may provide a unique opportunity to develop a new polymer material as a flexible combination of various constituents. In particular, blends that contain a semicrystalline polymer and an amorphous polymer have potentially synergistically balanced properties. Over recent years, miscibility studies on blend systems of polyesters and polyetherimides have attracted extensive interest [1–6]. Aryl polyesters are an interesting class of semicrystalline polymers with favorable mechanical character-

istics and can be used for packaging and synthetic in fiber. Conversely, poly(ether imide) (PEI) is a high-performance engineering thermoplastic polymer known for its thermal stability, toughness, high  $T_g$ , and other excellent mechanical properties. However, its amorphous nature makes the chemical resistance of PEI poor. Accordingly, the blending of polyester and PEI is expected to provide great opportunities for balancing properties for particular applications. Similar studies of poly(ethylene terephthalate) (PET)/PEI [1,2], poly(trimethylene terephthalate) (PTT)/PEI [3, 4] and poly(butylenes terephthalate) (PBT)/PEI [5, 6] blends were reported in recent years. These works have aimed

to improve understanding of the morphology, crystallization, processing and properties of miscible blend systems. Notably, PET, PTT and PBT, which have two, three and four methylene moieties in the repeating unit, respectively, are linear aromatic polyesters with similar chemical structures.

The thermal analysis of polymer blends has shown that a miscible polymer blend exhibits a single glass transition temperature between the  $T_g$ s of the constituents [7–9], while, in partially miscible systems, the  $T_g$ s approach each other but do not become identical [10, 11]. Additionally, some investigators have used the specific heat increment ( $\Delta C_p$ ) at  $T_g$ , to examine the compatibility of polymer blends using differential scanning calorimetry [9, 12]. However, most polymer blends, whose morphology appears heterogeneous, are immiscible or partially miscible. Normally, the compatibility of different blended polymers follows from the interactions between various components. In earlier studies [12–15], several methods have been used to determine the thermodynamic polymer–polymer interaction parameter ( $\chi_{12}$ ) of a miscible blend, including melting point depression [12], vapor sorption [13], inverse-phase gas chromatography [14] and light-scattering methods [15]. Only a few methods that can be applied to incompatible polymer blends have been developed. For examples, Kim et al. [10] considered the thermal transition temperatures of polymers to study the polymer–polymer interaction parameter ( $\chi$ ) in partially miscible blend systems.

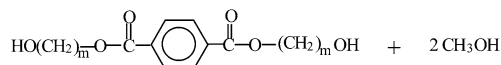
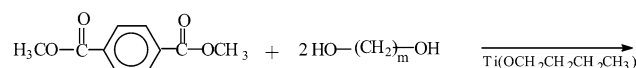
This study investigated the compatibility of blends of poly(pentamethylene terephthalate)/poly(ether imide) (PPT/PEI) and poly(hexamethylene terephthalate)/poly(ether imide) (PHT/PEI) by experimentally determining the glass transition temperature ( $T_g$ ) of the blends using differential scanning calorimetry, and the morphology of blends of aryl polyester and PEI is examined by optical microscopy. Moreover, the polymer–polymer interaction parameter ( $\chi_{12}$ ) in immiscible or partially miscible systems is determined by experimentally measuring the glass transition temperature. The results of this study can contribute to efforts to investigate how the number of methylene moieties in the repeating unit of the aryl polyester affects the compatibility of the aryl polyester/PEI blend systems.

## Experimental

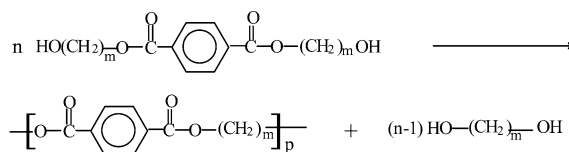
### Materials and sample preparation

Poly(pentamethylene terephthalate) (PPT) and Poly(hexamethylene terephthalate) (PHT) were synthesized from the appropriate glycol (1, 5-pentanediol for PPT; 1, 6-hexanediol for PHT) and dimethyl terephthalate using 0.1% butyl titanate as a catalyst by a two-step polymerization. Both PPT and PHT had been

### (1) Transesterification



### (2) Polycondensation

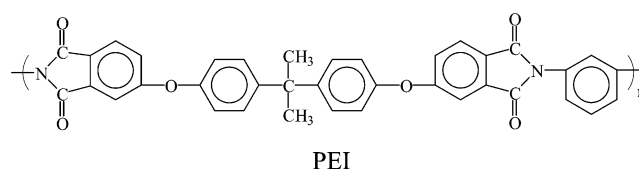


$m=5$  for poly(pentamethylene terephthalate)  
 $m=6$  for poly(hexamethylene terephthalate)

**Scheme 1** Synthetic pathways for PPT and PHT

synthesized in this laboratory earlier [16]; however, for better clarity, brief procedures are reiterated here as following. The first step was a transesterification process, and the second step involved polycondensation. The synthesis of PPT and PHT is illustrated as Scheme 1. The molecular weights of PPT and PHT were determined by GPC (Waters) using polystyrene as a standard. The weight-average molecular weights ( $M_w$ ) of PPT and PHT are 16,600 and 13,800 g/mol, respectively.

Poly(ether imide) (PEI) was a commercial-grade resin (Polysciences, Inc.,  $M_w = 30,000$  g/mol). The asymmetry of its chemical structure makes it amorphous, but it has a high  $T_g$  of 215.6°C because of the aromatic and imide rings in the backbone chains. Table 1 characterizes in details the polymers used in this study. The chemical structure of the repeating units of PEI is as follows.



Two methods of blend preparation were used. In PPT/PEI blends, direct melt-mixing (at 280°C) and co-precipitation were used to prepare the samples for comparison. In PHT/PEI blends, only co-precipitation was used because of the poor heat-resistance of PHT, according to thermogravimetric analysis (TGA) results. In direct melt-mixing, a specially designed aluminum mold with a small mixing chamber (with a capacity of about 2 g) was used for blending purposes. Heating was performed by mounting the mold on a hot stage and mixing was by manual stirring. Throughout the mixing,

**Table 1** Characterization of polymers used in this study

Polymer	$\overline{M}_n$ (g/mole)	$T_g$ (°C)	$\Delta C_p$ (J/g°C)	$\rho$ (g/cm <sup>3</sup> )	$m^c$
PPT	10,800	8.1	0.367	1.21 <sup>a</sup>	19.2
PHT	6,700	-2.0	—	1.31 <sup>a</sup>	11.0
PEI	17,000	215.6	0.263	1.27 <sup>b</sup>	28.7

<sup>a</sup>Van Krevelen [17]<sup>b</sup>Kuo et al. [3]<sup>c</sup> $m$  degree of polymerization

dry nitrogen was continuously purged over the mixing chamber to minimize degradation/oxidation. In co-precipitation, polymers were dissolved in chloroform at room temperature, yielding a 4% (w/w) solution. The blends were subsequently recovered by precipitating them in excess methanol. The precipitates were washed with a large quantity of hot water, and the residual solvent was removed in a vacuum oven at 80°C over 96 h.

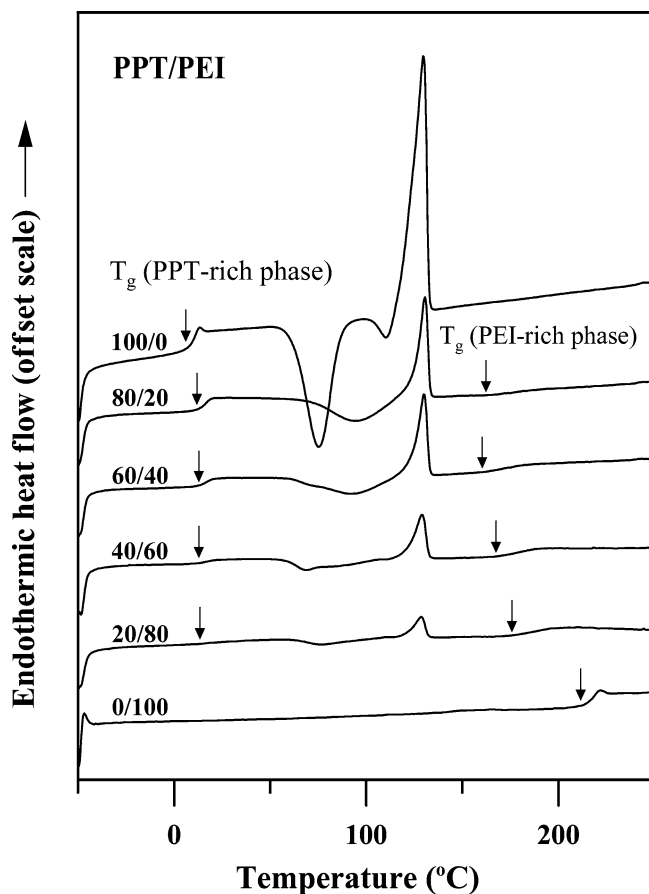
### Apparatus

The glass transition temperatures ( $T_g$ ) and apparent melting temperatures ( $T_m$ ) of the blend samples of various compositions were measured using a differential scanning calorimeter (Perkin–Elmer DSC-7) equipped with an intracooler (down to -50°C) and a computer for data acquisition/analysis. All measurements of  $T_g$  and  $T_m$  were made at a scan rate of 20°C/min following quenching from the melt at 320°C/min. The reported  $T_g$  values were taken as the temperatures of the onset of the glass transition (or the change in the specific heat) in the DSC thermograms, and the  $T_m$  values were taken as the peak of the endothermic.

## Results and discussion

### Thermal transition temperatures

Figure 1 shows thermograms of the melt-blended PPT/PEI with various compositions. Thermal analysis of PPT/PEI blends exhibited the two glass transition temperatures between the  $T_g$ s of the components; the  $T_g$ s approach each other but do not become identical. Apparently, PPT and PEI are immiscible or partially miscible, and two glass transition regions, designated by  $T_g$  (PPT) associated with PPT-rich regions, and  $T_g$  (PEI) associated with PEI-rich regions, are observed. Additionally, DSC thermograms of the samples were obtained by co-precipitation and comparison with thermal transition temperatures of blends using the method of melt-mixing of the PPT/PEI blends. Figure 2 plots the  $T_g$ -compositions of the PPT/PEI blends, which were prepared by the melt-mixing and co-precipitation approaches, respectively. One explanation of the difference



**Fig. 1** DSC traces for co-precipitated PPT/PEI blends of various compositions (wt. ratio), as indicated

between the two blending methods is that in co-precipitation blends, the difference between the solubility of polymers in the solvent and in the nonsolvent facilitates phase separation in the final precipitate. However, the effect of solubility is not apparent in the preparation of the PPT/PEI sample. Both figures exhibit similar trends of change in the thermal transition temperatures ( $T_{g,PEI}$ ,  $T_{g,PPT}$ , and  $T_{m,PPT}$ ) with composition. The  $T_g$ s of PPT in the PPT/PEI blends increase almost linearly with the PEI weight fraction in the figures; in contrast, the  $T_g$ s of PEI in the PPT/PEI blends fall as the PEI weight fraction in the figures declines. In the literature, similar studies of thermal analysis of polymer blends have shown that the  $T_g$ s of the immiscible systems approach

each other but do not become identical for the polycarbonate (PC)/poly(methyl methacrylate) (PMMA) [11, 18, 19], PC/polystyrene (PS) [18] and poly[(phenylene oxide)-co-(sulfonylated phenylene oxide)]/PS [20] blends. The crystallization behaviors, following glass transition, at PPT contents that exceed 20%, are indicated by a crystallization exotherm, whose crystallization temperature was also shown in Fig. 1. As the PEI content of the blend increases, the width of the exotherm increases, and the  $T_c$  measured at the minimum of the exotherm increases slightly. This fact indicates that a small quantity of PEI suppresses the crystallization of PPT from the glassy state, which could be expected to be partially miscible in the blend. Nevertheless, calorimetric scans of blends with PPT contents exceeding 20 wt% exhibit endothermic melting of PPT.  $T_m$  also slightly declined as the PEI content increases, as observed in Fig. 2. With small amounts of PEI present, thin crystalline lamellae were found to be located between thicker lamellae, forming spherulites in the PPT/PEI blends. This fact also demonstrates partial miscibility of the PPT/PEI blend [21, 22].

Figure 3 shows thermograms of the co-precipitated PHT/PEI blends of various compositions. Apparently, the PHT/PEI blends are also immiscible or partially miscible. In the experiment, the PHT/PEI samples were

first heated to 250°C for 5 min to eliminate fully the crystalline residues generated before the PHT/PEI samples undergo the thermal procedures.  $T_g$  and  $T_m$  were measured at a scan rate of 20°C/min, following quenching from melting at 320°C/min. However, the poly(hexamethylene terephthalate) (PHT) segment is easily re-arranged, promoting crystallization when the samples are quenched from the melting state. Finally, the  $T_g$  (PHT) associated with PHT-rich regions in the PHT/PEI blends is not as evident as the  $T_g$  (PEI) associated with the PEI-rich regions. Figure 4 plots the  $T_g$ -compositions of the PHT/PEI blends, which were prepared by co-precipitation methods. The PHT/PEI blends also exhibit a similar trend in thermal transition temperature ( $T_{g,PEI}$ ,  $T_{g,PHT}$ , and  $T_{m,PHT}$ ) as the PPT/PEI blends do. This observation suggests that the number of methylene moieties in the repeating unit of aryl polyester affect the compatibility of the aryl polyester/PEI blend systems. The above results demonstrate that the aryl polyester/PEI systems are immiscible when aryl polyester has more than five methylene moieties in the repeating unit. Given the above interesting findings,

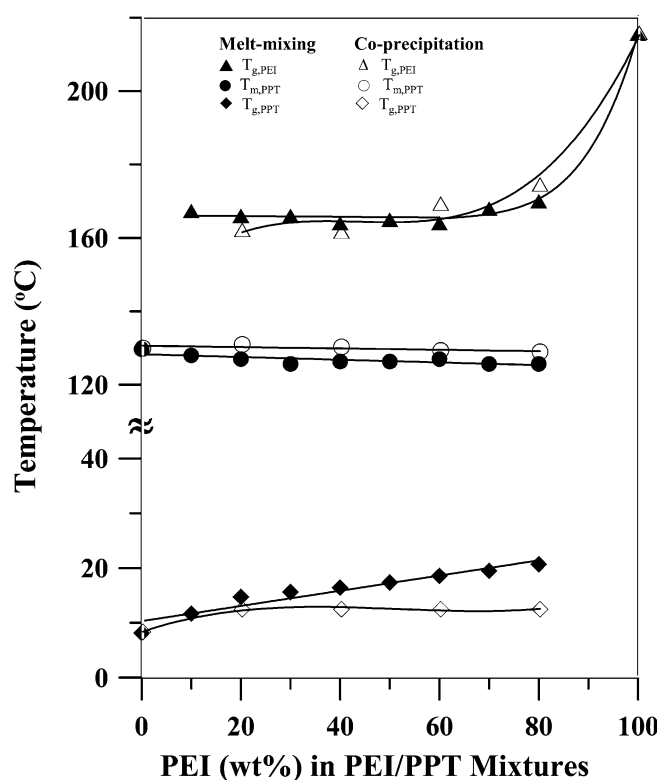


Fig. 2  $T_g$  and  $T_m$  versus composition plot of PPT/PEI blends by a melt-blending, b co-precipitation

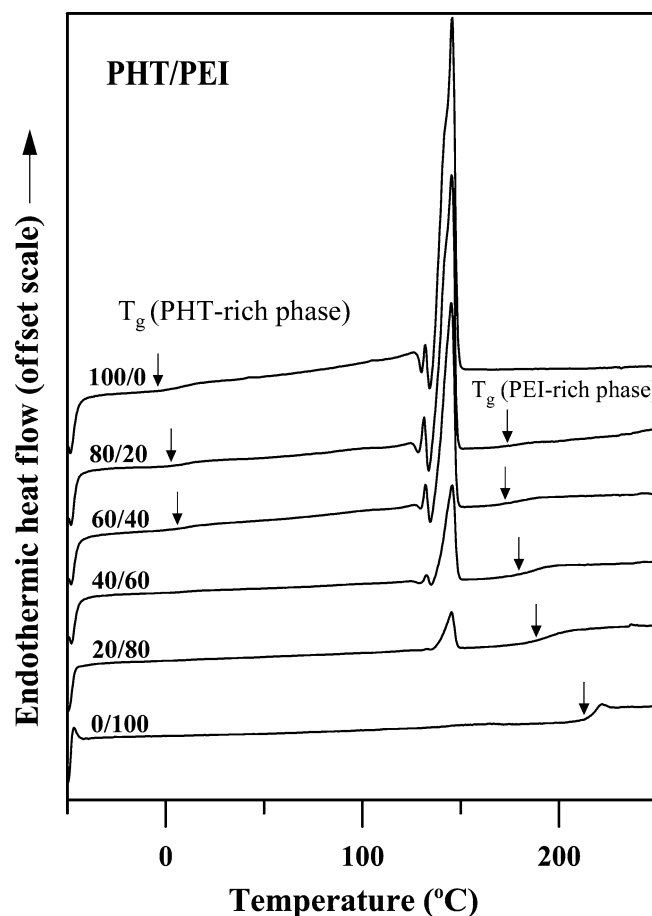


Fig. 3 DSC traces for co-precipitated PHT/PEI blends of various compositions (wt. ratios), as indicated

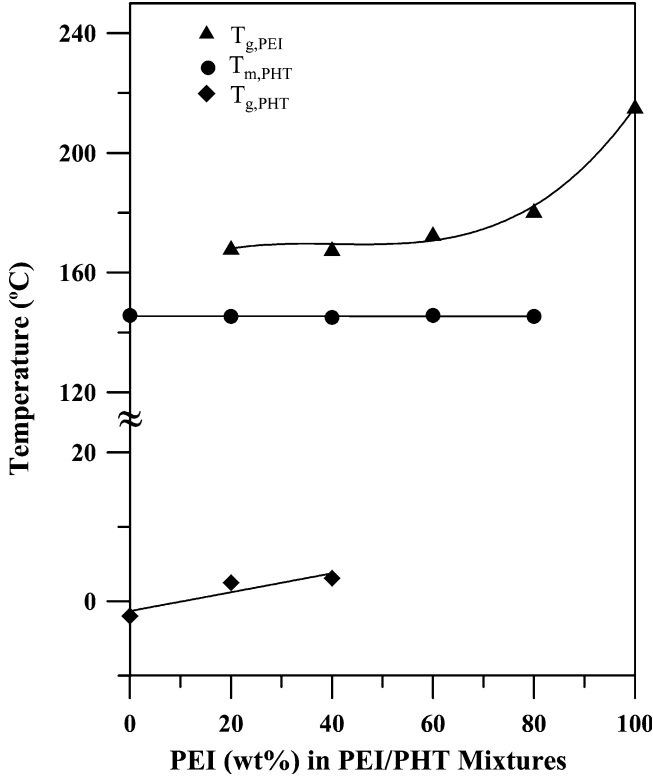


Fig. 4  $T_g$  and  $T_m$  versus composition plot of co-precipitated PHT/PEI blends

the compositions of the heterogeneous phase and the polymer-polymer interaction parameter ( $\chi_{12}$ ) between PPT/PEI and PHT/PEI blends will further be investigated in the following part.

#### Compositional analysis in the heterogeneous phase

The PPT/PEI and PHT/PEI blends are either fully immiscible or partially miscible at most. Two glass transition regions are observed: an aryl polyester-rich region, designated as  $T_g$  (aryl polyester), and PEI-rich region designated as  $T_g$  (PEI). The blends of compositions in the aryl polyester-rich regions contain a substantially larger amount of the aryl polyester phase and a smaller amount of the PEI phase. In the PEI-rich region, the blends also include a substantial amount of PEI and little amount of aryl polyester. Notably, the phase distribution is expected to be asymmetric, with the aryl polyester being more soluble in the PEI than the PEI in the aryl polyester in the aryl polyester/PEI blends. In the partially miscible blends, the calculated apparent weight fractions of the aryl polyester-rich phase ( $\omega_{1,I}$  and  $\omega_{2,I}$ ) and the PEI-rich phase ( $\omega_{1,II}$  and  $\omega_{2,II}$ ) were predicted using the Fox equation [23] and the Couchman equation [24].

The Fox equation is

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \quad (1)$$

where  $T_g$  is the observed  $T_g$  of the blend;  $\omega_1$  represents the weight fraction of polymer 1 with  $T_{g1}$ , and  $\omega_2$  ( $= 1 - \omega_1$ ) is the weight fraction of polymer 2 with  $T_{g2}$ . Equation 1 can be re-arranged to

$$\omega_1 = \frac{T_{g1}(T_g - T_{g2})}{T_g(T_{g1} - T_{g2})} \quad (2)$$

Both PPT/PEI and PHT/PEI blends exhibit discrete morphologies. For ease of treatments, the phase-heterogeneous blends can be considered to contain two separately homogeneous domains. Furthermore, the apparent weight fraction of the aryl polyester in the PEI-rich regions can be expressed as

$$\omega_{1,II} = \frac{T_{g1}(T_{g,II} - T_{g2})}{T_{g,II}(T_{g1} - T_{g2})} \quad (3)$$

where 1 and 2 refer to aryl polyester and PEI, respectively. I and II refer to the aryl polyester-rich phase and the PEI-rich phase, respectively.  $\omega_{1,II}$  is the apparent weight fraction of aryl polyester in the PEI-rich phase, and  $T_{g,II}$  is the observed  $T_g$  of PEI in the blends. Similarly, the apparent weight fraction of PEI in the aryl polyester-rich phase ( $\omega_{2,I}$ ) can be expressed as

$$\omega_{2,I} = \frac{T_{g2}(T_{g1} - T_{g,I})}{T_{g,I}(T_{g1} - T_{g2})} \quad (4)$$

The Couchman equation is given by

$$\ln T_g = \frac{\omega_1 \Delta C_{p1} \ln T_{g1} + \omega_2 \Delta C_{p2} \ln T_{g2}}{\omega_1 \Delta C_{p1} + \omega_2 \Delta C_{p2}} \quad (5)$$

where  $\Delta C_p = C_p^l(T_g) - C_p^s(T_g)$  is the difference between molar heat capacities at  $T_g$ , where  $C_p^l(T_g)$  is the molar heat capacity of the liquid polymer at  $T_g$  and  $C_p^s(T_g)$  is the molar heat capacity of the solid polymer at  $T_g$ . Equation 5 can be rearranged to

$$\omega_{1,II} = \frac{\Delta C_{p2}(\ln T_{g,II} - T_{g2})}{\Delta C_{p1}(\ln T_{g1} - \ln T_{g,II}) + \Delta C_{p2}(\ln T_{g,II} - \ln T_{g2})} \quad (6)$$

Similarly, the apparent weight fraction of PEI in the aryl polyester-rich phase ( $\omega_{2,I}$ ) can be expressed as

$$\omega_{2,I} = \frac{\Delta C_{p1}(\ln T_{g1} - \ln T_{g,I})}{\Delta C_{p1}(\ln T_{g1} - \ln T_{g,I}) + \Delta C_{p2}(\ln T_{g,I} - \ln T_{g2})} \quad (7)$$

Table 2 lists the apparent weight fractions of PPT and PEI in the PPT-rich phase and in the PEI-rich phase, which are determined from the Fox equation and the Couchman equation. The table shows similar apparent weight fractions for the two equations for the

**Table 2** Apparent weight fraction ( $\omega$ ) and polymer–polymer interaction parameter ( $\chi_{12}$ ) of co-precipitated PPT/PEI blends were determined from the Couchman equation and the Fox equation

PEI wt%	$T_{g,I}$ (°C) <sup>a</sup>	$T_{g,II}$ (°C)	Couchman equation			Fox equation		
			$\omega_{2,I}^b$	$\omega_{1,II}$	$\chi_{12}^c$	$\omega_{2,I}$	$\omega_{1,II}$	$\chi_{12}$
0	8.1	—	—	—	—	—	—	—
20	12.3	161.9	0.037	0.161	0.125	0.034	0.167	0.125
40	12.3	161.4	0.037	0.162	0.125	0.034	0.169	0.125
60	12.3	169.1	0.037	0.137	0.127	0.034	0.143	0.127
80	12.3	174.3	0.037	0.120	0.129	0.034	0.125	0.130
100	—	215.6	—	—	—	—	—	—

<sup>a</sup>I and II denote PPT-rich phase and PEI-rich phase, respectively

<sup>b</sup> $\omega_{2,I}$  is weight fraction of PEI in PPT-rich phase, and  $\omega_{1,II}$  is weight fraction of PPT in PEI-rich phase

<sup>c</sup>All  $\chi_{12}$ s were calculated from Eq. 8

PPT/PEI blends of the same composition. Apparently, the weight fraction of PPT dissolved in the PEI-rich phase ( $\omega_{1,II}$ ) exceeds that of the PEI component dissolved in the PPT-rich phase ( $\omega_{2,I}$ ) in the PPT/PEI blends. In the PHT/PEI blends, PHT crystallizes and quenches from the melting state, because the PHT segment is easily rearranged during cooling, reducing the specific heat increment ( $\Delta C_p$ ) in the experiment. Table 3 presents the predicted apparent weight fractions of PHT and PEI in the PHT-rich phase and in the PEI-rich phase, using the Fox equation, to avoid experimental errors. Similarly, in the PHT/PEI blends, the weight fraction of PHT dissolved in the PEI-rich phase ( $\omega_{1,II}$ ) exceeds that of the PEI component dissolved in the PHT-rich phase ( $\omega_{2,I}$ ). The weight fractions of PPT and PHT dissolved in the PEI-rich phase ( $\omega_{1,II}$ ) appear to exceed the weight fraction of the PEI component dissolved in the PPT-rich phase and PHT-rich phase ( $\omega_{2,I}$ ), as indicated in Tables 2 and 3, respectively. According to the result, Figs. 1, 2, 3 and 4 reveal that as the weight fraction of the aryl polyester increases, the fall of  $T_g$  (PEI-rich region) is very significant. It is even more significant than the increase in  $T_g$  (aryl polyester-rich region) as the weight fraction of PEI increases.

#### Polymer–polymer interaction parameter of aryl polyester/PEI blends

The Flory–Huggins polymer–polymer interaction parameter ( $\chi_{12}$ ) can be estimated if the system is at equilibrium [10].

where  $\phi$  represents the volume fraction of the component, which can be determined from  $\omega/\rho$ ;  $m$  is the degree of polymerization of the polymer, and is defined as

$$m = \frac{\bar{M}_n}{\rho} / V_r \quad (9)$$

$\bar{M}_n$  is the number-average molecular weight, and  $\rho$  is the density of the polymer. In this study,  $V_r$ , the reference molar volume of the repeat unit in PEI is 466.2 cm<sup>3</sup>/mol. The degrees of polymerization of the PPT, PHT and PEI are obtained from Table 1. The values  $m_{PPT} = 19.2$ ,  $m_{PHT} = 11$  and  $m_{PEI} = 28.7$  were used for PPT, PHT and PEI, respectively.

In Table 2, the values of  $\chi_{12}$  are compared among the various treatments of the PPT and PEI components using the Fox equation and the Couchman equation. Table 2 reveals that  $\chi_{12}$  are 0.12 ± 0.01. By comparison,  $\chi_{12}$  obtained from the Fox equation agrees closely with those obtained from the Couchman equation. For the PHT/PEI blends,  $\chi_{12}$  was determined to be 0.17 ± 0.01 according to the Fox equation, as stated in Table 3. The positive values of  $\chi_{12}$  indicate the observed immiscibility of the two blends. In the aryl polyester/blends, the values of  $\chi_{12}$  between PPT and PEI are smaller than those between PHT and PEI because the PPT/PEI blends interact more strongly than the PHT/PEI blends. Interestingly, some relationship exists between the methylene moiety in the repeat unit of the aryl polyester and the polymer–polymer interaction parameter ( $\chi_{12}$ ). Table 4 presents  $\chi_{12}$  between aryl polyester and PEI, for a series of aryl polyesters with various methylene moieties in the repeating unit ( $m = 2 \sim 6$ ). For the aryl polyester/PEI blends, the polymer–polymer interaction parameter ( $\chi_{12}$ )

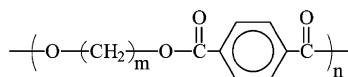
$$\chi_{12} = \frac{(\phi_{1,I}^2 - \phi_{1,II}^2)[m_2 \ln(\phi_{1,II}/\phi_{1,I}) + (m_1 - m_2)(\phi_{2,I} - \phi_{2,II})] + (\phi_{2,I}^2 - \phi_{2,II}^2)[m_1 \ln(\phi_{2,II}/\phi_{2,I}) + (m_2 - m_1)(\phi_{1,I} - \phi_{1,II})]}{2m_1m_2(\phi_{1,I}^2 - \phi_{1,II}^2)(\phi_{2,I}^2 - \phi_{2,II}^2)} \quad (8)$$

**Table 3** Apparent weight fraction ( $\omega$ ) and polymer–polymer interaction parameter ( $\chi_{12}$ ) of co-precipitated PHT/PEI blends were determined from the Fox equation

PEI wt%	$T_{g,I}$ (°C) <sup>a</sup>	$T_{g,II}$ (°C)	$\omega_{2,I}^b$	$\omega_{1,II}$	$\chi_{12}^c$
0	−2.0	—	—	—	—
20	2.5	168.4	0.037	0.133	0.175
40	3.1	168.0	0.041	0.134	0.173
60	5.0	173.0	0.057	0.119	0.173
80	5.7	180.8	0.062	0.096	0.180
100	—	215.6	—	—	—

<sup>a</sup>I and II denote PHT-rich phase and PEI-rich phase, respectively<sup>b</sup> $\omega_{2,I}$  is weight fraction of PEI in PHT-rich phase, and  $\omega_{1,II}$  is weight fraction of PHT in PEI-rich phase<sup>c</sup>All  $\chi_{12}$ s were calculated from Eq. 8**Table 4** Polymer–polymer interaction parameter ( $\chi_{12}$ ) between aryl polyester and PEI for a series of aryl polyesters

Aryl polyester/PEI blends	$T_g$ of polyester (°C)	$\chi_{12}$	Compatibility
PET/PEI	76.0	−0.66 <sup>a</sup>	Miscible
PTT/PEI	42.8	−0.10 <sup>b</sup>	Miscible
PBT/PEI	32.0	−0.62 <sup>c</sup>	Miscible
PPT/PEI	8.1	0.12	Immiscible
PHT/PEI	−2.0	0.17	Immiscible

<sup>a</sup>Martinez et al. [1]<sup>b</sup>Wu and Woo [4]<sup>c</sup>Woo and Yau [5]

m = 2 PET

m = 3 PTT

m = 4 PBT

m = 5 PPT

m = 6 PHT

between the aryl polyester and PEI increases with the number of methylene moieties in the repeating unit of the aryl polyester, causing a morphological change from a homogeneous phase to heterogeneous phase, indicating that more methylene moieties in the repeating unit of the aryl polyester weaken the interaction between the aryl polyester and PEI. In the aryl polyester/PEI blends, the dipole–dipole ( $-C=O \cdots OCN-$ ) interaction between the carbonyl group of PET and the imide ring of PEI increases the miscibility of the aryl polyester/PEI blends [25]. The structure of aryl polyester reveals that increasing number of methylene moieties in the repeating unit decreases the density of the carbonyl groups and, ultimately, reduces the dipole–dipole interaction between aryl polyester and PEI. Finally, phase separation in the PPT/PEI blends and the PHT/PEI blends is observed.

## Conclusion

A heterogeneous phase is observed in both the PPT/PEI blends and the PHT/PEI blends, and the compositions of each phase were obtained, where two  $T_g$ s were determined. They are  $T_g$  (aryl polyester) associated with

the aryl polyester-rich regions, and  $T_g$  (PEI) associated with PEI-rich regions, respectively. The  $T_g$  (PEI) for PPT/PEI blends declined more quickly as the PPT weight fraction increased, as also evidenced by the thermograms for the PHT/PEI blends. Although the heterogeneous regions are present in both PPT/PEI and PHT/PEI blends, the DSC thermograms reveal that some of the PPT (or PHT) is dissolved in the PEI-rich phase, and some of the PEI is dissolved in the PPT-rich (or PHT-rich phase). The above  $T_g$  at various blend compositions indicates that PPT (or PHT) dissolves more in the PEI-rich phase than PEI does in the PPT-rich (or PHT-rich) phase. Calculation results indicate that the apparent weight fraction of the PPT (or PHT) component in the PEI-rich phase exceeds that of the PEI component in the PPT-rich (or PHT-rich) phase. The behavior of  $T_g$  of the blend with various compositions demonstrates that compatibility increases more in regions rich in PEI than in the regions rich in aryl polyester. Moreover, the polymer–polymer interaction parameter ( $\chi_{12}$ ) between PPT/PEI and PHT/PEI blends was calculated and found to be 0.12 and 0.17, respectively. A comparison with a series of aryl polyester ( $m=2\sim6$ ) reveals that the increase in the number of

methylene moieties in the repeating unit of the aryl polyester weakens the interactions between the aryl polyester and PEI, reducing the compatibility between the aryl polyester/PEI blends.

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