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ORIGINAL CONTRIBUTION

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Miscibility and transesterification in ternary blends of poly(ethylene naphthalate)/poly(trimethylene terephthalate)/poly(ether imide)

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Abstract Miscibility and morphology of poly(ethylene 2,6-naphthalate)/poly(trimethylene terephthalate)/poly(ether imide) (PEN/PTT/PEI) blends were investigated by using a differential scanning calorimeter (DSC), optical microscopy (OM), wide-angle X-ray diffraction (WAXD), and proton nuclear magnetic resonance (^{1}H-NMR). In the ternary blends, OM and DSC results indicated immiscible properties for polyester-rich compositions of PEN/PTT/PEI blends, but all compositions of the ternary blends were phase homogeneous after heat treatment at 300 °C for more than 30 min. An amorphous blend with a single T_g was obtained in the final state, when samples were annealed at 300 °C. Experimental results from ^{1}H-NMR identified the production of PEN/PTT copolymers by so-called transesterification. The influence of transesterification on the behaviors of glass transition and crystallization was discussed in detail. Study results identified that a random copolymer promoted the miscibility of the ternary blends. The critical block lengths for both PEN and PTT hindered the formation of crystals in the ternary blends. Finally, the transesterification product of PEN/PTT blends, ENTT, was blended with PEI. The results for DSC and OM demonstrated the miscibility of the ENTT/PEI blends.

Keywords Miscibility · Morphology · Ternary blends · Transesterification · Copolymer

Introduction

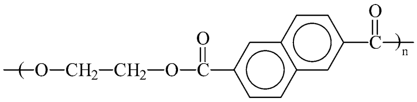
Multicomponent blends are gaining an important share in the field of polymer property diversification through blending. In ternary blends, a third component is usually added to an immiscible pair to achieve miscibility in cases where the third component is miscible with each of the other two polymers as a result of hydrogen bonding or van der Waals physical forces [1–3]. Additionally, miscibility and phase homogeneity in polymer blends are enhanced owing to chemical interactions in the ternary blends. Poly(trimethylene terephthalate) (PTT) is an interesting class of semicrystalline polymers that possess good mechanical properties and are applied as a material for film, fiber and engineering thermoplastic. Above all, naphthalene groups in the repeated structure of poly(ethylene 2,6-naphthalate) (PEN) provide rigidity to the polymer backbone, elevate the transition temperature for glass and enhance its mechanical properties. On the contrary, poly(ether imide) (PEI) is amorphous and serves as a high-performance engineering thermoplastic polymer known for its thermal stability, toughness, high T_g, among other excellent mechanical properties; its one shortcoming is its weakness against organic solvents. In the literature [4–6], binary blends comprising a semicrystalline polymer and an amorphous polymer have been widely investigated and offer a potential, synergistic balance of polymer properties. The PEN/PEI blends have been reported to be completely miscible over the whole composition range. In the UCST phase diagram, PEN/PEI blends exhibited simultaneous liquid–liquid phase separation and crystallization [4, 5]. In aryl polyester/PEI blends, Woo et al. [6, 7] reported discontinuity and asymmetry in the T_g-composition relationship for miscible PTT/PEI blends, which were attributed to the PTT crystalline domain-induced variations in the intermolecular interactions. Nevertheless, a significant amount of research has been directed at gaining a better understanding of miscibility, crystallization, mechanical properties, and processing of the blend system comprising PEI and other aryl polyesters (PET and PBT) [8–10]. Blends of aryl polyester and PEN obtained by solvent precipitation are immiscible and, when the extent of transesterification reaches 50% of the completely randomized state independent of blend composition, the blends show a single glass transition temperature between those of starting polymers [11–18]. Given that the process is not completely understood, previous literature suggests three possible mechanisms: alcoholysis, acidolysis, or direct ester exchange [13, 15, 18]. Whatever mechanism is at work, it is generally agreed that the interchange reactions first lead to the formation of block copolymers, and then random copolymers that promote the miscibility of the blend [13]. Studies of miscibility and transesterification in blends of polycarbonate (PC) and aryl polyester [19–21], as well as PC and tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) identified that transesterification plays an important role in these systems [22].

As expected, the transesterification reactions also occur between PEN and PTT in the ternary PEN/PTT/PEI blends which include two polyesters with different repeating structures. In this study, the effects of transesterification on the miscibility of ternary systems are examined by using a differential scanning calorimeter (DSC) and optical microscope (OM) techniques. The relationship between crystallization and transesterification was also evaluated by employing wide angle X-ray diffraction (WAXD). Furthermore, the sequence distribution and degree of randomness for the copolyesters (ENTT), transesterification products of PEN/PTT, were studied by applying high-resolution nuclear magnetic resonance (^{1}H-NMR).

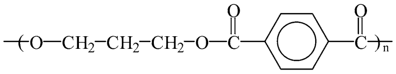
Experimental

Materials

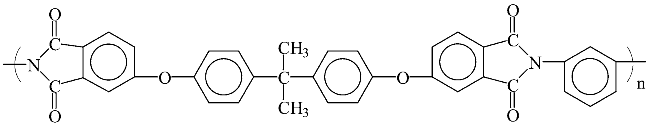
Poly(ethylene naphthalate) (PEN) was purchased from Aldrich Inc. with $M_w = 43{,}000$. Poly(trimethlene terephthalate) (PTT) was synthesized as a research-grade resin with $M_w = 58{,}000$ and supplied by Industrial Technology Research Institute (ITRI). Poly(ether imide) (PEI) was obtained from Polysciences Inc. with $M_w = 30{,}000$. The chemical structures of the repeating units of PEN, PTT and PEI are shown as the following.



PEN



PTT



PEI

Co-precipitation was applied to produce ternary PEN/PTT/PEI blends. Polymers of various fractions were co-dissolved in dichloroacetic acid at 120 °C to yield a 4% (w/w) solution and then precipitated in an excess volume of methanol. The blends were washed with a large amount of hot water, and left to dry at 60 °C for several days. Residual solvent was then removed from the blends after being left in a vacuum oven at 80 °C for about 1 week.

Apparatus

The ^{1}H-NMR analysis of the blend was performed at room temperature by applying a Bruker AMX-400 NMR spectrometer operating at 400.13 MHz. The blend was dissolved in a 1/9 (v/v) mixture of deuterated trifluoroacetic acid (CF_3COOD)/deuterated chloroform ($CDCl_3$) solution. The central peak of $CDCl_3$ was assigned as 7.27 ppm with respect to tetramethylsilane (TMS) as the internal standard.

The thermal behaviors of blend samples were measured with a differential scanning calorimeter (Perkin-Elmer DSC-7) equipped with an intracooler. The glass transition temperature (T_g), cold-crystallization temperature (T_{cc}) and melting temperature (T_m) were each measured at 20 °C/min after heat treatment at 300 °C for a desired period of time. The obtained T_g values were taken as the onset of the glass transition (i.e., change in the specific heat) in the DSC thermograms.

A polarized-light optical microscope (POM) (Nikon Optiphot-2 POL) with UFX-DX automatic exposure was used to examine and confirm the phase structure of the polymer mixtures. Samples for microscopy were placed between two micro glass slides, then heated and gently pressed by hand to reduce film thickness for the microscopic heating stage (Linkam THMS-600 with a TP-92 temperature programmer).

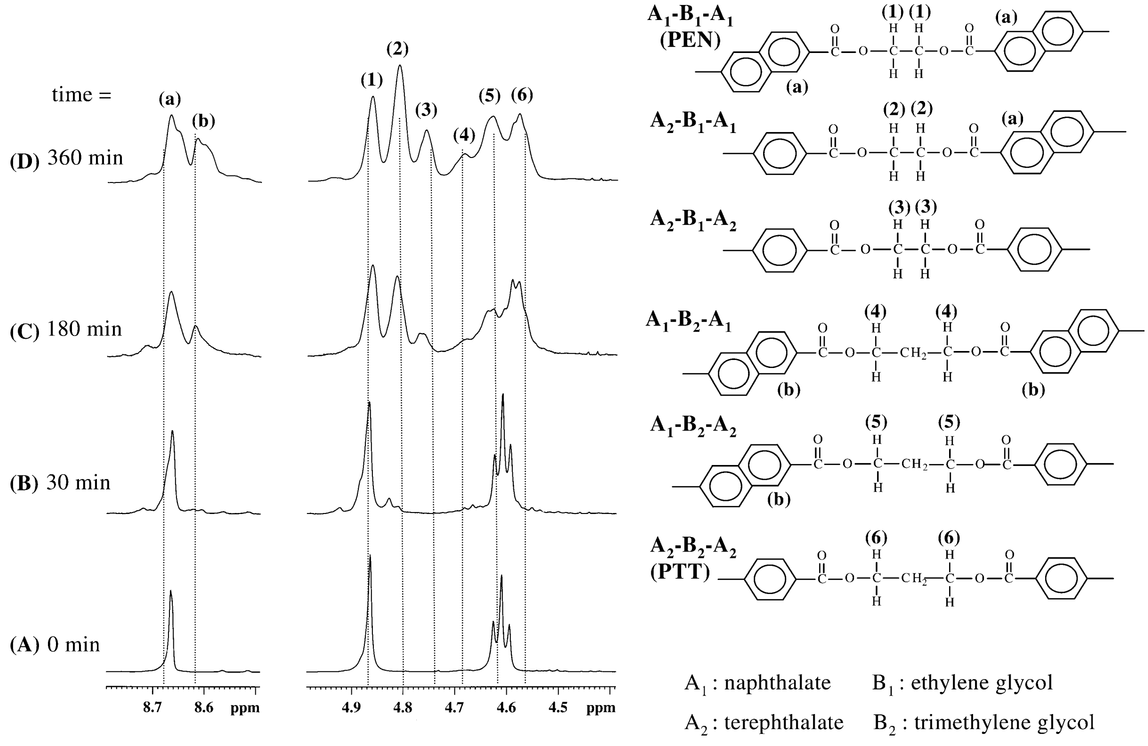
The WAXD experiments were performed with a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα X-rays at a voltage of 40 kV and a 30 mA current in the 2θ range of 5–35° with a step scanning of 2°/min. The blends encapsulated in DSC cells were heat treated at 300 °C for different time periods, then quickly transferred to the microscopic heating stage, preheated to 200 °C, for 8 h to attain maximum crystallinity. The DSC cells were then opened and the crystallized blends were subjected to WAXD measurements.

Results and discussion

NMR analysis

In the PEN/PTT/PEI blends, the interchange reaction in the carbonyl group of PEN and PTT resulted in the change in chemical shift and intensity of the methylene moieties and naphthalate proton resonances in the copolyesters. The extent of interchange of the blends was determined by using the methylene moieties region of the ^{1}H-NMR spectrum. Figure 1 shows the proton NMR spectrums of the PEN/PTT/PEI blends after different annealing time periods at 300 °C. The PEN peaked at approximately 4.87 ppm, while the peak for PTT occurred at approximately 4.60 ppm. This region of the NMR spectrum for a mixture of the two homopolymers prepared in solution (no interchange reaction) is shown in Fig. 1a. During the start of transesterification, all the methylene moieties proton resonances (4.55–4.90 ppm) of the PEN/PTT copolyesters were split into multiplets as a result of the six possible environments for ethylene and trimethylene units: A_1-B_1-A_1, A_2-B_1-A_1, A_2-B_1-A_2, A_1-B_2-A_1, A_1-B_2-A_2, and A_2-B_2-A_2, where A_1 and A_2 represent naphthalate and terephthalate units, respectively, and B_1 and B_2 represent ethylene units and trimethylene units, respectively, as shown in Fig. 1. In this figure, new ethylene proton signals, such as A_2-B_1-A_1, A_2-B_1-A_2, were caused by the substitution of a terephthalate unit for a naphthalate unit. Additionally, new trimethylene proton signals, such as A_1-B_2-A_1, A_1-B_2-A_2, were also identified, which were caused by the substitution of a naphthalate unit for a terephthalate unit. As PEN and PTT reacted, an increasing number of terephthalate-ethylene-naphthalate (A_2-B_1-A_1), terephthalate-ethylene-terephthalate (A_2-B_1-A_2), naphthalate-trimethylene-naphthalate (A_1-B_2-A_1), and naphthalate-trimethylene-terephthalate (A_1-B_2-A_2) residues were found in the blend; the concentration of PEN and PTT decreased with increases of reaction time. The ^{1}H-MMR signals from these units was at 4.82, 4.77, 4.68, and 4.63 ppm and was easily differentiated from

Fig. 1 ^{1}H-NMR of PEN/PTT/PEI = 33/33/33 with assignment of the main peaks after different reaction times at 300 °C: time **a** 0 min, **b** 30 min, **c** 180 min, **d** 360 min



the resonance of the A_1-B_1-A_1 (4.87 ppm) and A_2-B_2-A_2 (4.61 ppm) sequences. Moreover, changing the methylene moieties caused the new proton resonance (8.62 ppm) signals for naphthalate units, including A_1-B_2-A_1 and A_1-B_2-A_2. In the copolyesters, experimental results indicated that the amount of hetero units in the copolyesters increased. Additionally, the interchange reactions led initially to the formation of block copolyesters and, then, to random copolyesters in the ^{1}H-NMR spectrums.

Analyzing sequence distribution

In the PEN/PTT/PEI blends, transesterification played a significant role in the formation of block or random copolyesters between PEN and PTT. The transesterified polymers were analyzed by using ^{1}H-NMR. The NMR data were applied to calculate the randomness factors and average sequence lengths, as transesterification progresses, of the terephthalate and naphthalate sequences in the copolymers. The amplitude of these A_2-B_1-A_1, A_2-B_1-A_2, A_1-B_2-A_1, and A_1-B_2-A_2 signals was in direct proportion to the mole fractions for A_2-B_1-A_1, A_2-B_1-A_2, A_1-B_2-A_1, and A_1-B_2-A_2 sequences in the polymer. Furthermore, the signal amplitudes for the A_1-B_1-A_1 and A_2-B_2-A_2 sequences in the original unreacted mixtures were direct measures of their mole fraction compositions in the polyester mixtures. Devaux et al. [18] investigated the sequence distribution and randomness of copolyester by using NMR to identify the transesterification in bisphenol-A polycarbonate (PC) and poly(butylenes terephthalate) (PBT). In this study, only copolycondensates resulting from an exchange reaction in two linear polycondensates PEN and PTT possess such a high degree of polymerization, explaining why the chain ends are neglected in the calculation. Mole fractions for naphthalate (F_N) and terephthalate (F_T) groups were defined by the concentration ratios

$$F_N = \frac{A_{8.67}}{A_{2.38} + A_{8.67}} \tag{1}$$

$$F_T = \frac{A_{2.38}}{A_{2.38} + A_{8.67}} \tag{2}$$

where $A_{8.67}$ and $A_{2.38}$ represent the area of characteristic peak for naphthalate and trimethylene glycol, respectively. Furthermore, the mole fraction of$F_{A_iB_jA_k}$ can be calculated from the area of characteristic peak between 4.5 and 5.0 ppm, respectively, and can be defined as

$$F_iB_jA_k = \frac{A_iB_jA_k}{\sum_{i,j,k=1}^{2} A_iB_jA_k} \tag{3}$$

The mole fractions of A_1 B_1 A_1, and A_2 B_2 A_2 can be expressed as

$$F_{A_1B_1A_1} = \frac{A_{A_1B_1A_1}}{A_{A_1B_1A_1} + A_{A_2B_1A_1} + A_{A_2B_1A_2} + A_{A_1B_2A_1} + A_{A_1B_2A_2} + A_{A_2B_2A_2}} \tag{4}$$

$$F_{A_2B_2A_2} = \frac{A_{A_2B_2A_2}}{A_{A_1B_1A_1} + A_{A_2B_1A_1} + A_{A_2B_1A_2} + A_{A_1B_2A_1} + A_{A_1B_2A_2} + A_{A_2B_2A_2}} \tag{5}$$

Similarly, the mole fractions of A_2-B_1-A_1, A_2-B_1-A_2, A_1-B_2-A_1, and A_1-B_2-A_2 in the copolyesters were also obtained. During the process of transesterification, the mole fractions of copolyesters containing two methylene moieties in their structures can be expressed as

$$F_{A_2B_1A_k} = F_{A_2B_1A_1} + F_{A_2B_1A_2} \tag{6}$$

Likewise, the mole fraction of copolyesters containing three methylene moieties in the structure can be expressed as

$$F_{A_1B_2A_k} = F_{A_1B_2A_2} + F_{A_1B_2A_1} \tag{7}$$

The probability of finding an A_2-B_1-A_k sequence in copolyester can be expressed as

Table 1 Sequence-distribution analysis of PEN/PTT/PEI = 33/33/33 heated at 300 °C for different times

Time	Composition molar fraction[a]		Fraction of dyads centered in the glycol unit[c]				Probability		Average sequence length		Degree of randomness
t (min)	F_N[b]	F_T	$F_{A_1B_1A_1}$	$F_{A_2B_1A_k}$	$F_{A_1B_2A_k}$	$F_{A_2B_2A_2}$	$P_{A_2B_1A_k}$	$P_{A_1B_2A_k}$	$L_{A_1B_1A_1}$	$L_{A_2B_2A_2}$	B
0	0.437	0.563	0.437	0.000	0.000	0.563	0.000	0.000	–	–	0.000
30	0.472	0.528	0.379	0.076	0.024	0.521	0.161	0.045	6.024	22.272	0.206
180	0.452	0.548	0.226	0.271	0.206	0.298	0.599	0.376	1.670	2.662	0.974
360	0.496	0.504	0.160	0.357	0.287	0.196	0.720	0.570	1.389	1.755	1.290

[a] The molar fraction of PEI is not included

[b] F_N: mole fraction of naphthalate; F_T: mole fraction of terephthalate

[c] $F_{A_2B_1A_k} = F_{A_2B_1A_1} + F_{A_2B_1A_2}; F_{A_1B_2A_k} = F_{A_1B_2A_1} + F_{A_1B_2A_2}$

$$P_{A_2B_1A_k} = \frac{F_{A_2B_1A_K}}{F_N} \tag{8}$$

and the probability of finding an A_1-B_2-A_k sequence in copolyester can be expressed as

$$P_{A_1B_2A_k} = \frac{F_{A_1B_2A_K}}{F_T} \tag{9}$$

The degree of randomness, B, of a copolymer is defined as the summation of two probabilities [23].

$$B = P_{A_2B_1A_k} + P_{A_1B_2A_k} \tag{10}$$

For $B = 0$, a mixture of two homopolymers is indicated. Additionally, values for $B < 1$ indicate that the units tend to cluster in blocks of each unit. For random copolyesters, B is unity; and B values between 1 and 2 denote a tendency of A_1 and A_2 to alternate around B_j. If $B = 2$, the distribution of units are alternated in the copolymers. The degree of randomness was interpreted as the content of hetero sequence in the PEN/PTT blends divided by that which corresponds to the random copolymer with the same composition of PEN and PTT. In this study, the degree of randomness was used as a parameter that describes the extent of transesterification [11, 23]. Additionally, the average length of the PEN sequence$(L_{A_1B_1A_1})$ in copolyester, is defined as [12, 18, 23]

$$L_{A_1B_1A_1} = \frac{1}{(1 - F_{A_1B_1A1})}B \tag{11}$$

where $F_{A_1B_1A_1}$ is the mole fraction of the A_1 B_1 A_1 sequence. The average length of the PTT sequence$(L_{A_2B_2A_2})$ in copolyester, is defined as

$$L_{A_2B_2A_2} = \frac{1}{(1 - F_{A_2B_2A_2})}B \tag{12}$$

where $F_{A_2B_2A_2}$ is the mole fraction of the A_2 B_2 A_2 sequence.

Table 1 lists the following: the molar fractions of compositions; the fraction for$F_{A_iB_jA_k}$; probability of the A_2-B_1-A_k and A_1-B_2-A_k sequences forming in a copolyester; average sequence length of A_1-B_1-A_1 and A_2-B_2-A_2; and the degree of randomness of PEN/PTT/PEI = 1/1/1 heated at 300 °C for different periods of time. In the copolyesters, our results indicate that both the content of hetero sequences $(F_{A_2B_1A_k})$ and$(F_{A_1B_2A_k})$ and the probability of obtaining the A_2-B_1-$A_k(P_{A_2B_1A_k})$ and A_1-B_2-A_k sequences$(P_{A_1B_2A_k})$ increased with annealing time. The average sequence length of homo segments $L_{A_1B_1A_1}$ and$(L_{A_2B_2A_2})$ decreased and the degree of randomness (B) increased as the transesterification reaction progressed. This finding suggests that the transesterification produced a block copolymer and then proceeded to form a random copolymer in the ternary blends. Such behaviors reveal that the transesterification in PEN and PTT occurred at 300 °C, and that the blend system became randomized as the transesterification progressed.

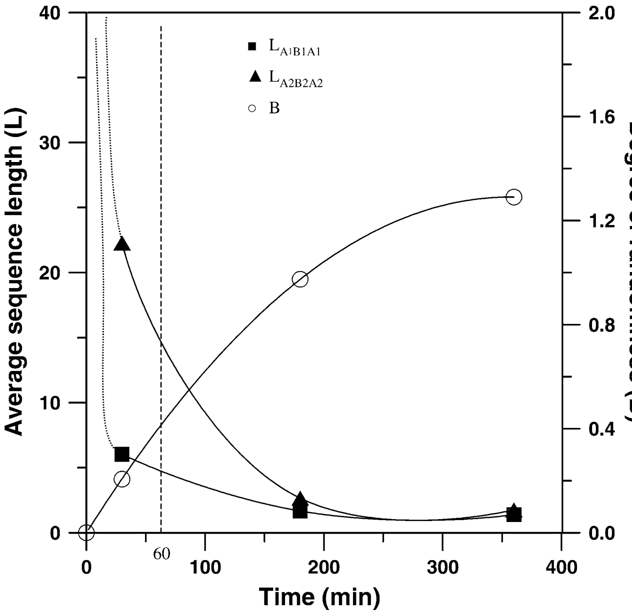


Fig. 2 The average sequence length for PEN and PTT repeat units and the degree of randomness in the copolymer mixtures obtained as a function of reaction times

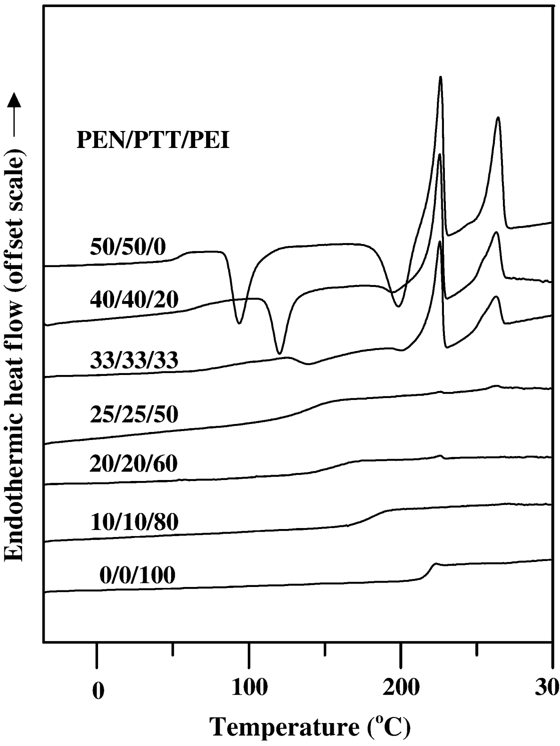


Fig. 3 DSC traces for different compositions (wt. ratio) of PEN/PTT/PEI blends heated at 300 °C for 1 min

The average sequence length for PEN and PTT repeated units and the degree of randomness of PEN/PTT copolyesters dependent on annealing time are shown in Fig. 2. The degree of transesterification increased with an increase in annealing time. The average sequence length for PEN and PTT declined sharply until the reaction was 180 min in the figure. The randomness of samples also increased with an increase in annealing time, finally achieving the value close to 1.30, which denotes random distribution, i.e., a tendency of A_1-B_1-A_2 and A_1-B_2-A_2 to dominate A_1-B_1-A_1 and A_2-B_2-A_2 units in the copolyesters. In Fig. 2, the values obtained for the block length of PEN/PTT block copolyesters indicated that although$L_{A_1B_1A_1}$ and$L_{A_2B_2A_2}$ decreased with the onset of heating, both$L_{A_1B_1A_1}$ and$L_{A_2B_2A_2}$ decreased slightly in the final period of annealing time. The variations in block lengths in each unit was closely related to the change in chemical structure, in particular, for intermolecular chain reactions that denotes a transesterification reaction in two polymers.

Phase behavior

In the ternary PEN/PTT/PEI systems, blends were obtained by applying solution precipitation at room temperature to avoid transesterification during blend preparations. The effect of composition on the thermal behavior of the PEN/PTT/PEI blends is shown in Fig. 3. Notably, the samples were heated at 300 °C for 1 min to eliminate thermal history in the blends. Heating, however, did not alter the morphology of the samples. The thermograms curve indicated that PTT had a low crystallization temperature ($T_{\mathrm{c,PPT}}$) and a low melting temperature ($T_{\mathrm{m,PPT}}$). Additionally, PEN had a relatively high crystallization temperature ($T_{\mathrm{c,PEN}}$) and a high melting temperature ($T_{\mathrm{m,PEN}}$). Moreover, a T_g in blends was found to be extremely close to the same temperature as the T_g of the pure PTT, and T_g referred to as PTT-rich regions in the blends. This finding suggests immiscibility in the blends. Apparently, the exothermic crystallization peak of either the PTT or PEN component obscured another T_g in PEN-rich regions blends. As the PEI content of the blend increased, the $T_{\mathrm{c,PTT}}$ measured at the minimum of the exothermic of PTT increased. This fact indicated that some PEI suppressed the crystallization of PTT from its glassy state; its glassy state could be expected to be miscible for the PTT and PEI components. This finding correlates with the findings that PTT and PEI were completely miscible over the whole composition range [7]. Conversely, the crystallization temperature of PEN ($T_{\mathrm{c,PEN}}$) was nearly independent of the PEI concentrations in these compositions. This finding suggests that only a slight amount of interaction occurred between PEN and PEI. Additionally, the melting peaks associated with PTT and PEN appeared at the same temperatures, regardless of the concentration of PEI in the ternary blends (Fig. 3). When amorphous PEI was present, the thin crystalline lamellae, i.e., not formed or located between the thicker lamellae, formed the spherulites of PTT and PEN in the PEN/PTT/PEI blends, respectively. These findings identified the immiscibility of the PEN/PTT/PEI blends in polyester-rich components. In contrast, the thermal behavior in the PEI-rich compositions (PEI > 50 wt%) showed a clear T_g in the DSC traces, and the T_gs of the PEN/PTT/PEI blends increased with increased PEI weight fractions. In the PEN/PTT/PEI blends, a homogeneous system is formed when PEI concentration is high (> 50 wt%).

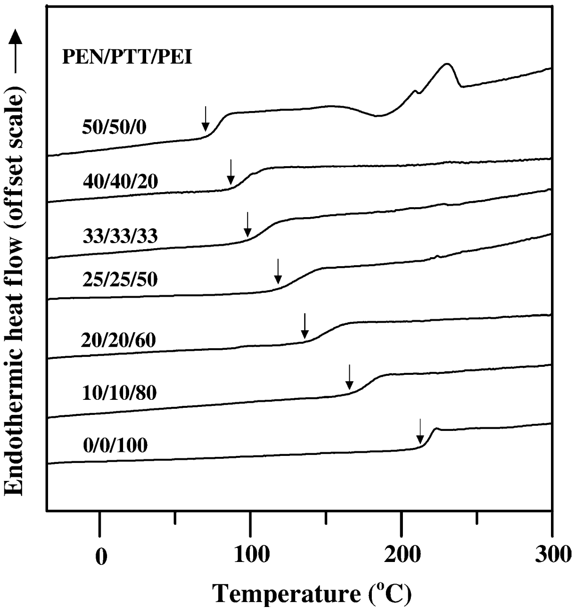


Fig. 4 DSC traces for different compositions (wt. ratio) of PEN/PTT/PEI blends heated at 300 °C for 30 min

The DSC thermograms of PEN/PTT/PEI blends obtained by heating the quenched samples after melting at 300 °C for 30 min are shown in Fig. 4. The cold crystallization and melting were virtually eliminated by the increased annealing time. The thermal behavior suggested that crystallization of PEN and PTT was inhibited due to the disruption of the chain periodicity, a consequence of transesterification in PEN and PTT. In the ternary blends, a single glass transition was observed; the glass transition range narrowed with an increasing reaction time, indicating that transesterification enhanced miscibility. Table 2 lists the T_gs of PEN/PTT/PEI blends heated at 300 °C for 1 min and 30 min. In the polyester-rich compositions, T_g significantly increased, i.e., around 30 °C, owing to transesterification in PEN and PTT. The transesterification led to a morphological change from a heterogeneous phase to a

Table 2 The glass transition temperature of PEN/PTT/PEI blends heated at 300 °C for 1 and 30 min

PEN/PTT/PEI	T_g (°C), (300 °C, 1 min)			T_g (°C), (300 °C, 30 min)
	Homogeneous phase	Heterogeneous phase		Homogeneous phase
		PTT-rich regions	PEN-rich regions	
100/0/0	117.0	–	–	117.0
0/100/0	40.0	–	–	40.0
50/50/0	–	49.0	Obscure[a]	72.5
40/40/20	–	54.8	Obscure[a]	85.9
33/33/33	–	66.9	Obscure[a]	97.0
25/25/50	118.1	–	–	117.5
20/20/60	139.0	–	–	136.5
10/10/80	167.0	–	–	167.0
0/0/100	215.6	–	–	215.6

[a] The exothermic crystallization peak of either the PTT or PEN component obscured another T_g in PEN-rich regions in the blends

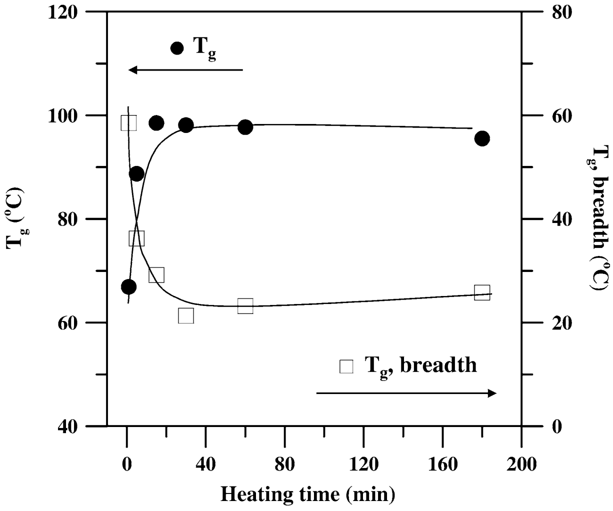


Fig. 5 Change of T_g and T_g breadth for PEN/PTT/PEI = 33/33/33 heated at 300 °C for different times

homogeneous one. Although transesterification occurred in the PEI-rich compositions, T_gs had nearly the same value. Meanwhile, PEN/PTT/PEI blends were heated at 300 °C for 1 min and 30 min, respectively. Moreover, both the phases remained homogeneous. In the ternary systems, the transesterification reaction affected the formation of copolyesters of the polyester-rich compositions more than the polyester-poor compositions did.

Figure 5 describes how annealing time affects the glass transition behavior for the compositions of PEN/PTT/PEI = 33/33/33 blend. Initially, T_g of the blends increased rapidly with the reaction time. After 30 min, T_g of the blends remained consistent and independent of annealing time. The glass transition range narrowed with an increasing reaction time and, then, rapidly declined over the reaction time. In the later stages of the reaction, the breadth of the glass transition range remained consistent and independent of reaction time. From the above results, transesterification enhanced the miscibility of the ternary blends, and the transreaction was almost completed in early stages of the reaction. Restated, the miscibility of the ternary blends increased with the concentration of the product, ENTT copolymer, subsequently forming in the copolymerization of PEN and PTT. Therefore, a consistent T_g and a narrow glass transition range appeared when the blends were heated at 300 °C for more than 30 min. A single T_g in the mixture correlated with a degree of randomness, 0.20, and an average PEN and PTT repeating unit sequence lengths of 6.15 and 22.40 in the copolyester formed by transesterification. Moreover, sequences of PEN and PTT were also shortened with the concentration of the ENTT copolymer, which suppressed the crystallization of PEN and PTT in the ternary blends.

Figure 6 shows the optical micrographs (A–F) of the co-precipitated PEN/PTT/PEI samples with five compositions after being heated at 300 °C for 1 min and 30 min. When the blends were heated at 300 °C for 1 min, experimental results showed a phase separation in blends with polyester-rich components and a homogeneous phase in the PEI-rich compositions. For the immiscible compositions, the phase domain sizes depended on the composition and declined with the increase of the PEI weight fractions in the micrographs. Both PEN/PEI [4, 5] and PTT/PEI [6, 7] blends are miscible throughout the compositions, but PEN/polyester [11–18] are immiscible in all the compositions. Before transesterification, miscibility increased with the PEI concentration in the PEN/PTT/ PEI blends. Furthermore, the PEI concentration increased the miscibility of PEN and PTT, as attributed to the interaction of PEN and PEI, and PPT and PEI. After the compositions were heated at 300 °C for 30 min, their morphologies were homogeneous. This suggests that the transesterification in PEN and PTT can enhance the miscibility in the PEN/PTT/PEI blends.

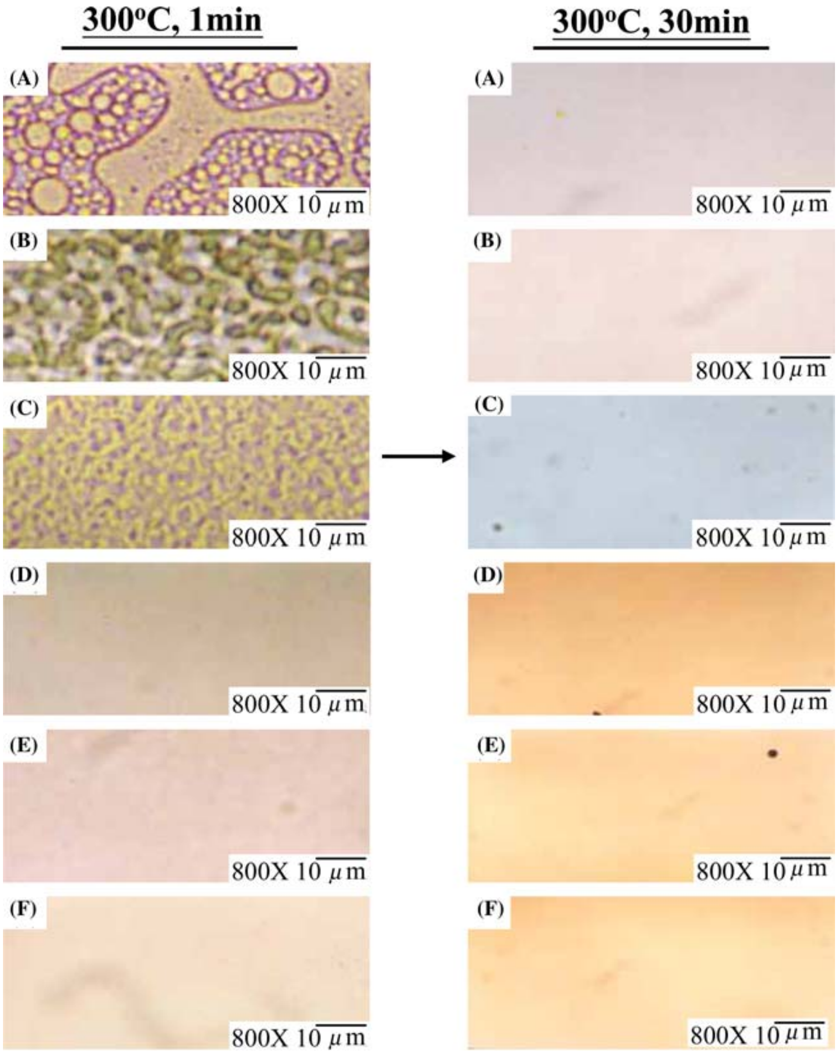


Fig. 6 OM graphs for PEN/PTT/PEI blends of different compositions: **a** 50/50/0, **b** 40/40/20, **c** 33/33/33, **d** 25/25/50, **e** 20/20/60, **f** 10/10/80 (wt. ratio)

Crystallization behavior

Figure 7 shows the relative intensity of the wide-angle X-ray diffractograms (WAXD) patterns for samples crystallized at 200 °C for 8 h. For the PEN homopolymer, the peak at the diffraction angle of 15.5° was assigned to (010) plane, while peaks at diffraction angles of 23.4° and 26.8° corresponded to (100) and$(\bar{1}10)$ planes, respectively [24]. Additionally, the WAXD patterns of crystals for PEN depended on the prior melting temperature [25]. In this study, the blends previously melted at 300 °C obtained the α form for PEN crystallized at 280 °C. In the PEN/PTT/PEI = 33/33/33 blends, the scattering patterns contain features of both PEN and PTT when the peak positions of the two polymers were mixed. Peak position shifting was not observed in blends crystallized at 280 °C. The arrangement of unit cells remained the same as in the original PEN and PTT sequences, and co-crystallization did not occur in the PEN/PTT/PEI blends.

Figure 8 shows the WAXD diffractograms for annealed samples (PEN/PTT/PEI = 33/33/33) which were heat treated at 300 °C for different periods of time, then quiescently crystallized at 200 °C for 8 h to attain maximum crystallization. The peaks in the diffractograms for PEN were clearly identifiable in the ternary blends up until annealing time reached 60 min. Experimental results in Fig. 2 indicate not only that the sequence length for PEN and PTT was short, but also that the sequence distribution of PEN/PTT copolymer was more random than usual as the reaction progresses, subsequently decreasing the crystallization for PEN and PTT in the PEN/PTT/PEI = 33/33/33 blend. Furthermore, the critical average sequence length for crystallization was about 4.70 and 12.50 for PEN and PTT, respectively; the degree of randomness reached 0.41 at a reaction time of $t = 60$ min. The above results correspond to the results of the DSC thermograms of the composition of PEN/PTT/PEI = 33/33/33 blend (Fig. 4), where the melting peaks of PEN and PTT disappeared

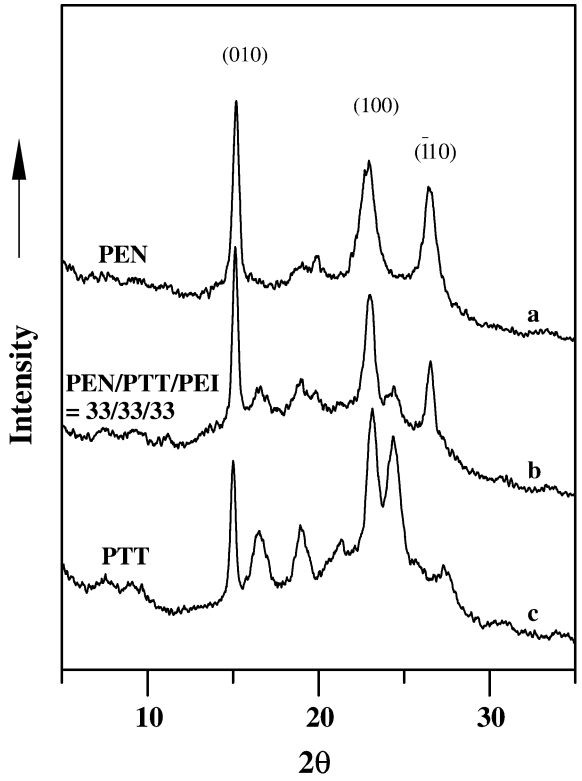


Fig. 7 WAXD profiles of samples heated at 300 °C for 1 min: **a** PEN, **b** PEN/PTT /PEI = 33/33/33, **c** PTT (isothermal crystallization at 200 °C for 8 h)

as the heating time approached 60 min. However, when the transesterification reaction has progressed to such an extent that the sequence length for both PEN and PTT is too short, crystallization is hindered. This finding indicates that the length of homo segments in polymer chains decreased and crystal formation was disturbed due to the irregularity of structure as the exchange reaction progressed.

Miscibility of ENTT copolymer/PEI blends

The ^{1}H-NMR result identified that when the samples were heated at 300 °C for 360 min, there existed a random copolymer in the PEN/PTT/PEI blends, which improved the miscibility of the PEN/PTT/PEI blends. Furthermore, the miscibility between the transesterification product of PEN/PTT blends (ENTT) and PEI was investigated. In this study, the composition of PEN/PTT = 50/50 was preheated at 300 °C for 360 min to form the random copolymer first, and then the product of ENTT copolymer was blended with PEI. Figure 9 shows the DSC thermograms for ENTT/PEI blends of different compositions. The thermograms indicate that the blends possessed a clear and single T_g that increased with the concentration of PEI in the blends. The above experimental results indicated the miscibility of the blends. Notably, PEI was not only miscible with PEN and PTT but also with their ENTT copolymers. Moreover, after using an optical microscope to preliminarily examine the ENTT/PEI blends, the samples were found to be plain and transparent with no discernible phase domains/boundaries at 800X (not shown for brevity). The phase of all ENTT /PEI blend compositions, as revealed by OM, was domain-free and transparent.

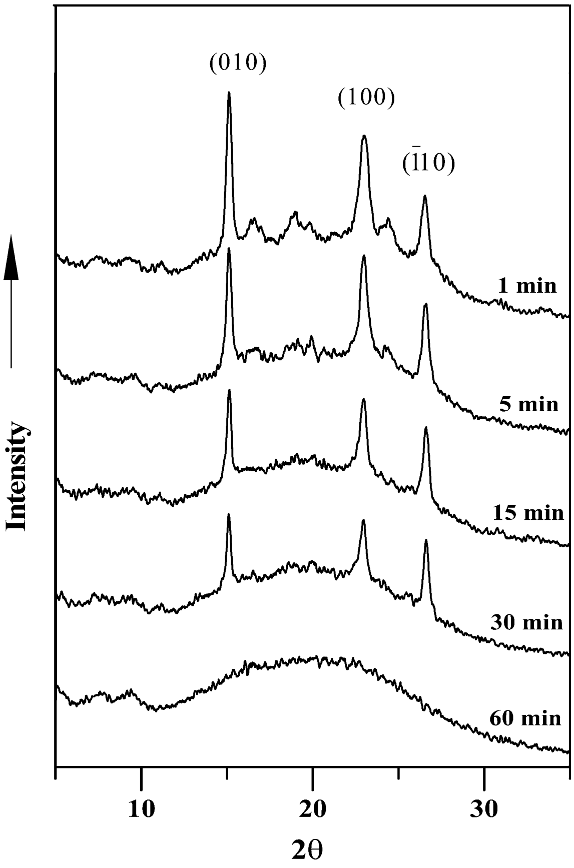


Fig. 8 WAXD diffractograms for the PEN/PTT/PEI = 33/33/33 blends heated at 300 °C for different times (isothermal crystallization at 200 °C for 8 h)

As shown in Fig. 10, the composition effect on T_g of ENTT/PEI blends followed the Fox equation [26]

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \tag{13}$$

where ω_i is the weight fraction and $T_{g\ i}$ is the glass transition temperature of component i. In Fig. 10, the experimental T_gs for each composition show negative deviations from the expected T_g values obtained using the Fox equation. This suggests that the miscibility observed in the blends was caused by the interactions between the two components [22, 27]. Additionally, the T_g

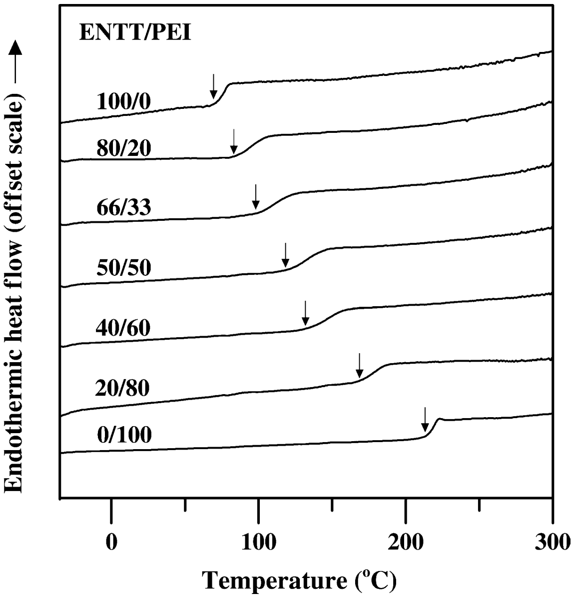


Fig. 9 DSC traces for ENTT/PEI blends of different compositions (wt. ratio), as indicated

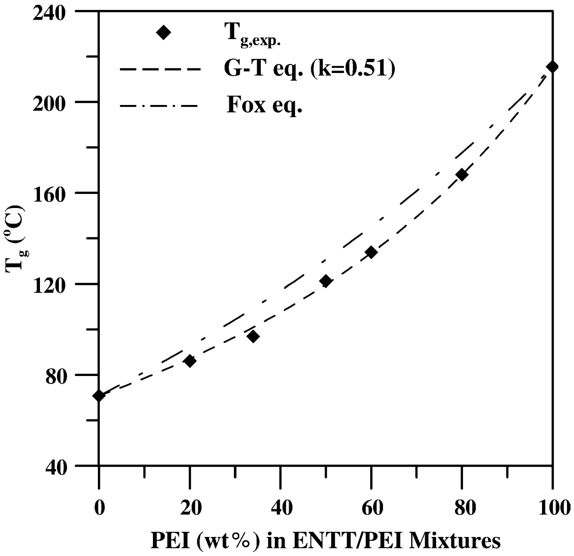


Fig. 10 T_g composition plot of ENTT/PEI blends. The data are compared with Fox and Gordon–Taylor equation

versus composition data was best correlated by the Gordon–Taylor equation [28, 29] for ENTT/PEI blends:

$$T_g = \frac{T_{g1}\omega_1 + kT_{g2}\omega_2}{\omega_1 + k\omega_2} \tag{14}$$

where k represents the ratio of the thermal expansion coefficients of ENTT and PEI. The Gordon–Taylor equation with an adjustable parametric constant seems to best describe the T_g data of the ENTT/PEI blends. The parameter, k, was found to be 0.51. It can be easily concluded from these T_g results that the ENTT/PEI blends were indeed a homogeneous and single phase.

Conclusions

In the PEN/PTT/PEI blends, two polyesters, PEN and PTT, created copolymers through transesterification when the samples were annealed at 300 °C. Before heat treatment, PEN and PTT were immiscible; adding PEI increased the miscibility in the ternary PEN/PTT/PEI systems. Additionally, the transesterification in PEN and PTT enhanced the miscibility of the PEN/PTT/PEI blends that were annealed at 300 °C for more than 30 min. The extent of transesterification in PEN and PTT appears to be a threshold value of miscibility for PEN/PTT/PEI blends in the exchange reaction. The degrees of randomness and average sequence lengths were calculated by applying the ^{1}H-NMR data. These findings indicated that the final product was a statistically random copolymer of the two polyesters. In the ternary blends, partial compositions of the ternary blends were immiscible; but after a sufficient reaction time, a single T_g was obtained, indicating the homogeneous phase in the ternary systems. The initially immiscible blends became miscible after a critical amount of transesterification occurred; specifically, this homogenization occurred when the randomness factor was a value of 0.20. This did not completely correspond to random copolymer formation, but suggested that the average sequence lengths of the PEN and PTT repeating units in the copolyester were 6.15 and 22.40, respectively. Furthermore, the critical value of the average sequence length required to form the crystallites was approximately 4.70 and 12.30 for PEN and PTT, respectively. In the PEN/PTT/PEI blends, the miscibility of the ternary systems enhanced not only the interaction of van der Waals forces among the three components, but also transesterification in PEN and PTT.

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