

Phase separation and homogenization in poly(ethylene naphthalene-2,6-dicarboxylate)/poly(ethylene terephthalate) blends

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Competitive domain-structure development and homogenization under annealing were investigated via time-resolved light scattering and ^1H n.m.r. in melt-quenched blends of partially miscible poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) and poly(ethylene terephthalate) (PET) loaded with/without PEN–PET random copolymer as a compatibilizer. In the early stage the domain structure formation took place presumably by demixing via spinodal decomposition (SD). In the intermediate stage, the domain growth was retarded by transesterification between the two polyesters through the domain interphase, and the whole system was gradually homogenized due to the miscibility enhancement by the produced PEN–PET multiblock copolymer species, as revealed by ^1H n.m.r. analysis. Incorporation of the random copolymer also suppressed the domain growth and resulted in acceleration of the homogenization. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: PEN/PET blends; spinodal decomposition; transesterification; homogenization)

INTRODUCTION

In many industrial areas, polyesters and their blends have been enjoying a wide variety of application for fibres, films and bottles. Poly(ethylene terephthalate) (PET) is an excellent material especially for beverage bottles, and its blends with poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) are expected to be still better because of their low permeability toward oxygen. For example, the oxygen permeability of 40 wt% PEN containing PEN/PET blend is only a half of pure PET bottles. A drawback, however, is the opacity of the bottles resulting from phase separation due partly to the immiscibility and partly to different crystallization behaviour of the component polyesters.

During the melt-blending of two polyesters transesterification often takes place^{1–10}. Undoubtedly the reaction leads to the formation of block copolyester species that enhance their miscibility, which in turn influences the gross structure through their phase behaviour and ultimately the final properties of the product blends^{5,6}. However, the details of such processes have not yet been completely understood. Thus, to obtain well-designed materials one has to be able to control these competitive processes of domain growth and homogenization induced by the transesterification occurring simultaneously in the blend during the melt-extrusion processes. Recently, in both academic and industrial perspective, much attention has been paid to understand and control these complex processes^{11–13}.

In this study, we undertook an analysis of the structure

development by time-resolved light scattering to clarify the mechanism for the PEN/PET blends loaded with or without random PEN–PET copolymer as a compatibilizer. Here we will report the results and discuss the phase behaviour of the blends involving the domain growth due to spinodal decomposition and simultaneous phase homogenization resulting from spontaneous compatibilization through the transesterification of the two polyesters.

EXPERIMENTAL

Polyester samples were commercial grade PET ($M_n = 2.6 \times 10^4$) and PEN (intrinsic viscosity = 0.77 dl g⁻¹ (in a mixed solvent of *p*-chlorophenol and tetrachloroethane (7/3 v/v) at 30°C), $T_g = 118^\circ\text{C}$, ethylene terephthalate content = 8 mol%, PTN92)¹⁴ and a random PEN–PET copolymer ($M_n = 2.0 \times 10^4$, ethylene naphthalate content = 50 mol%, PTN50)¹⁴ supplied by Toyobo Co. PEN/PET blends (40/60 w/w) loaded with or without the random copolymer were prepared by melt extrusion, using a co-rotating twin screw extruder (Ikegai Machinery Co.; the length/diameter ratio L/D of 16 with $D = 30$ mm) operated at the barrel temperature of 280°C.

In each run the extrudate was quickly quenched in ice water to freeze the structure in the melt. The quenched blend was placed between two cover glasses and remoulded at 250°C for 30 s on a hot stage to a thin film of ~ 20 μm thick. Immediately after the melt-pressing, the molten specimen was quickly transferred to the hot chamber of a light scattering apparatus equipped with a

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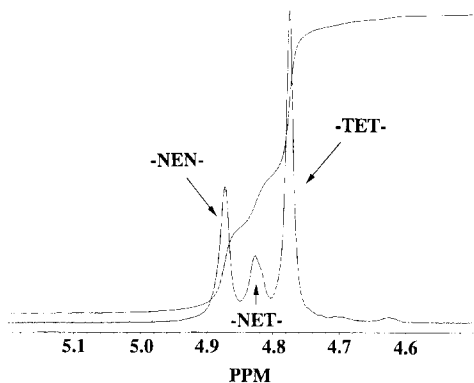


Figure 1 ¹H n.m.r. spectrum of ethylene region of a PEN/PET 40/60 blend annealed at 300°C for 400 s

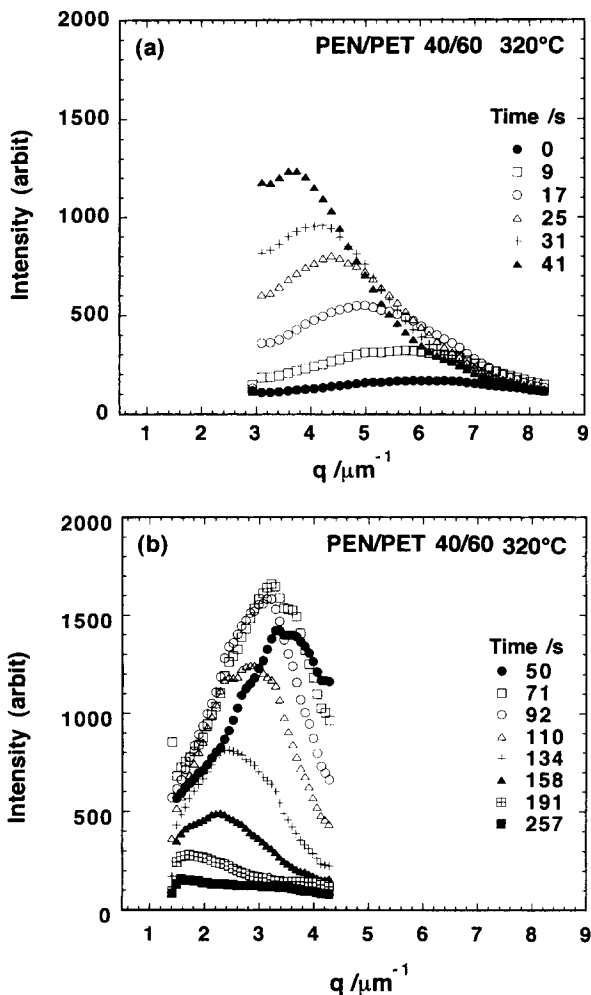


Figure 2 Time evolution of the light scattering profile during isothermal annealing of (a) in the initial stage ($t < 45$ s) and (b) after the initial stage ($t \geq 50$ s) for a PEN/PET 40/60 blend at 320°C

highly sensitive charge coupled device camera (Princeton Instruments, Inc.)¹⁴ and subjected to time-resolved light scattering measurement. The 632.8 nm wavelength beam from a 5 mW He-Ne laser was applied vertically to the film, and the scattering profiles under V_v (parallel polarization) optical alignment were observed with time after the specimen was placed in the hot chamber.

For ¹H n.m.r. test to determine the extent of transesterification, the blends were dissolved in a mixture of deuterated chloroform and trifluoroacetic acid (9/1 v/v)

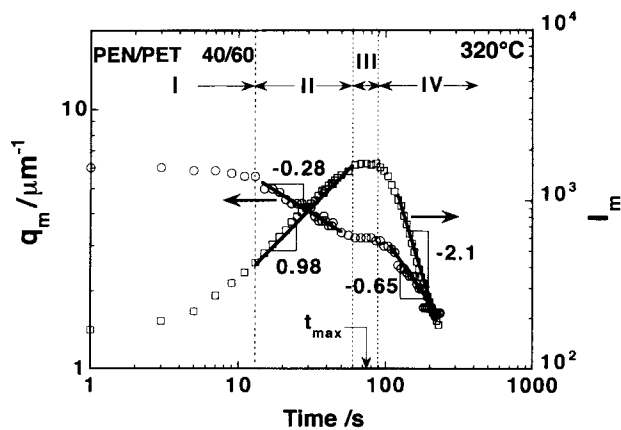


Figure 3 Log-log plots of q_m and I_m vs annealing time and a classification of state of the blend into four regimes. t_{max} is a time of maximum I_m in regime III

and subjected to a ¹H n.m.r. spectrometer (Varian Unity-500, 500 MHz), using tetramethylsilane as an internal standard¹⁵. The evaluation of the amount of heterojunctions due to transesterification was made by comparing the peak for ethylene links (N-E-T) between naphthalate (N) and terephthalate (T) with those between naphthalates (N-E-N) and between terephthalates (T-E-T). According to the assignment of Stewart *et al.*⁷ the ethylene peak for N-E-T appears at approximately 4.82 ppm, while those for N-E-N and T-E-T links appear at ~ 4.86 ppm and at ~ 4.76 ppm, respectively, as demonstrated in Figure 1. The evaluation of the extent of transesterification and the resulting sequence distribution were made from the areas under these peaks according to the method reported previously¹⁵.

RESULTS AND DISCUSSION

Figure 2a shows a typical example of time evolution of the one-dimensional V_v scattering profile in the early stage ($t < 45$ s) of the annealing at 320°C of a PEN/PET (60/40) blend (without the copolymer). Here, the scattered light intensity I is shown as a function of the magnitude of the scattering vector q [$= (4\pi/\lambda') \sin(\theta/2)$ with λ' being the wavelength of light in the specimen and θ , the scattering angle]. Note that, even at time $t = 0$, a weak scattering peak appears at large q . Then the peak intensity I_m increases with time up until 60 s with its position q_m further shifting to the smaller angles, which fact implies that the domain growth is taking place with the regularity keeping unchanged. Figure 2b is the development of the scattering profile after the initial stage: In the intermediate stage the profile remains essentially the same for a short while, and then the peak intensity I_m quickly decreases and broadens with q_m further shifting toward the much smaller angles. The latter result suggests that now the phase homogenization is proceeding in the blend. Finally at $t = 257$ s the intensity becomes very weak and shows hardly any q -dependence, presumably by the completion of the homogenization.

Figure 3 summarizes these features of the scattering profiles, in which q_m and I_m are plotted against time t in a double logarithmic scale. We can clearly see that four regimes do exist in the demixing process: (1) In the early stage of $t < 10$ s, q_m is constant but I_m increases with t

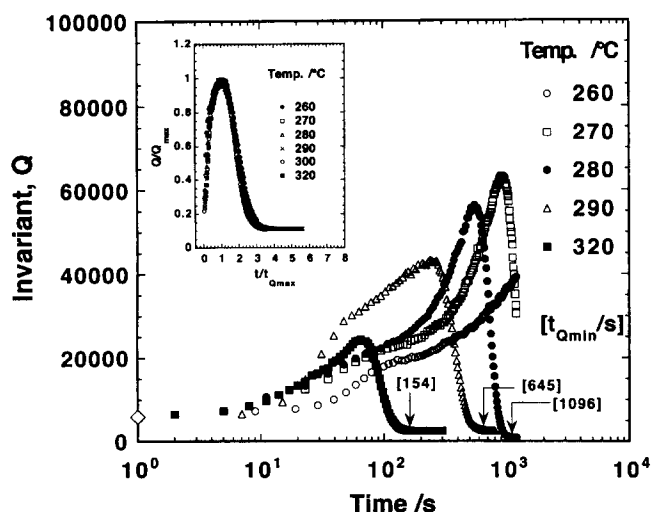


Figure 4 Time dependence of the light scattering invariant Q for a PEN/PET 40/60 blend at various temperatures. The large diamond-shaped mark indicates the Q values of several annealing temperatures for $t = 0$ s. The arrows indicate the time $t_{Q_{\min}}$ at which the minimum value of Q was attained at each annealing temperature. The reduced plot of Q/Q_{\max} vs $t/t_{Q_{\max}}$ is shown in the upper left-hand corner of the figure. Q_{\max} is the maximum value of Q at each annealing temperature and $t_{Q_{\max}}$ is the time at which Q_{\max} was achieved

(regime I); (2) during $10 \text{ s} < t < 60 \text{ s}$ both $\log q_m$ and $\log I_m$ vary linearly with $\log t$ (regime II); (3) then q_m stays constant at $\sim 3.2 \mu\text{m}^{-1}$ and I_m reaches to and stays at maximum for about 30 s around t_{\max} ($\sim 75 \text{ s}$) (regime III); and finally (4) both $\log q_m$ and $\log I_m$ decrease linearly with $\log t$ (regime IV).

Another important parameter that describes the features of the scattering profile is the time variation of the light scattering invariant Q defined by

$$Q \propto \int q^2 I(q) dq \propto \langle \eta(t)^2 \rangle = \phi_1 \phi_2 (\rho_1 - \rho_2)^2 \quad (1)$$

where $\langle \eta(t)^2 \rangle$ is the mean-square fluctuation for the spatial variation of scattering contrast and ϕ_i and ρ_i are the volume fraction and the polarizability of phase i , respectively¹⁶. Figure 4 shows the time development of Q for the PEN/PET blend annealed at different temperatures, and the insert is a normalized Q/Q_{\max} vs $t/t_{Q_{\max}}$ curve of these data. We can see nicely superposition in the insert figure, suggesting the domain growth is closely related to the homogenization and the domain formation in the early stage through homogenization proceeds with the same kinetics at several temperatures in the PEN/PET blend.

From Figures 2 to 4, we see several interesting features of the structure development in the PEN/PET blend. First of all, the weak scattering peak at large q found at $t = 0$ suggests that the blend already has a two-phase structure with a certain regularity in the beginning. Secondly, the behaviour in the early to intermediate stages (regimes I to II where q_m is constant and then decrease with time as $t^{-0.28}$ while I_m increases as $t^{0.98}$ with the invariant Q also increasing with t) resembles those in the early-to-intermediate stages of *spinodal decomposition* (SD). These results suggest that the structure development occurring in these stages is certainly *not* due to the reorganization of the domains of the pure components such as expected in strongly *segregating* blends, in which case Q must stay constant during the structure development.

However, the reason for the two-phase structure already existing at $t = 0$ is not obvious at present. One possible explanation is the following. Recently, a large body of evidence has been accumulated for the influence of high shear rates such as encountered in a melt-extrusion process on the phase behaviour of a weakly segregating blend. Under high shear rates in an extruder, spinodal temperature T_s might be elevated over the barrel temperature in lower critical solution temperature phase diagram^{17–19}. This could be the case for the present PEN/PET blends. Thus, melt mixing took place in a wide temperature window for the dissolution of the two components to yield a homogeneous mixture. However, once the melt was extruded from the nozzle, the shear rate turned to zero and T_s immediately fell to the static value so that SD proceeded forming a regular domain structure until the system cooled down below the static T_s for the PEN/PET blend. For this blend we could not apply the linear Cahn–Hilliard theory²⁰ because a homogeneous mixture was not obtained and the T_s value could not be evaluated by the theory.

The behaviour in regimes II and IV seen in Figure 3 can be interpreted by the power law relationship developed for the late stage of SD. This problem was discussed by Langer based on non-linear statistical consideration^{21,22}. The theory predicts the power law scheme for the intermediate-to-late stages of SD as

$$q_m(t) \propto t^{-\alpha} \quad (2)$$

$$I_m(t) \propto t^{\beta} \quad (3)$$

where α and β are the critical exponents.

In regime II, we see that the β/α ratio is 3.5, which is higher than the theoretical value 3.0 predicted for the late stage of SD by Binder and Stauffer using cluster dynamics²². In this regime II the phase separation appears to proceed as predicted for the intermediate stage of SD with $\beta > 3\alpha$.

After passing regime III where q_m and I_m stay constant for about 30 s around t_{\max} ($\sim 75 \text{ s}$) the blends go into regime IV where both $\log q_m$ and $\log I_m$ decrease linearly with $\log t$ as seen in Figure 3. Then finally the scattering intensity becomes very weak and almost independent of the scattering vector q . The result suggests that the blend tends to become homogeneous again.

However, this homogenization is quite different from the behaviour due to the mixing or phase dissolution induced by temperature drop across the T_s from the two-phase region down to the one-phase region^{18,23}. In such a case while I_m decreases q_m stays constant. A possible mechanism to explain this homogenization is the creation of PEN–PET block and/or random copolymer species through the transesterification of the two polyesters during the annealing process. An interesting feature is that in the blend the demixing and domain growth proceed first and the phase homogenization follows. In fact, in the temperature range from 270 to 320°C, the demixing proceeds much faster than the phase homogenization, and below 260°C the phase homogenization does not occur within 1000 s. Presumably in this system the transesterification reaction takes place between the two polyesters forming block and/or random copolymer species as a compatibilizer.

To confirm this point, we estimated from ¹H n.m.r. spectra increments of the content of hetero N–E–T linkages, $\Delta(N-E-T)$, as a function of the annealing time

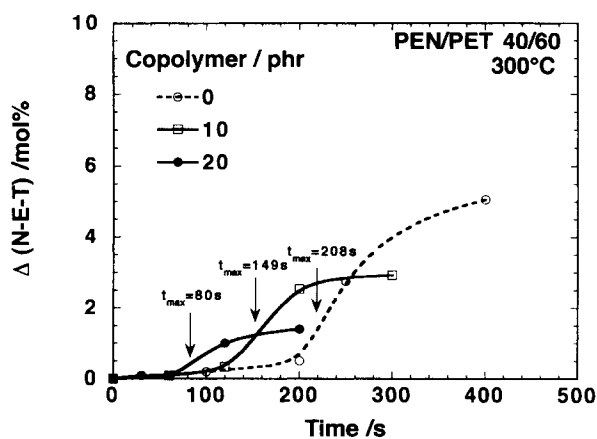


Figure 5 Time variation of $\Delta(N-E-T)$ for PEN/PET 40/60 blend at 300°C and various copolymer content. The arrows indicate the t_{\max} in each system estimated from regime III

Table 1 Characteristic parameters specifying the scattering profiles from regimes II to IV isothermally annealed at 300°C (cf. Figure 3)

Copolymer content (phr)	Regime II		Regime III	Regime IV	
	α^a	β^b	t_{\max} (s ⁻¹) ^c	α^a	$-\beta^b$
0	0.33	1.04	208	1.00	3.37
10	0.30	1.10	149	0.71	3.10
20	0.24	0.86	80	0.53	1.98

^a Exponent of domain growth estimated by equation (2)

^b Exponent of maximum peak intensity development estimated by equation (3)

^c Time of maximum peak intensity reached

t. Figure 5 shows change of $\Delta(N-E-T)$ with *t* for the blend annealed at 300°C. In Figure 5, we see that in the beginning $\Delta(N-E-T)$ remains almost zero until a certain induction period. The period roughly corresponds to t_{\max} , as indicated with the downward arrow, at which the peak intensity I_m or the domain growth reaches the maximum extent (cf. Figure 3). The implication of these results is that in this PEN/PET blend the demixing and domain formation proceed first, the polyesters encounter with a high probability in the domain interphase through which transesterification takes place, and the product block copolymer reduces the density fluctuation, and thus the system is slowly homogenized. Then a puzzling question was *why* the transesterification did not take place in an initial homogeneous or near-homogeneous mixture? An answer may be the rate of SD is much faster than that of the transesterification reaction.

Anyway, in this regime III, the domain growth continues until it is suppressed by the formation of compatibilizing block copolymer species in the interface that decreases the interfacial tension and then reduces the driving force for demixing. The following rapid increase in $\Delta(N-E-T)$ after t_{\max} in regime IV (cf. Figures 3 and 5) is presumably due to the further transesterification of the block copolymers into PEN-PET random copolymers.

If this is the case, we expect that addition of PEN-PET random copolymer species to the blend should enhance the tendency of phase homogenization. This was tested by observing $\Delta(N-E-T)$ and the change of scattering profiles for the PEN-PET random copolymer added blends annealed at 300°C. Figure 5 shows the results of $\Delta(N-E-T)$ plotted against annealing time *t*,

and Table 1 lists the characteristic parameters specifying the scattering profiles. We see that the higher the copolymer content, the shorter is the t_{\max} and the smaller is the change of $\Delta(N-E-T)$. Also the higher is the copolymer content, the smaller is the exponent α and β in regimes II and IV (cf. Table 1). Addition of the random copolymer certainly accelerates the homogenization, as anticipated.

Another interesting feature to be noted is that the exponent α is larger in regime IV compared to that of regime II. That is, the rate of the domain growth due to the homogenization in regime IV is much faster than that due to the demixing in regime II, both defined as the rate of decrease in q_m or that of increase in the periodic distance. The reason why this is so is not clear at present. However, the same trend was found also in our previous study on the late stage of SD in melt-extruded poly(butylene terephthalate)/polycarbonate blends. The deviation from theoretical expectations is presumably caused by transesterification¹⁷.

Now we turn our attention to the kinetics of transesterification: The reaction obviously involves exchange of the chemical units between PEN (A) and PET (B). That is, the segments -AAAAA- and -BBBBB- transforms, for example, to the segments -AABABA- and -BBABAB- after the exchange. We define temporal change of the composition of two copolymer chains initially having the A/B ratio of $x/(1-x)$ units after the reaction time *t* as $A_{x+\Delta x(t)}B_{1-x-\Delta x(t)}$ and $A_{x-\Delta x(t)}B_{1-x+\Delta x(t)}$. We further assume that the initial values of $x = 1/2$ and $\Delta x(t=0) = 1/2$, i.e. initially we have two homopolymer chains. According to Devaux⁵, Zachmann¹⁰ and Tanaka¹³ with an additional assumption of no change in the degrees of polymerization and of first-order reaction scheme for the transesterification, we arrive at

$$\Delta x(t) = \Delta x(t=0) \exp(-k_1 t) \quad (4)$$

where k_1 is the first-order rate constant.

Flory's interaction parameter χ_{12} between two random copolymers with composition difference of $2\Delta x$ is given by $\chi_{12} = (2\Delta x)^2 \chi_{AB}$ with χ_{AB} being the interaction parameter for A and B homopolymers²⁴. Then according to the Flory-Huggins theory²⁵, when a condition that $\chi_{12} \leq \chi_c$ (interaction parameter at the critical point) is met, phase homogenization occurs. Then for the blend of two copolyesters undergoing transesterification and thus the composition changing with time as $2\Delta x(t)$ the critical condition may be given by

$$\chi_c \approx \chi_{12} = [2\Delta x(t=0)]^2 \chi_{AB} \exp(-2k_1 t) \quad (5)$$

Now, assuming that the rate constant k_1 is of Arrhenius-type, the minimum time $t_{Q_{\min}}$ (indicated with the arrows in Figure 4) required for the completion of the phase homogenization or the time required for the invariant $Q(t)$ becoming minimum may be written by

$$t_{Q_{\min}} \sim 1/k_1 \sim \exp(E_a/RT) \quad (6)$$

where E_a is the activation energy for transport, RT is the thermal energy.

To confirm our consideration for the phase homogenization mechanism, we plotted $t_{Q_{\min}}$ against $1/T$ for the blends with and without the compatibilizing random

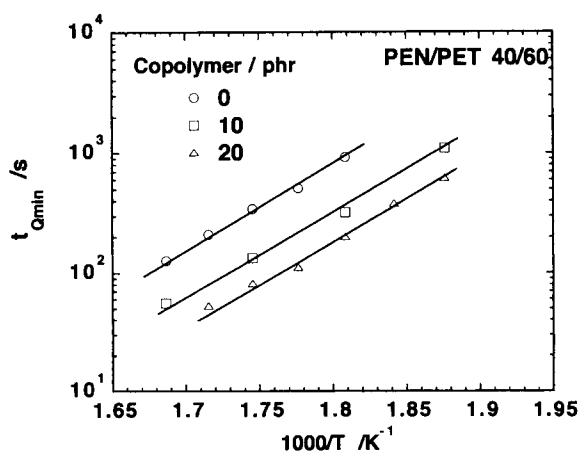


Figure 6 Temperature dependence of $t_{Q_{min}}$ for PEN/PET 40/60 blend and various copolymer contents

Table 2 Sequence distributions in the phase homogenized blends recovered at $t_{Q_{min}}$ annealed at 300°C

Copolymer content (phr)	$P_{T/N}^a$	$P_{T/N}^b$	L_N^c	L_T^d	B
0	0.192	0.092	5.2	10.9	0.28
10	0.215	0.101	4.7	9.9	0.32
20	0.223	0.120	4.5	8.3	0.34

^a Fraction of N units linked with T given by $(N-E-T)/2N$

^b Fraction of N units linked with T given by $(N-E-T)/2T$

^c Number-average sequence length of N unit given by $1/P_{T/N}$

^d Number-average sequence length of T unit given by $1/P_{N/T}$

copolymer annealed at various temperatures. The results are shown in Figure 6. For all the blends examined the plots nicely conform to straight lines, as predicted by equation (6). The slopes of the plots are unchanged, indicating that the activation energy of the transesterification is unchanged regardless of the random copolymer content, as anticipated. The estimated values of E_a are of the order of $\sim 133 \text{ kJ mol}^{-1}$ for the PEN/PET blends, which are in good agreement with E_a of other polyester/polyester blends^{7,9}.

Finally, we discuss the sequence distribution in the copolyester chains in fully transesterified and homogenized PEN/PET blends recovered at $t_{Q_{min}}$ to clarify the degree of randomness. The results for the blends with or without the random copolymer annealed at 300°C are summarized in Table 2, which lists the fraction of N units linked with T, $P_{T/N}$, and vice versa $P_{N/T}$ and the number-average lengths of N, L_N , and T units, L_T and the degree of randomness defined as $B = P_{T/N} + P_{N/T}$. The number-average sequence length L_N of ethylene naphthalate units ranges approximately 5 to 4 and that L_T of ethylene terephthalate units, 10 to 8 for the blends, and both values slightly decrease with loading the random copolymer. The degree of randomness B also increases by adding the copolymer up to around 0.3. By definition $B = 0$ for a homopolymer mixture and virtually for pure block copolymers, and B increases with increasing block alteration or increasing fraction of heterolinkages, and finally $B = 1$ for random copolymers. The value of B about 0.3 implies that the blends are a mixture of the multi-block copolymers rather than a mixture of random copolymers.

In such blends for phase homogenization to occur, χ_{12}

must become smaller than χ_c . For PEN/PET blends χ_{AB} appears to be considerably larger. However, as the transesterification proceeds, $\Delta x(t_{Q_{min}})^2$ may become quite close to zero, reducing χ_{12} significantly and enhancing the miscibility.

CONCLUSIONS

We found that the phase separation in melt-extrudates of the PEN/PET blends during the early stage of annealing of the melt-extruded PEN/PET blends proceed mainly through the demixing due to SD. After the formation of the sharp interface in the intermediate stage of annealing, transesterification starts to occur through the domain interface, enhancing their miscibility. Thus the PEN/PET blends slowly undergo homogenization, and end up as a nearly homogeneous mixture of multi-block copolyesters. Addition of random PEN-PET copolyesters to the blend accelerates the phase homogenization.

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