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ORIGINAL CONTRIBUTION

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A comparative study on transreactions induced phase changes in blends of poly(trimethylene terephthalate) and poly(ethylene naphthalate) upon annealing

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Abstract By using wide-angle X-ray diffraction (WAXD), thermal analysis, scanning and optical microscopy, and nuclear magnetic resonance (NMR) analyses, this study has demonstrated that blends of two semicrystalline polyesters, poly(trimethylene terephthalate) and poly(ethylene naphthalate) (PTT/PEN), were initially immiscible in as-blended state. The process of blend phase/morphology changes upon extended heating/annealing at elevated temperatures was monitored and probed. With reactions induced at heating/annealing at high temperatures (300°C) for long enough times, the original two phases quickly merged into a single phase. NMR analyses have shown that the products of the transreactions are identified as the random copolyesters (termed as EN-TT). From the NMR results, statistical analyses revealed that the average sequence lengths decreased upon heating, and the degree of chain randomness increased with time of heating at the fixed temperature. Upon extended heating, all PTT and PEN chains could be fully transformed into random copolymers of higher randomness with only a single but amorphous phase. Results are compared to another blend system comprised of PEN and a homologous polyester, PPT, of different structure. Influence of polyester structure on transreactions and phase homogenization process is analyzed.

Keywords NMR · Transreaction · Poly(trimethylene terephthalate · Poly(ethylene naphthalate

Introduction

Blends of two different polymers are not always miscible or of one phase. It is known that temperature can have a thermodynamic effect on phase behavior of blends owing to the variation of free energy of mixing. For blends of polyesters (or some polyamides), temperature effects on phase behavior can be more complex than just variation of free energy. Transreactions can induce variation in chemical structures of the polymer constituents in blends. Blends of similar naphthalate aryl polyesters have been extensively studied [1–12] such as poly(ethylene naphthalate)/poly(ethylene terephthalate) (PEN/PET) [4–7], poly (ethylene naphthalate)/poly(butylene terephthalate) (PEN/PBT) [8], or poly(ethylene terephthalate)/poly(butylene terephthalate) (PET/PBT) [9]. Of the many that are known and have been investigated, the PEN/PET blend seems to offer the most commercial interests. Upon melt processing at high enough temperatures, it is known that polyester blends may undergo transesterification and/or exchange reactions. These exchange reactions can lead to the formation of block/random copolyesters from the original binary pair. The resultant initial block or eventual random copolymers, owing to the transesterifications, are expected to exhibit better mutual miscibility than the original unreacted components based on theoretical and experimental results concerning the constituent polymers [13]. This means that when polyester blends are held at higher temperatures, i.e., near or above their melting points, an interchange reaction can occur among the component polyesters, leading eventually to exchanged copolymers of various sequences/blocks.

Many studies on polyester exchange reactions [10, 11] have concluded three most likely routes including: (a) intermolecular alcoholysis, (b) intermolecular acidolysis, or (c) direct midchain ester exchange (transesterification), etc. Porter and Wang [10] have extensively studied on blends of polyesters and carefully examined whether or not transreaction is a prerequisite for forming a single-phase system for polyester blends. It is generally reported that heating-induced transesterification can lead to blend miscibility or, more correctly speaking, can enhance compatibility between phases in blends of polyesters. Kimura and Porter [14] have reported that transreacted blends of PBT and a poly(aryl polyester) (PAr, a copolyester of bisphenol-A of 50% terephthalate and 50% isophthalate) are obtained by holding the physical blends at 250°C for up to 16 h. The transesterified systems show higher glass transitions (T_gs) than the corresponding physical blends and also show a marked melting point depression and lesser PBT crystallinity at the corresponding increased PAr content. However, Guo and Brittain [15] have argued that this statement may not be completely correct. Some blends, such as PET/PHB-co-PEN and PEN/PET-co-PHB [poly(β-hydroxybutyrate)], are miscible without any transreactions, while in other blends, transreactions may be necessary to bring in a single-phase mixture. Indeed, depending on the chemical structures of constituents, some blends of polyesters can be miscible without reactions. It has been recently reported that three aryl polyesters, PET, PTT, and PBT, of a homologous series may form miscible ternary blends without transreactions [16].

However, for some polyester blends processed at high temperatures, exchanged reactions may be inevitable. Kenwright and Peace [17] and Collins et al. [18] have studied effects of end group on transreaction kinetics and claimed that alcoholysis and acidolysis are two key mechanisms. In addition, Montaudo and Puglisi [19] have used nuclear magnetic resonance (NMR) in characterizing transreaction mechanisms. Regardless of ongoing arguments on proposals of likely mechanisms, it is more uniformly agreed that transreactions lead to, first, block copolymers and then random copolymers, which may be responsible for the final uniform phase upon heating. Devaux et al. [20] have proposed a terminology of block lengths of sequence, from which the randomness in the copolymers may be calculated.

Issues of miscibility in blends of polyesters must be dealt with correctly, especially in situations where heating-induced exchange reactions in blend constituents may be involved. Shi and Jabarin [21] have studied on PEN/PET blends, and they found that an originally immiscible PEN/PET blend can turn into a homogeneous single-phase blend with a negative value of interaction parameter χ. However, it may be argued here that if the chemical constituents in a blend have changed, interactions per se for a physically blended system vs a chemically reacted one should be interpreted differently. An important issue is whether the final phase homogeneity of these blended materials is a result from purely physical miscibility (no reactions) or, alternatively, from interchange reactions leading to structures of copolymer formation. This is because the interactions may no longer be between PET and PEN but, rather, it may be between PEN (or PET) and a copolymerized species yet to be determined. In addition, the observed single phase may no longer be referred to miscibility in a physical blend but, rather, transreactions (transesterification) can occur between two aryl polyesters, as well as between an aryl polyester and a polycarbonate at sufficiently high temperatures [22].

We tried to further answer the following questions. If the formation of a single phase in a polyester blend system is a consequence of transesterification, then how much transesterification is necessary to bring in such single phase? That is, where is the onset point for a single phase if a polyester blend turns from a two-phase to a homogeneous one? Furthermore, what is the role of the intermediate block copolymers (products of exchange reactions between polyesters A and B)? An earlier published work has indicated that the blend of PEN and PPT, originally immiscible with two T_gs, may turn into a homogeneous amorphous mixture (PEN, PPT, and copolymer of EN-co-PT of various segment lengths, etc.) upon heating at 300°C for long enough times [23]. As PPT in the blend is replaced with PTT, would the difference in structure lead to different consequences? Understanding the relationships between transesterification and miscibility is important. The experiments in this study have been designed by taking the following considerations. By varying the structure in one of the constituents in the polyester–polyester blends, the objectives of this work were, firstly, to investigate the influence of polyester structure on physical phases of blends before heating and, secondly, to further understand the effects of polyester structure on segmental sequences/distribution upon transreactions.

Experimental

Materials and methods

PTT, alternatively named as poly(propylene terephthalate), was synthesized by Industrial Technology Research Institute (ITRI, Taiwan) and supplied to us as a courtesy sample material of a research-grade resin with no additives. As-received PTT has a T_g of ~43°C and apparent T_m of 228°C. PEN was obtained from Aldrich (USA), with a T_g of ~116°C and apparent T_m of 268°C. The T_g and T_m of PEN are higher owing to the naphthalate rings in the backbone. The chemical structures of the repeating units of PEN and PTT are shown as following:

Blends of polyesters were in two different methods for comparisons. To ensure that inherent phase behavior of the physical blends was understood first, the blend specimens were prepared by solution-blending method to avoid any possible effect of thermal heating at elevated temperatures that is inevitable in melting blending. The first series of binary blend samples were prepared by solution mixing in dichloroacetic acid (4 wt% polymer solution) at 60°C, followed by coprecipitation in methanol. The repeated precipitation and washing would help further ensure that any impurities be removed from the polymers. The finally precipitated blend was filtered, washed, and finally dried in vacuum at 80°C for 7 days. The solution mixing and coprecipitation for the preparation of blend samples were used to ensure the absence of possible transesterification and/or chemical reactions that might occur in these two polyesters at high temperatures. A study was also conducted to the analyze effects of thermal heating on changes of miscibility and morphology that might be attributed to possible reactions between these two polymers at high temperatures. For these purposes, the physical blends were further thermal annealed at 260~300°C for different times (0–180 min) to induce various extents of reactions between these two polymers.

Apparatus

T_g temperatures, crystallization, and melting temperatures of the blend samples of various compositions were measured with a differential scanning calorimeter (DSC) (Perkin–Elmer DSC-7) equipped with an intracooler. Measurements of T_g, cold crystallization, and melting transitions were made at a scan rate of 20°C/min in the range of −60~300°C. The T_g values were taken as the onset of the T_g (i.e., change in the specific heat) in the DSC thermograms, while the values of T_c (cold crystallization) and apparent melting point (T_m) were taken as the peak of the exotherms or endotherms. The DSC sample size was around 5 mg for all studies. For temperature accuracy, all thermal treatments imposed on the blend samples were performed in the precision-temperature cells of the DSC. Melt crystallization of all samples was performed by melting at ~300°C (in DSC cells) for 5 min, and then they were quenched quickly to a desired isothermal temperature for a specified period of time.

A polarized light optical microscope (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 microglass slides and then heated and gently pressed by hands to thin films in the microscope heating stage (Linkam THMS-600 with TP-92 temperature programmer). To further confirm the phase homogeneity, the morphology of the fracture surfaces of the blends (compression molded to films) was also examined using a scanning electron microscope (SEM) (JEOL, Model JXA-840). Thicker-blend films (0.3 mm in thickness) for SEM were prepared by compression molding. They were then fractured across the thickness after dipping into liquid nitrogen; subsequently, the fractured surfaces were sputter-coated with gold for SEM characterization.

^{1}H NMR spectra were recorded using a Bruker AVANCE-400 spectrometer operating at 400 MHz. Tetramethylsilane was used as an internal standard for chemical shift references. The 2D ^{1}H COSY (correlated spectroscopy) experiment was performed to correlate pairs of protons through their spin–spin coupling. Coprecipitated PEN/PTT blend (fixed at 50/50 by weight) was heated at 300°C and then held for various times to induce unspecified extents of reactions. The heated blends were dissolved in $CF_3COOD/CDCl_3$=10/90 (v/v) for NMR experiments. ^{1}H NMR measurements were also performed on a sample of neat PET to obtain the chemical shift value of the ethylene unit between two terephthalates.

The WAXD instrument was Shimadzu XRD-6000 with copper K_α radiation (40 kV and 45 mA) and a wavelength of 1.542 Å. The scanning angle ranged from 2θ=5° to 35°, with a step scanning of 2° for 1 min. Thermal treatments of blend samples for both X-ray diffraction and SEM characterization were performed in the DSC cells for precise temperature control of intended thermal treatments.

Results and discussions

Phase-separated morphology in coprecipitated PTT/PEN blends

Figure 1 shows the DSC thermograms (heating rate of 20°C/min) of the PEN/PTT blends (prepared by solution

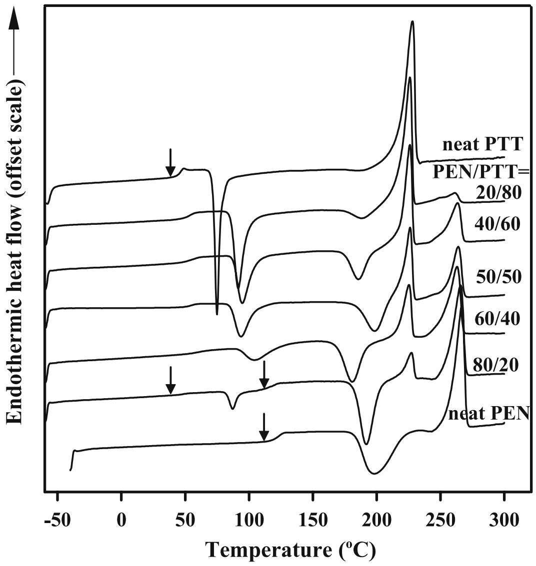
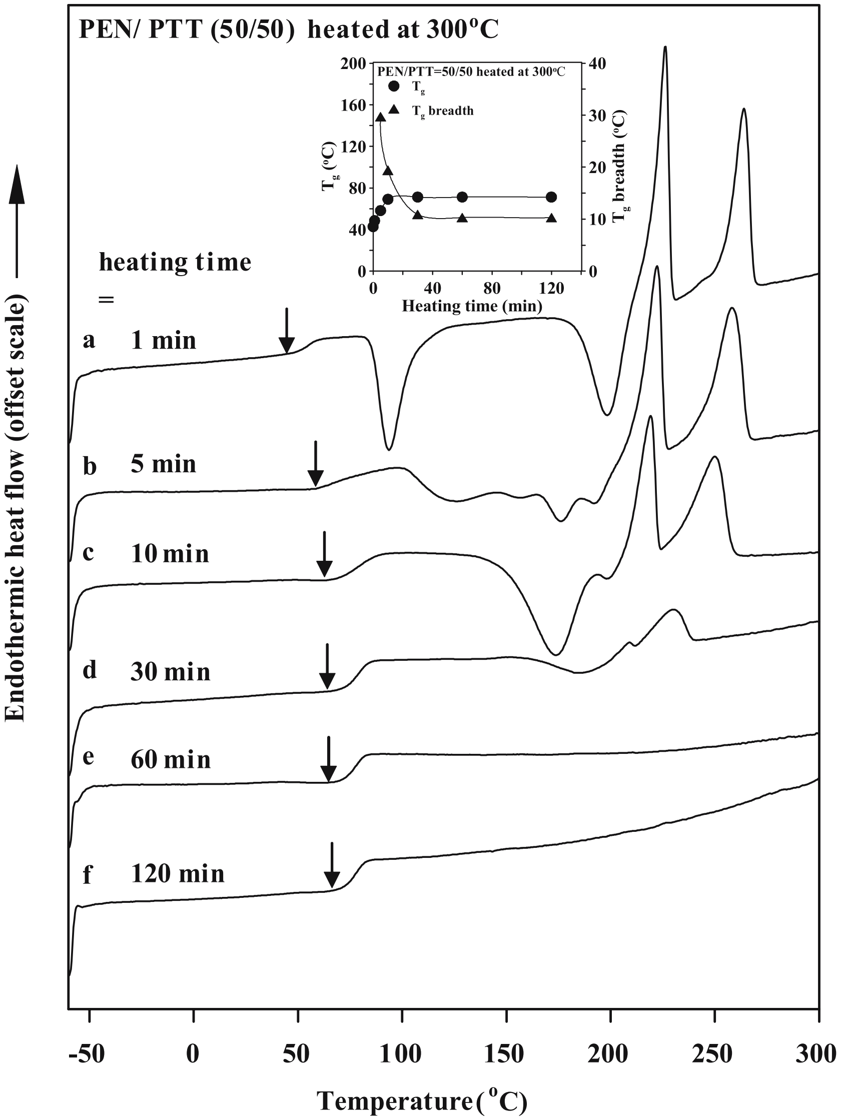


Fig. 1 DSC thermograms (20°C/min) for PEN/PTT blends (solvent coprecipitated) and two neat polymers (PEN and PTT)

blending and coprecipitation) and two neat polymers (PEN and PTT). The DSC traces show that two T_gs (marked on onset positions indicated with arrows) are seen. Note that the second T_g for some of the blends may be masked or overlapped with the cold crystallization peaks, while the first T_g pretty much stays at the same position regardless of the composition. The morphology was grossly phase-separate as revealed in the actual POM images for the coprecipitated PEN/PTT blends (which were heated briefly above melting point to press into uniform films for OM characterization). Except for the two neat polymers that are naturally homogeneous, quite apparent phase domains are observed in the blends, indicating apparent phase immiscibility. Both DSC and POM studies concluded a phase-separated morphology in the as-prepared PTT/PEN blend system (coprecipitated before annealing at high temperatures).

The effect of heating on the blends was examined. Figure 2 shows DSC traces of coprecipitated PEN/PTT (of a fixed composition 50/50) heated at 300°C for times of (a) 1, (b) 5, (c) 10, (d) 30, (e) 60, and (f) 120 min. Significant changes are seen in $T_{c,c}$ and T_m. For heating time of 20 min or longer, the crystallinity and tendency for crystallization in the blend gradually diminish or finally disappear according to the DSC traces. The T_g of the blends also underwent significant changes upon heating at 300°C. The inset shows plots of T_g and its breadth variation with the heating time. The T_g first increases slightly but steadily with respect to time of heating at 300°C up to 20 min and then stays almost constant further until 120 min. The breadth of T_g, however, becomes narrower to a fixed breadth with the increase of heating time. Both facts suggest that the imposed heating might have induced homogenization of structure on the blend.

Fig. 2 DSC traces of coprecipitated PEN/PTT=50/50 heated at 300°C for different times: **a** 1, **b** 5, **c** 10, **d** 30, **e** 60, and **f** 120 min. *Inset* shows T_g and its breadth variation with heating time



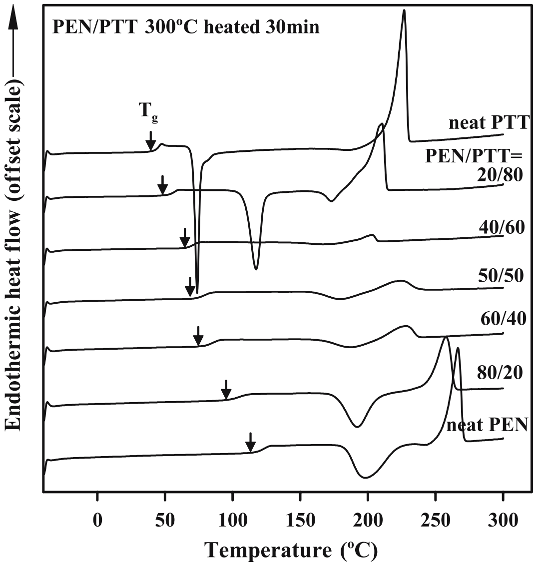


Fig. 3 DSC traces of coprecipitated PEN/PTT blends of different compositions (weight ratio) after heating at 300°C for 30 min

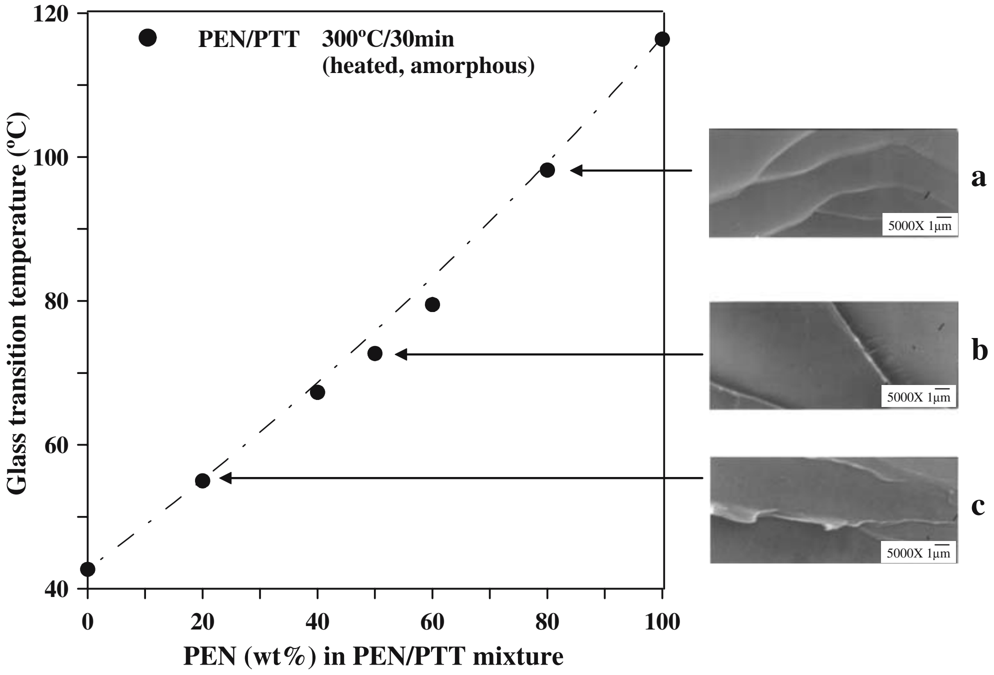
Similarly, the effects of heating on blends of various different compositions were compared by examining the blend T_gs. Figure 3 shows the DSC thermograms of coprecipitated PEN/PTT (two neat polymers and five blend compositions) annealed/heated at 300°C for 30 min. Three features are noted. One is that all blends exhibit a depressed crystallization tendency. The second feature is a narrow T_g breadth. The third is that all heated blends now exhibit a single T_g, indicating that heating at 300°C for 30 min has induced a certain extent of phase/morphology homogenization, as evidenced by the T_g behavior.

Phase homogenization owing to physical miscibility or copolymerization

The effect of annealing at high temperatures on the PEN/PTT blends was also examined by analyzing its T_g vs composition plot in Fig. 4. In addition, the inset blocks show the corresponding SEM morphology of the heated blends (three compositions). The T_g data in this plot were obtained from the coprecipitated PEN/PTT blends that were post-annealed at 300°C for 30 min, where the coprecipitated blends had been homogenized into one amorphous phase, or in other words, turned into single-T_g blends. Apparently, the figure shows that the classic Fox equation [24] for the binary blend systems: $1/T_g = \left(w1/T_{g1} + w2/T_{g2}\right)$ describes quite reasonably the observed T_g–composition relationship. However, one cannot yet conclude a physical miscibility by just judging this figure, as a random copolymer comprising these two units (or a copolymer of short blocks) may also exhibit such a relationship. The morphology and the T_g–composition relationship both show clearly that the annealed/heated PTT/PEN blends are of a single phase.

However, one must determine whether this observed single phase is a result of physical miscibility or copolymerization of two homopolymers. For this objective, WAXD determination of the crystallinity of the heated blends may be a key. Two sets of blends were prepared for comparisons. One set of samples was prepared by coprecipitation and involved no

Fig. 4 T_g (onset values) vs compositions for the PEN/PTT blends heated at 300°C for 30 min. *Inset* shows SEM morphology of the heated blends of compositions: **a** 20/80, **b** 50/50, and **c** 80/20 (weight ratios)



subsequent heating, which was used as basis of references for comparison. The coprecipitated blends were melted briefly at 300°C (1 min) and then quenched to 200°C for crystallization (8 h). The second set of samples was heated at 300°C for various times (1 to 60 min), and the heated blends were again melted briefly at 300°C (1 min) and then quickly quenched to 200°C for crystallization (8 h). Note that crystallization at 200°C would induce crystallization of only the PEN species, and not the PTT, in the blends. Figure 5 shows comparisons of these two sets: (a) WAXD diffractograms for PTT, PEN/PTT (50/50) and PEN (unheated), and (b) PEN/PTT (50/50) 300°C heated for various times as indicated on diffractograms. Figure 5a shows that the PEN/PTT (50/50) blend contains almost as much PEN crystallinity as the neat PEN. The PTT crystallinity in the PEN/PTT blend is not discussed here, as the 200°C crystallization would have prohibited any PTT crystallization. Figure 5b apparently shows that depending on the length of time heated at 300°C, the PEN crystallinity in the PEN/PTT (50/50) blend is depressed to different degrees. PEN/PTT blends heated for 30 min contain minimum PEN crystallinity. However, the same blend heated for 60 min virtually shows no crystallinity at all, suggesting that the PTT/PEN blend heated at 300°C for 60 min or longer cannot crystallize easily (even after being held isothermally at 200°C for as long as 8 h).

NMR characterization

Figure 6 demonstrates the 400-MHz ^{1}H NMR spectra, in the range of chemical shifts from 4.5 to 5.0 ppm, of the PEN/PTT blend (50/50, w/w) heated at 300°C for times between 0 (unheated) and 480 min. From spectrum a (unheated blend), the singlet at 4.86 ppm represents the ethylene protons (1) in PEN, and the triplet at 4.60 ppm results from the methylene protons (6) adjacent to oxygen in PTT. With the increase of the heating times (up to 480 min) imposed on the PEN/PTT blend, the new peaks appeared and are shown in spectra b, c, and d. The new peaks, assigned as 2 through 5, are to be identified.

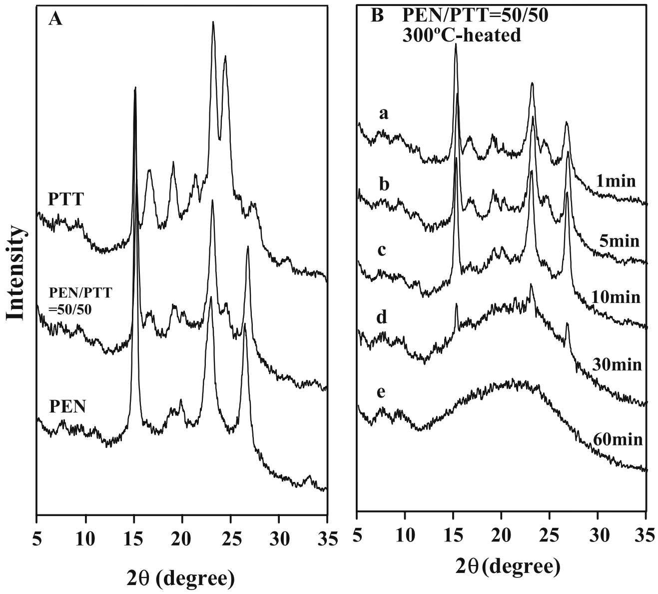


Fig. 5 X-ray diffraction patterns of coprecipitated PEN/PTT=50/50 melt crystallized at 200°C for 8 h. **a** Without reaction and **b** after heating at 300°C for different times: (a) 1, (b) 5, (c) 10, (d) 30, and (e) 60 min

Figure 7 summarizes the possible sequences of various blocks in PEN/PTT blends upon annealing at high temperature. In this scheme, A_1 represents the naphthalate unit, A_2 the terephthalate, B_1 the glycol unit (oxy-ethylene-oxy), and B_2 the oxy-trimethylene-oxy unit. For examples, the $A_1B_1A_1$

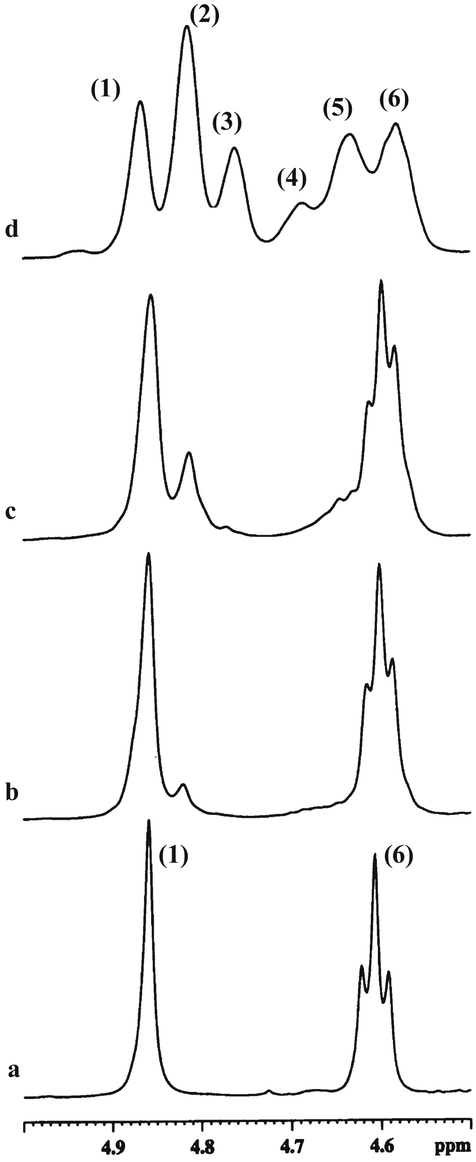


Fig. 6 ^{1}H NMR spectra of coprecipitation PEN/PTT=50/50 after heating at 300°C for different times: **a** 0, **b** 60, **c** 120, and **d** 480 min

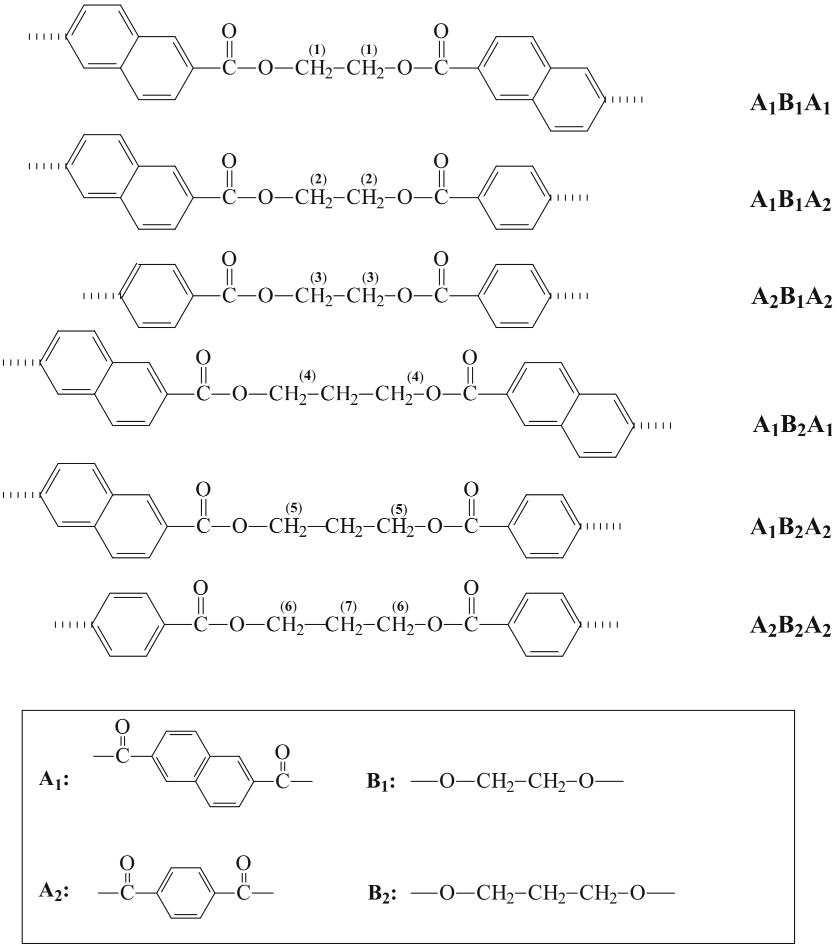


Fig. 7 Possible sequences of the copolymer on the glycol units of PEN/PTT=50/50 after heating at 300°C for a period of time

block is the original ethylene naphthalate unit, while $A_1B_1A_2$ represents one of the exchanged blocks where the terephthalate of PTT has been exchanged with PEN.

A new singlet appears at 4.82 ppm after the sample was heated for 60 min, indicating that transesterification reaction occurs between PEN and PTT. This peak is assigned to protons of the ethylene group (2) between the 2,6-naphthalate and terephthalate units. With increasing reaction times, the intensity of this peak increases. After annealing at 300°C for 120 min, another singlet at 4.77 ppm shows up and becomes distinct after 480 min. The chemical shift of 4.77 ppm is also seen in the spectra of neat PET (the original PET spectra not briefly shown here). This means that the singlet at 4.77 ppm can be assigned to the protons of ethylene group (3) bonded between two terephthalates. On the other hand, after 60 min of heating on the sample, a shoulder peak at 4.64 ppm is seen. This implies that the chemical environment of trimethylene protons has been changed by tansesterifications between PEN and PTT, relative to the singlet at 4.82 ppm. In the range of 4.59–4.70 ppm, the proton singlets were found to split into three sets of peak: (4), (5), and (6) for the samples heated at 300°C for 480 min.

From the results of NMR analyses, the segmental sequence structures of the copolyesters produced by transesterification may be determined by using the statistical methods earlier demonstrated by Devaux et al. [20]. A four-segment copolyester may be generated from the exchange reaction(s) between PEN and PTT, shown as following:

$$[(A_1{-}B_1)_x{-}(A_2 - B_1)_y]_m - [(A_1 - B_2)_z - (A_2 - B_2)_w]_n$$

In this formula, A_1, A_2, B_1, and B_2 are the monomer units of different chemical structures (refer to schemes in Fig. 7) but of the same functionality; x, y, z, and w represent the average length of the various sequences; m and n are the mean lengths of blocks having in common the same B_1 or B_2 unit.

By following the procedures of Devaux et al. [20] and using the results from the NMR analysis, the distribution of the copolyester sequence and the randomness (based on an analysis of triads centering on the ethylene unit, B_1) may be calculated. Summary results of the triad analysis for the PEN/PTT (50/50) blend upon heating at 300°C (for various times from 0 to 480 min) are demonstrated in Table 1. The theoretical values for the statistical copolyester of the same composition are also included in the table. The triad fractions $fA_iB_1A_k$ around the ethylene unit (B_1) is defined by the concentration ratio and can be determined from previous ^{1}H NMR assignments.

$$f_{A_iB_1A_k} = \frac{[A_iB_1A_k]}{[B_1]}$$

Note that $fA_1B_1A_2 = fA_2B_1A_1$, and the degree of randomness around B_1 (BB_1) is given by

$$B_{B_1} = f_{A_1B_1A_2}\left(\frac{1}{F_{EN}} + \frac{1}{F_{TT}}\right)$$

where F_{EN} and F_{TT} are the mole fractions of 2,6-naphthalate and terephthalate group, respectively. The degree of randomness is associated with the distribution of monomer units in the copolyester produced by exchange reactions. In a mixture of polyesters or in a copolyester with long homogeneous sequences, B_{B_1} equals to 0. The value $B_{B_1}=1$ indicates a copolyester with a random distribution of A_1 and A_2 units around B_1; whereas, B_{B_1} between 1 and 2 means a tendency of A_1 and A_2 to alternate around B_1 [20]. Because the resolution of ^{1}H NMR is not enough to deconvolute the proton peaks 4, 5, and 6 except for the reaction time which is 480 min, we only calculated the evolution of the mean lengths of the ethylene 2,6-naphthalate (x) and ethylene terephthalate (y) sequences. The average lengths of A_1B_1 (x) and A_2B_1 (y) sequences can be determined from the fraction of $A_iB_1A_k$ triads and is given by

$$x = \frac{f_{A_1B_1A_1} + f_{A_1B_1A_2}}{f_{A_1B_1A_2}}$$

$$y = \frac{f_{A_2B_1A_1} + f_{A_2B_1A_2}}{f_{A_2B_1A_1}}$$

Table 1 reveals that the degrees of randomness increase, while the average sequence lengths decrease with time of 300°C annealing imposed on the PEN/PTT blend. Up to 480 min of reaction, the degree of randomness B_{B_1} is 0.94. The degrees of randomness (B_{B_1} or B_{B_1}) are approaching 1.0 upon extended heating, indicating that fully random copolyesters (with B=1) are finally formed after extensive reactions at 300°C. For comparison, a slightly different value ($B_{B_1}=0.92$) has been obtained for another heating-homogenized polyester blend of PEN/PPT annealed at the same temperatures (300°C) for the same time [23]. The values of B are slightly different for the PEN/PTT and PEN/PPT blends. This fact suggests that the polyester structure may slightly influence the final segmental distribution in the random copolyesters; however, the major trends of gradual phase homogenization and chain randomness owing to transreactions at 300°C are similar between PEN and aryl polyesters.

The DSC and X-ray results have demonstrated that the PEN/PTT (50/50) blend gradually lost its crystallizing ability upon heating at 300°C. By combination of the NMR, DSC, and X-ray analyses, it can be proposed that in the PEN/PTT binary blends, transesterification has occurred between PEN and PTT chain segments upon annealing. Accompanying this reaction is the fact that the originally semicrystalline blends gradually lose their crystallizability and transfer into amorphous random chain copolyesters. At this state, not only that the mean sequence length is shorter than the critical sequence for crystallizing but, also, the polymer chain contains irregular and different units. Table 1 shows that the mean sequence lengths of PEN (x values) decrease with increasing time of annealing until they finally reach a constant value.

Interactions between the exchanged product and the homopolyesters

Ma et al. [24, 25] have studied on transesterification in PC/PET and PET/PCL blends and pointed out that introduction of the reacted product (copolymers) into blends of homopolymers may lead to changes in the interfacial

Table 1 Segmental sequence structures for likely PEN/PTT copolyesters as determined by ^{1}H NMR and triad analysis[a]

Reaction time	$fA_1B_1A_1$[b]	$fA_1B_1A_2+fA_2B_1A_1$	$fA_2B_1A_2$	x[c]	y[c]	B_{B_1}[d]
0 (unheated)	1.00	0	0	–	–	0
60 min (1 h)	0.88	0.12	0	15.67	1.00	0.24
480 min (8 h)	0.31	0.47	0.22	2.32	1.94	0.94
Theoretical values for a statistical copolyester	0.21	0.50	0.29	1.84	2.16	1

[a] Reaction products at temperature of 300°C; PEN/PTT mole ratio=45.8/54.2

[b] $fA_iB_1A_k$ represents the fraction of triads centering on B_1 (ethylene unit)

[c] x, the average length of A_1B_1 sequences; y the average length of A_2B_1 sequences

[d] B_{B_1} represents the degree of randomness around B_1 (ethylene unit)

forces and morphology. It would be interesting to examine what role the copolymer from exchange reaction of PTT and PEN may play during heating. For this comparison, we prepared a PEN/PTT=50/50 blend, which was heated at 300°C for 8 h. DSC, X-ray, and NMR characterizations all confirmed that a random and amorphous copolyester was formed from the original PEN/PTT=50/50 blend upon being heated at 300°C for 8 h. This random copolyester was code-named as EN-co-TT. A physical blend of EN-co-TT with PTT homopolymer (1/1 weight ratio) and another blend of EN-co-TT with PEN homopolymer (1/1 weight ratio) were prepared by coprecipitation. Both blends (prepared by coprecipitation without further heating) were examined using OM and DSC. OM revealed no apparent phase domains, and DSC showed that a single T_g was found in either EN-co-TT/PTT or EN-co-TT/ PEN blend.

Comparison with model-designed blends

Furthermore, the copolymer, EN-co-TT, was blended with both neat PEN and PTT in such a fashion that they formed a ternary blend system. This was so designed to simulate the actual PEN/PTT blend system upon heating at 300°C, where some portions of PTT and PEN might initially remain unchanged but the other portions might have been transformed into random EN-co-TT. The ternary blends of various compositions were prepared by coprecipitation to ensure that no further thermal heating was imposed. The DSC was performed to reveal their T_gs. Figure 8 shows the DSC traces for the ternary blends of EN-co-TT/PEN/PTT, where the compositions were varied in such ways that EN-co-TT was increased while PEN/PTT was decreased proportionally. In all blends, the PEN and PTT weight fractions were maintained equal. The DSC traces show that with no EN-co-TT (trace a) or at small contents of EN-co-TT (traces b and c), PEN and PTT phases are separated and two corresponding T_gs are seen in the DSC traces. However, as the content of EN-co-TT reaches 50 wt% (trace-d), the ternary blend EN-co-TT/PEN/PTT exhibits a single T_g. The evidence shows that partial miscibility between EN-co-TT and PEN (or PTT) exists. Thus, it may be realistically conceived that a PEN/PTT blend may initially develop two phases/domains upon heating: (a) a PEN-rich phase with minor EN-co-TT and PTT, and (b) a PTT-rich phase with minor EN-co-TT and PEN. In addition, there exists an interfacial boundary phase comprising mainly the reacted EN-co-TT. In between the phases, gradient changes in compositions may be present. However, upon extensive heating, these three phases finally collapse into a uniform phase of random EN-co-TT, and the phase domains or their boundaries disappear.

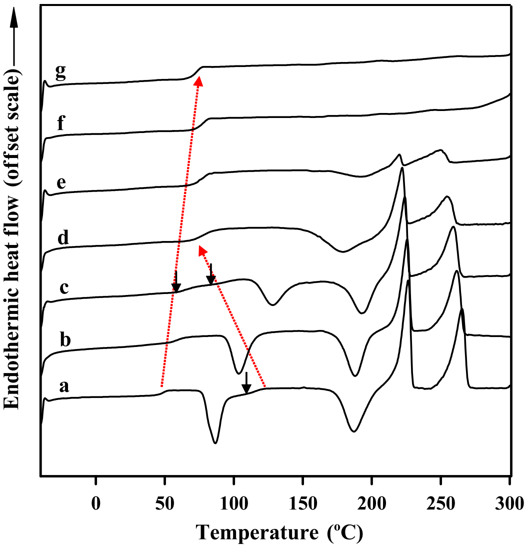


Fig. 8 DSC traces of coprecipitated ternary ENTT/PEN/PTT blends of different compositions: a 0/50/50, **b** 10/45/45, **c** 30/35/35, **d** 50/25/25, **e** 70/15/15, **f** 90/5/5, and **g** 100/0/0 (weight ratios)

Conclusion

The PEN/PTT blends (naphthalate/aryl polyester blends) were initially immiscible when physically blended. The blends without heating would initially exhibit two T_g temperatures with also a heterogeneous morphology, indicating at least two phases. With heating/annealing of the blends at high temperatures (e.g., 300°C or near) for long times, the original two phases quickly merged into one single phase showing a single T_g, which is similar in major characteristics to other previously investigated blend systems of naphthalate/aryl polyester blends. NMR analyses performed on the transreacted products of PEN/PTT (50/50) blend heated at 300°C revealed that the average sequence lengths decreased, and the degree of randomness increased with time of heating. Partially or fully amorphous EN-TT random copolyesters of various compositions with several phase domains are intermediate products resulting from various extents of transreactions between PTT and PEN. These copolyesters at intermediate stages could initially form blends with PTT and PEN of various ternary compositions. Eventually upon extended heating, all PTT and PEN chains could be fully transformed into likely mixtures of copolymers of various degrees of randomness, which, however, show a single and amorphous phase. In comparison to earlier reported transreactions between PEN and another aryl polyester of different structures (PEN/PPT), it can be summarized that the polyester structure may slightly influence the final segmental distribution in the products of random copolyesters; however, the major trends of gradual phase homogenization and chain randomness owing to transreactions at 300°C are of similar mechanism between PEN and aryl polyesters.

Furthermore, this study clarifies that there is difference between physical miscibility and chemical-reaction-induced phase homogenization. If chemical reactions are involved in bringing the blends into a homogeneous phase, the term “miscibility” in blends may not be totally appropriate. “Miscibility” should refer to a single phase in physical blend system with no chemical reactions. However, for blends of PEN with aryl polyesters, phase homogeneity in the blend (after annealing at high temperatures) is achieved upon heating, which is partially attributed to the heat-induced exchange reactions between the aryl polyester and PEN constituents.

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