

Irreversible Phase Behavior of the Ternary Blends of Poly(ethylene terephthalate)/Poly(ethylene-2,6-naphthalate)/Poly(ethylene terephthalate-co-ethylene-2,6-naphthalate)

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ABSTRACT: The phase behavior of Poly(ethylene terephthalate)/Poly(ethylene-2,6-naphthalate)/Poly(ethylene terephthalate-co-ethylene-2,6-naphthalate) (PET/PEN/P(ET-co-EN)) ternary blends in molten state was evaluated from differential scanning calorimetry (DSC) and NMR results as well as optical microscopic observations. Copolymer of ethylene terephthalate and ethylene-2,6-naphthalate was prepared by a condensation polymerization, which was a random copolymer with an intrinsic viscosity (IV) of 0.3 dL/g. The phase diagram of the ternary blends revealed that the miscibility of ternary blends in molten state was dependent on the fraction of P(ET-co-EN) in the blends and holding time of the blends at high temperatures above 280°C. With increase in the holding time, the fraction of copolymer in the blends necessary to induce

the immiscible to miscible transition decreased. For the blends with longer holding time at 280°C, the phase diagram in molten state was irreversible against the temperature, although a reversibility was found for the blends with short holding time of 1 min at 280°C. The irreversibility of phase behavior was not explained simply by the increase of copolymer content produced during heat treatment. Complex irreversible physical and chemical interactions between components and change of phase structure of the blend in the molten state might influence on the irreversibility. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1814–1821, 2008

Key words: polyester; blends; phase diagrams; miscibility; differential scanning calorimetry (DSC)

INTRODUCTION

Both poly (ethylene terephthalate) (PET) and poly (ethylene-2,6-naphthalate)(PEN) are semicrystalline polymers. Thus, we can expect a variety of morphologies for the PET/PEN blends, which would lead to the production of higher thermal and mechanical performance polymeric materials, because both PET and PEN have excellent thermal and mechanical properties.

There are many reports on the phase structures of PET/PEN blends.^{1–15} The majority of studies in the literature concluded that PET and PEN were immiscible independent of the blend composition^{1,6,8} if there was no transesterification reaction between PET and PEN molecules. The blends became miscible when the blending was done at higher temperature around above 260°C, due to the development of poly (ethylene terephthalate-co-ethylene naphthalate) (P(ET-co-EN)) produced by the transesterification reaction in the PET/PEN blends.^{3,6,7} It was

reported^{5,7} that the transesterification reaction first produced a block copolymer and then proceeded to form a random copolymer. The transesterification in PET/PEN blends and its effects on miscibility have been reviewed.^{2,3,5–8,14} Stewart et al.³ reported that the primary factors controlling the transesterification were blending time and temperature, whereas the composition of the blend and the residual polyester catalysts had little or no effect on the ester interchange reactions. Okamoto and Kotaka¹⁴ examined the structure development in PET/PEN blends at high temperature by the time-resolved light scattering method. They found that competitive processes of liquid–liquid phase separation and phase homogenization induced by transesterification took place simultaneously during annealing. The results suggest that at a given temperature, the phase structure of PET/PEN blends in molten state changes with time and the effect of third component of P(ET-co-EN) on the phase diagram of PET/PEN blends should be taken into consideration.

In this study, we evaluated the effects of P(ET-co-EN) on the phase behavior of PET/PEN blends in molten state from differential scanning calorimeter (DSC) and NMR measurements as well as optical

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microscope observations. The binary blends of PET/PEN and ternary blends of PET/PEN/P(ET-co-EN) were prepared by solution-blending method to avoid any possible effect of thermal heating. Then, the blends obtained were annealed at 260–280°C at different times (0–5 min) to evaluate the effect of heat treatments on the phase behavior of the blends in molten state. On the basis of the results, the phase diagrams of ternary blends in molten state were constructed as functions of treatment time and temperature.

EXPERIMENTAL

Synthesis of P(ET-co-EN)

The starting materials used for the synthesis were commercial grades of terephthalic acid dimethyl ester (ET), 2,6-naphthalene dicarboxylic acid dimethyl ester (EN), and ethylene glycol (EG). Zinc acetate and antimony trioxide were used as catalysts. They were used without further purification.

The esterification was carried out for the blends of ET, EN, and EG (blend ratio: 1/1/2, mol %) using zinc acetate at 230°C for 2 h under the atmospheric pressure, followed by the polycondensation at 285°C for 2 h under a reduced pressure using antimony trioxide as a catalyst and trimethoxyphosphate as a stabilizer. The product was dissolved in a mixed solvent of trifluoroacetic acid/dichloromethane (TFA/DM) (30/70, v/v) and precipitated by methanol. The precipitate obtained was dried at room temperature under a reduced pressure for 48 h.

Preparation of blend samples

In this study, commercial grades of PET (intrinsic viscosity, $IV = 0.63$ dL/g) and PEN ($IV = 0.65$ dL/g) pellets, and P(ET-co-EN) synthesized were used as starting materials.

All blends were prepared by a solution blending to avoid the transesterification reaction during blending. Each polymer with desired weight was dissolved in a mixed solvent of TFA/DM (30/70, v/v) at room temperature. A desired volume of P(ET-co-EN) solution (3 wt %) was mixed with a desired volume of PET (3 wt %) and PEN (3 wt %) solution. Then the mixed solution was poured into methanol to obtain polymer precipitate. The precipitates were dried at room temperature under a reduced pressure for 48 h. The blend ratio was expressed by weight ratio of each polymer.

Measurements

The IV of the samples was measured in a mixed solvent of TFA/DM (50/50, v/v) with an Ubbelohde viscometer at 25°C.

^1H NMR measurements were carried out by using JEOL JNM-LA 500 at 25°C. The solvent used was a mixed solvent of TFA/deuterated chloroform (20/80, v/v). The chemical shift was referenced by tetramethylsilane. The amount of ethylene units in the copolymer was determined by the method reported by Stewart et al.³ The calculation was carried out by using software of ALICE2 (JEOL). The error of absolute value was less than ± 0.1 mol %.

The thermal analyses of the samples were carried out by a Seiko Instrument DSC (Model SSC-5200). The measurements were carried out in a dry nitrogen atmosphere at a heating rate of 10°C/min. The thermal history of the samples was as follows: as-prepared blends were inserted into preheated compression molding machine and they were held at a constant temperature in the range of 260–280°C for a constant time in the range of 1–5 min, followed by a rapid quenching into an ice water to preserve the phase structure in molten state. These were termed MQ samples.

The transparency of the samples in molten state was observed by an Olympus BH-2A optical microscopy. The sample temperature was controlled by a Mettler FP 80 hot stage. The thermal history of the samples was as follows: as-prepared blends were inserted into hot stage where temperature was controlled in the range of 260–280°C. The transparency of the samples at a given temperature was observed as a function of holding time.

RESULTS AND DISCUSSION

Characterization of synthesized P(ET-co-EN)

Figure 1 shows the ^1H NMR spectrum of the synthesized P(ET-co-EN) in the ethylene units region. Observed peaks at 4.79 and 4.90 ppm were attributed to ethylene units of PET and PEN homopolymers, respectively, as shown in Figure 1(a,c).^{3,15} The observed peak at 4.84 ppm was due to ethylene units that existed between terephthalic and naphthalic groups in the polymer backbone^{3,15} [Fig. 1(b)]. The degree of randomness (B) and the average block lengths of PET (L_{pet}) and PEN (L_{pen}) were calculated by using these peak intensities. Details of the calculation were reported by Yamada and Murano,¹⁶ which showed that the B values were 2, 1, and 0 for alternative copolymer, random copolymer, and block copolymer or physical blends, respectively. In this work, the calculated B value of synthesized P(ET-co-EN) was 1.01 indicating a random copolymer. The L_{pet} and L_{pen} were also determined to be 2.03 and 1.93, respectively. The IV of the P(ET-co-EN) was determined to be 0.30 dL/g.

The synthesized P(ET-co-EN) showed a specific heat transition corresponding to a glass transition

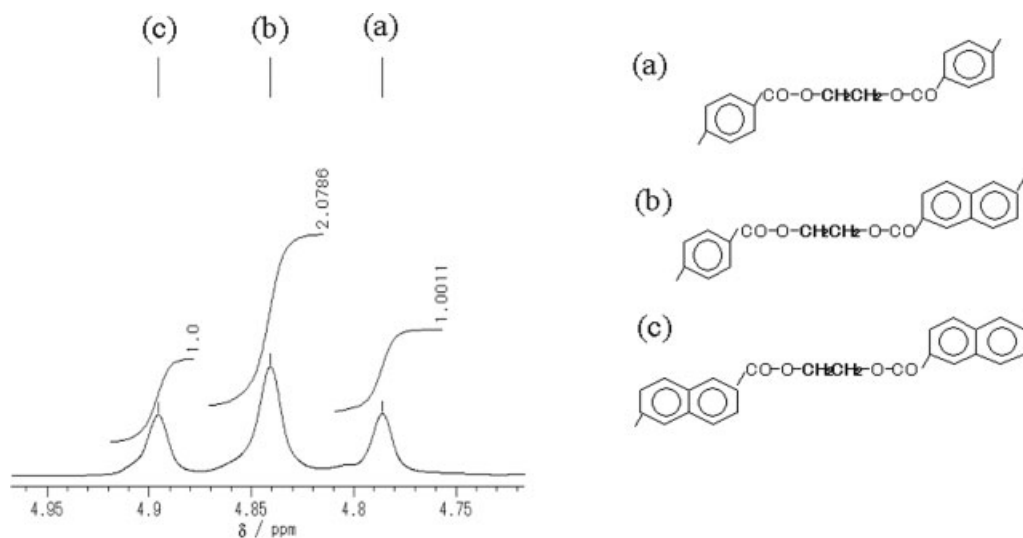


Figure 1 ¹H NMR spectrum of the ethylene unit region for P(ET-co-EN).

(T_g) of the sample at around 90°C (data not shown). T_g of P(ET-co-EN) can be expressed by the empirical Fox equation.¹⁷ The calculated T_g of P(ET-co-EN) (ET/EN, 50/50 mol) was 98.4°C by assuming the random copolymer, where T_{gs} of PET and PEN were 80 and 120°C,¹² respectively. The value was slightly different from the T_g of synthesized P(ET-co-EN) determined by DSC measurements. The T_g of polymer, especially, for low-molecular weight region decreases with decreasing molecular weight.¹⁸ The molecular weight of synthesized copolymer was about 0.3 dL/g, which was almost half compared with those for PET (0.63 dL/g) and PEN (0.65 dL/g). Thus, the difference of T_g between observed and calculated ones may result from the effect of molecular weight on the T_g .

Moreover, any exothermic peaks during heating process of P(ET-co-EN) corresponding to the cold crystallization were not observed. The lack of cold crystallization might be due to the small values of L_{pet} and L_{pen} .¹⁹ In addition, the synthesized P(ET-co-EN) showed no crystallinity even after heat treatment at 180°C for 2 h. All of the results support that the synthesized P(ET-co-EN) is a random copolymer.

Phase behavior of PET/PEN blends in molten state

The phase behavior of PET/PEN blends in molten state (above 260°C) is complex probably due to the development of P(ET-co-EN) produced by the transesterification reaction between PET and PEN in the PET/PEN blends.^{2,3} Thus, information on the effects of P(ET-co-EN) on the phase behavior of PET/PEN blends in molten state is necessary to understand the complexity.

In this work, we used two techniques to evaluate the phase behavior of the blends in molten state. The one is the utilization of MQ samples for the

DSC measurements. The preparation of the samples was described in the experimental part. The thermograms for the MQ samples were obtained by the heating process of DSC scan.

The other one is the optical microscope observations of the blends in molten state. The transparency determined by the optical microscope observation of the polymer blend is often used to evaluate the miscibility of the blends.²⁰ For PET/PEN blends, it was reported that there was a good relation between miscibility and transparency.³ In this study, we also confirmed that MQ sample with single T_g was transparent in molten state.

Figure 2 shows DSC thermograms of MQ PET/PEN blends (1/1, g/g) with different heat treatment times at 280°C. Both samples showed two clear transitions around 80 and 120°C which corresponded to

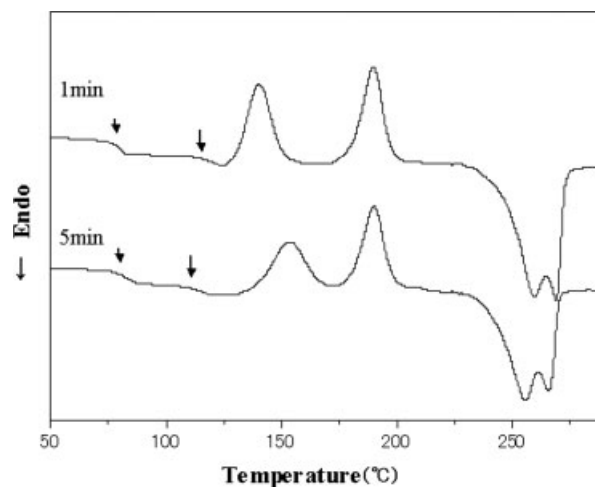


Figure 2 DSC thermograms on the heating process of MQ PET/PEN (1/1, g/g) blends annealed at 280°C for 1 and 5 min.

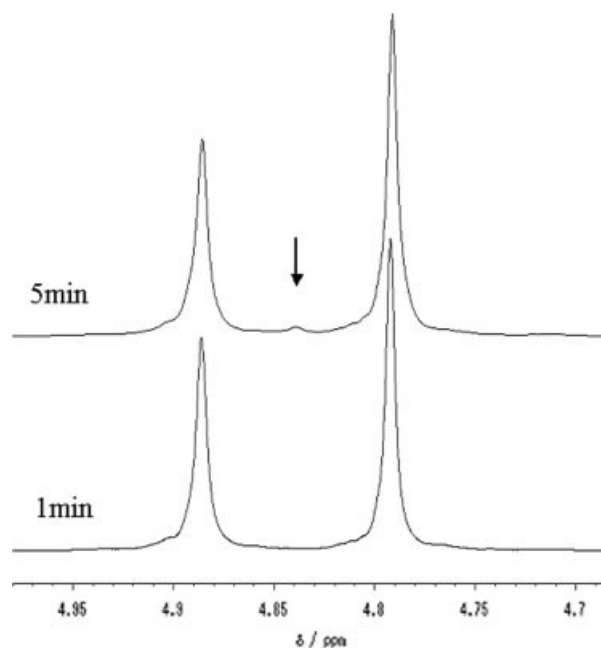


Figure 3 ^1H NMR spectra of MQ PET/PEN (1/1, g/g) blends annealed at 280°C for 1 and 5 min.

the T_{gs} of PET and PEN, respectively.¹² The two exothermic peaks around 130 and 190°C were attributed to the cold crystallization of PET and PEN, respectively, during heating process of DSC scan.¹² MQ samples with different blend ratios showed similar thermograms to those shown in Figure 2 (data not shown).

Figure 3 shows ^1H NMR spectra of MQ PET/PEN (1/1, g/g) samples annealed at 280°C for 1 and 5 min. For both the samples, observed peaks at 4.79 and 4.89 ppm were attributed to ethylene units of PET and PEN, respectively.^{3,15} MQ sample with the annealing time of 5 min showed an additional absorption peak at 4.84 ppm which was attributed to the ethylene backbone of P(ET-co-EN).^{3,15} The results indicate that it takes about 5 min at 280°C to produce the P(ET-co-EN). The amount of ethylene units produced was about 4 mol %, which was determined by the method reported by Stewart et al.³

Based on the results shown in Figures 2 and 3, it can be concluded that both PET and PEN phases in molten state of PET/PEN blends are immiscible state even though small amount of P(ET-co-EN) existed. This conclusion was also supported by the optical microscope observation of the blends. At 280°C , all blends were translucent even after a prolonged treatment time of 10 min, where about 6 mol % of the ethylene units produced. Stewart et al. reported that about 10 mol % of the ethylene units produced by transesterification between PET and PEN was necessary to enhance the miscibility of PET/PEN blends,³ whose value was almost twice compared with 6 mol %.

Phase behavior of PET/PEN/P(ET-co-EN) blends in molten state

P(ET-co-EN) has a possibility to act as a compatibilizer for the PET/PEN blends.^{5,7} A phase diagram of molten state for the ternary blends of PET/PEN/P(ET-co-EN) might be helpful to understand the role of P(ET-co-EN) on the phase behavior of PET/PEN blends.

Figure 4 shows DSC thermograms of MQ PET/PEN/P(ET-co-EN) blends (1/1/1, g/g/g) with different heat treatment times at 280°C . It is seen that the blend treated for 1 min showed two transitions corresponding to the T_{gs} of PET and PEN indicating that PET and PEN are immiscible state. On the other hand, the blend treated for 5 min showed only one T_g around 90°C , apparently, miscible state. There are two possibilities to explain the appearance of single T_g . This will be discussed in the following next section.

Optical microscope observations during the heat treatments were carried out for the ternary blends. It was found that at a given temperature, an opacity-transparency transition happened with increasing the treatment time. Further, the time necessary to induce the transition increased with decreasing the treatment temperature. The quenched sample from opaque state showed two T_{gs} in the DSC thermogram. On the other hand, the quenched sample from transparent state showed only one T_g around 90°C . These results indicate that the opaque and transparent states correspond to the immiscible and miscible states of PET and PEN domains, respectively, in molten state. That is, the opacity to transparency transition corresponds to the immiscible to miscible phase transition of PET and PEN domains in molten state. Based on opacity-transparency transition obtained by the optical microscope observations, the

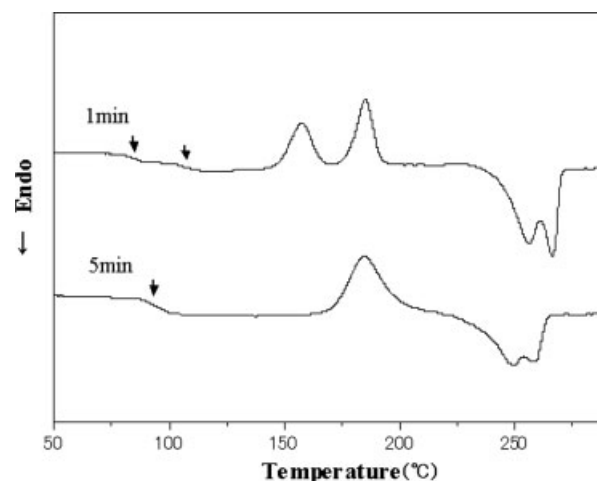


Figure 4 DSC thermograms on the heating process of MQ PET/PEN/P(ET-co-EN) (1/1/1, g/g/g) blends annealed at 280°C for 1 and 5 min.

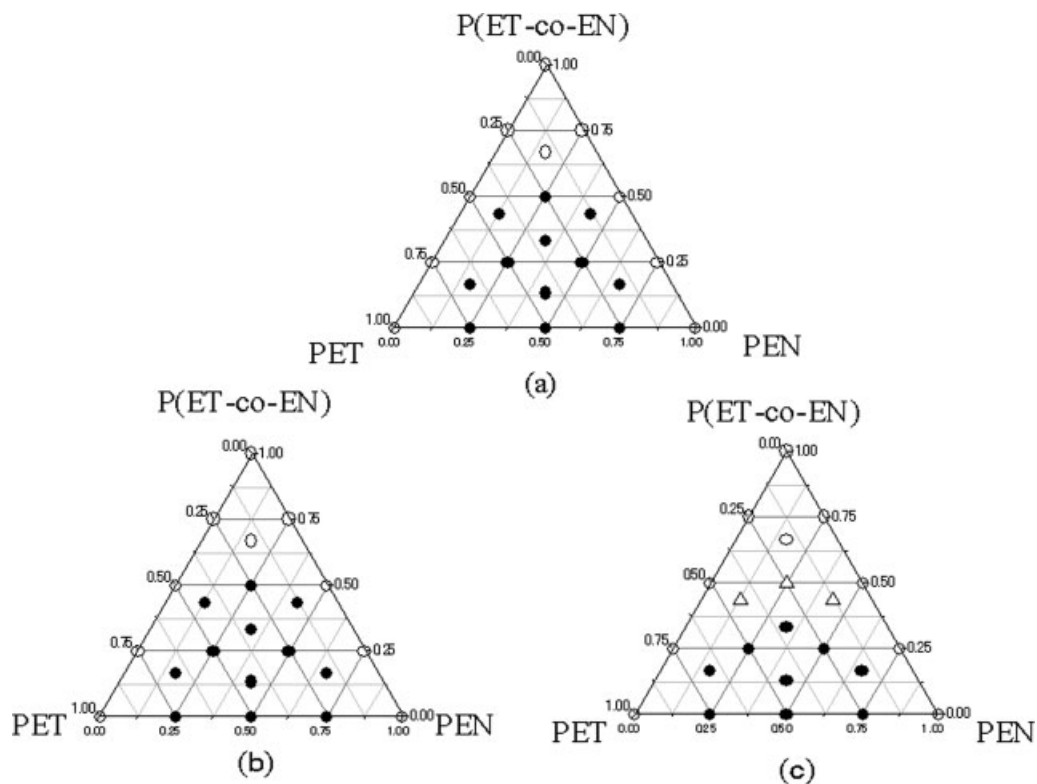


Figure 5 The phase diagrams in molten state of ternary blends with different annealing temperatures for 1 min. (a) 260°C, (b) 270°C (c) 280°C. ○ transparency △ translucency, and ● opacity.

phase diagrams in molten state for the ternary blends of PET/PEN/P(ET-co-EN) were constructed as a function of blend ratio for different treatment temperatures and times, and the results are shown in Figures 5 and 6. It is seen that the binary blends of PET/P(ET-co-EN) and PEN/P(ET-co-EN) are miscible in any cases (composition, treatment temperature, and time). On the other hand, most of the ternary blends treated below 270°C were immiscible even for long treatment time of 5 min. An interesting fact is that the ternary blends which treated at high temperature of 280°C for a long time of 5 min were miscible in a wide range of compositions. Mainly two reasons can be considered to explain the immiscible to miscible transition. The first is that the large PET and PEN domains which showed individual T_g were subdivided into small domains by the P(ET-co-EN), resulting in the mutual dissolution (physical blend). The copolymer with relatively small molecular weight (0.3 dL/g) might act as a surfactant for both PET and PEN domains and the copolymer can easily diffuse into PET and PEN domains, which enhances the subdivision of both the domains. The domain size responsible for a single T_g is reported to be about 100 Å.²¹

The other possibility is the development of copolymer produced by the transesterification reaction between PET and PEN domains during the heat

treatment (chemical blend). In fact, the mol fraction of ethylene unit between terephthalate and naphthalate (TEN) in the PET/PEN/P(ET-co-EN) blends increased with increasing the treatment temperature and time. The amount of increased TEN in the PET/PEN/P(ET-co-EN) blend (1/1/1, g/g/g) is plotted as a function of treatment time in Figure 7. The amount of increased TEN (mol %) was obtained by subtraction of TEN content in the as-prepared ternary blend from that in the heat-treated blend.

It is seen that an increase of TEN content due to the transesterification reaction was negligible when the heat treatment was carried out at 260°C, also, even at a high temperature of 280°C with short treatment time of 1 min. Therefore, it can be concluded that the appearance of mixed state of ternary blends at a short treatment time of 1 min shown in Figure 5 is due to the physical blend.

Above the treatment temperature of 270°C, the TEN increased steadily with increasing the treatment time with this tendency more prominent at high temperature of 280°C. However, the increased amount was only 1.5 mol % by the treatment at 280°C for 5 min. The increase seems to be too small to enhance the chemical blend. The increase was also quite small compared with the binary blend of PET/PEN, which was treated at 280°C for 5 min as described earlier. However, the miscible state was

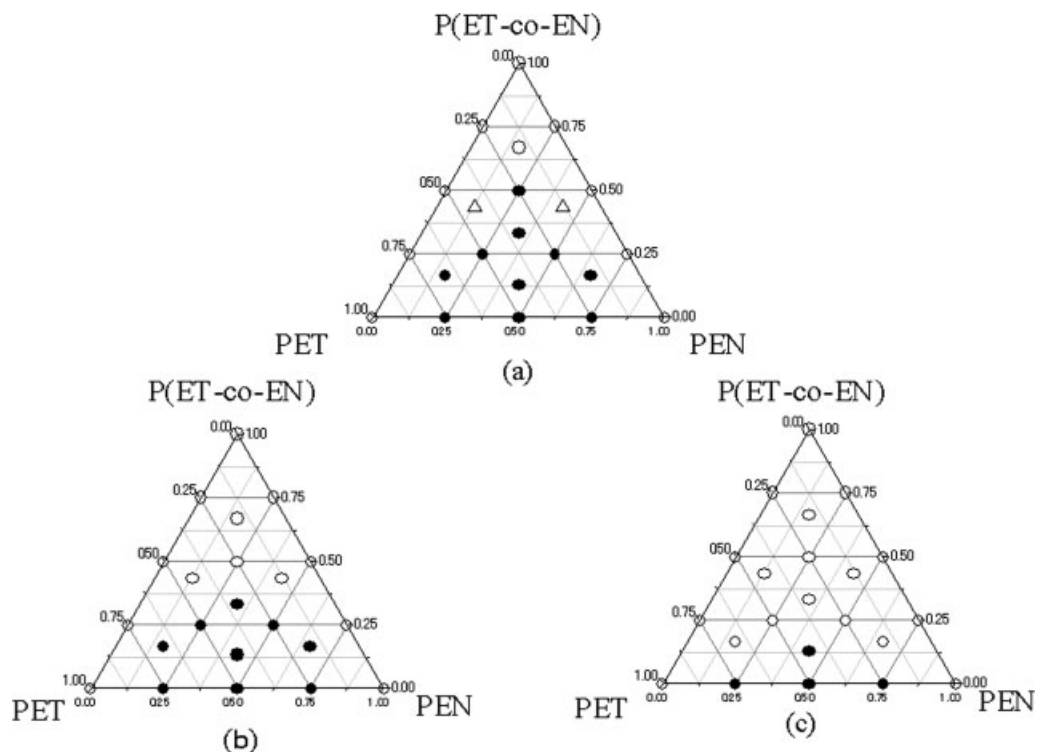


Figure 6 The phase diagrams in molten state of ternary blends with different annealing temperatures for 5 min. (a) 260°C, (b) 270°C, (c) 280°C. ○ transparency, △ translucency, and ● opacity.

achieved in the wide range of compositions of ternary blends when the blends were heat treated at 280°C. It is interesting that the increase of TEN by the heat treatment was larger for binary blend than for ternary blend. The transesterification reaction proceeds at the interface between PET and PEN phases. If P(ET-co-EN) existed between PET and PEN phases, the transesterification reaction cannot proceed. The details are currently studied.

The mechanisms of transesterification reactions in the polyester blends have been studied for a long time.^{22–25} Although three possible mechanisms (alcoholysis, acidolysis, or direct ester change) are reported,^{22–25} the details of them are not yet completely understood. Whatever the mechanism, it is generally agreed that interchange reactions lead to the formation of copolymers. In this case, the fraction of each component in the ternary blends used in this study changes, which induces the changes of phase diagram of ternary blends.

Figure 8 shows DSC thermograms for ternary blends of PET/PEN/P(ET-co-EN) (1/1/2, g/g/g) treated by various methods. The preparation of samples was as follows; the blend was heat treated at 280°C for 1 or 5 min, followed by a rapid quenching in an ice water [samples A (1 min) and B (5 min)]. Both samples were dissolved in a mixed solvent of TFA/DM (30/70, v/v), followed by coprecipitation in methanol, then the coprecipitates were dried in a

reduced pressure at room temperature for 48 h (Samples C and D).

Both Samples A and B showed a single T_g in the DSC thermograms indicating that the phases of the samples were miscible. Further, the treatment time of 1 min at 280°C was enough to induce the immiscible to miscible transition in the molten state of the ternary blend with the composition of 1/1/2 (g/g/g).

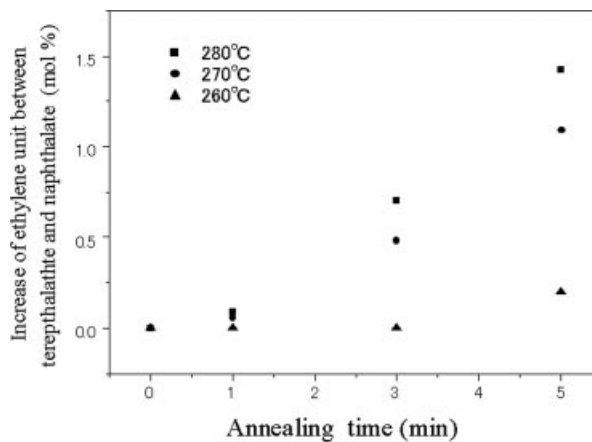


Figure 7 The increase of mol % for the ethylene moiety between terephthalic and naphthalic groups for the blends of PET/PEN/P(ET-co-EN) (1/1/1, g/g/g) as a function of heat-treatment time with different annealing temperatures.

The thermogram for Sample C was different from that for Sample A. That is, Sample C showed two T_{gs} which corresponded to the T_{gs} of PET and PEN. This means that the miscible state induced by the short heat treatment (Sample A) changed into immiscible one during the dissolution-co-precipitation process for the preparation of Sample C and suggests that the miscible state of Sample A was achieved by the physical blend by the help of P(ET-co-EN). That is, the P(ET-co-EN) acts as a plasticizer at high temperature for PET/PEN blends.

On the other hand, the thermogram for Sample D showed a single T_g , indicating that the ternary blend was miscible state even after the coprecipitation process. This suggests that the phase separation during dissolution-coprecipitation process which occurred in Sample C was less in Sample D.

As described, the increase of mol fraction of TEN was only 1.5 mol % by the increase of treatment time from 1 to 5 min at 280°C. Judging from the phase diagrams shown in Figures 5 and 6, the increase was too small to induce the immiscible to miscible transition of the ternary blends.

As-prepared blends with various compositions were heat treated at 280°C for 5 min, then cooled to 260°C at a cooling rate of 20°C/min and kept for 4 min at 260°C. The phase diagram at 260°C was constructed by observing the opacity of the samples, and the results are shown in Figure 9. It is evident that the phase diagram is different from that of the samples at 260°C kept for 5 min but quite similar to that of the samples at 280°C kept for 5 min (see Fig. 6). This means that the phase diagram for molten state of ternary blends changes with heat treatment

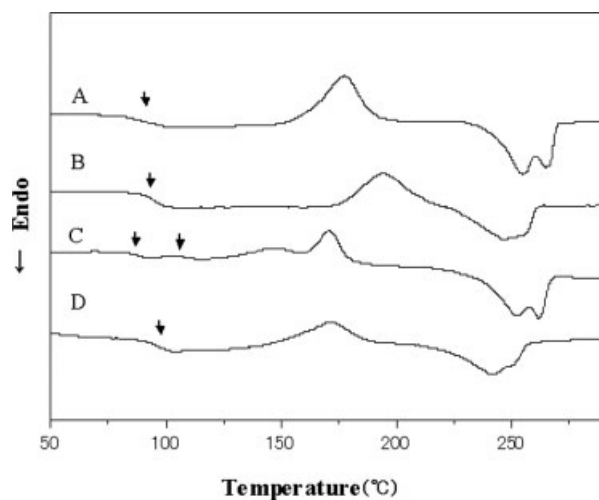


Figure 8 DSC thermograms on the heating process of MQ and re-precipitated PET/PEN/P(ET-co-EN) (1/1/2, g/g) blends with different annealing times at 280°C. A, MQ sample for 1 min; B, MQ sample for 5 min; C, reprecipitated sample from Sample A; D, re-precipitated sample from Sample B.

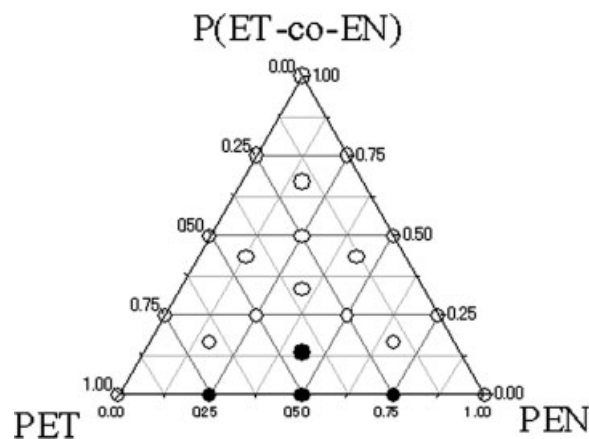


Figure 9 The phase diagram of ternary blends of PET/PEN/P(ET-co-EN) at 260°C (held at 280°C for 5 min followed by slow cooling to 260°C). ○ transparency and ● opacity.

time of the blends at high temperature and the change is not simply correlated to the change of component fraction in the ternary blends. Also, we could not find out any noticeable difference in chemical shift in the ^1H NMR spectra between A and B samples. Therefore, we cannot explain the difference of thermal behavior observed between Samples C and D.

During the heat treatment at high temperature, hydrolysis and degradation of polymer components in ternary blends might happen, which can significantly contribute to diffusion of molecules and forming of miscible blend. This phenomenon can markedly affect irreversibility of phase behavior. Therefore, the irreversibility of phase behavior might result from complex of irreversible physical and chemical interactions between components and change of phase structure of blend in the molten state of polyester blend.

CONCLUSIONS

The phase behavior in molten state of ternary blends of PET/PEN/P(ET-co-EN) was investigated by DSC, NMR, and optical microscopic observations, and phase diagrams of the ternary blends in molten state were constructed. The following conclusions were derived from the phase diagrams.

1. The random copolymer acts as a plasticizer at high temperature above 260°C for PET/PEN blends.
2. The miscibility of ternary blends in molten state was dependent on the fraction of P(ET-co-EN) in the blends and holding time at high temperature above 260°C.
3. The irreversibility of phase behavior observed in the molten state of ternary blends was not

explained by the increase of copolymer content produced during heat treatment. The irreversibility might result from complex of irreversible physical and chemical interactions between components and change of phase structure of blend in the molten state of polyester blend.

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