

The Changes of Transesterification Level in PET/PEN Blends with the Addition of PET–PEN Copolymer

Shin-Ichiro Ida, Hiroko Yamamoto, Masayoshi Ito

Department of Chemistry, Tokyo University of Science, Tokyo 162-8601, Japan

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ABSTRACT: The extent of transesterification in poly(ethylene terephthalate) (PET)/poly(ethylene-2,6-naphthalate) (PEN) blends with the addition of PET–PEN copolymers was examined by DSC and $^1\text{H-NMR}$ measurements to evaluate the factor affecting the reaction level at a given temperature and time. Both block (P(ET-*block*-EN)) and random (P(ET-*ran*-EN)) copolymers were used as the copolymers. At a given treatment temperature and time, the level was increased by the addition of P(ET-*block*-EN) into PET/PEN blends. On the other hand, a reverse

change was observed when P(ET-*ran*-EN) was mixed with PET/PEN blends. During the treatment, an inhomogeneous phase of the blends changed into the homogeneous one; however, the change showed little effect on the reaction level. The effects of molecular weight on the reaction level were also examined. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2716–2723, 2009

Key words: polyester blends; transesterification level; copolymer

INTRODUCTION

Blends of poly(ethylene terephthalate) (PET)/poly(ethylene-2,6-naphthalate) (PEN) are physically immiscible.^{1–3} However, the phase homogenization of the blends occurs at a high temperature, which may stem from transesterification reactions leading to copolymer formation.^{2–6}

There have been many studies and reviews the relations between transesterification reactions and phase homogenization of PET/PEN blends.^{2–9} The properties of PET/PEN blends prepared by melt processing are also the function of the extent of transesterification reactions occurring during blending.^{2–7} Therefore, it is important to know the factors affecting the extent of reaction.

Stewart et al.⁴ studied the effects of blending time, temperature, blend composition, and polyester catalyst on the transesterification in PET/PEN blends and reported that the amount of transesterification was determined primarily by the blending time and temperature. The composition of the blend and the residual polyester catalysts had little effect on the degree of transesterification. Golriz et al.¹⁰ proposed the kinetics of transesterification reaction in PET/PEN blends, which allowed the prediction of the extent of reaction as a function of the processing conditions such as temperature and time.

Since blends of PET and PEN are physically immiscible even at high temperature around 280°C, any transesterification reactions between them are initially limited to the interfacial zone where the two types of segments can exist. Thus, the progress of the reaction might depend on the interfacial area and the thickness of the interface, which change with the progress of homogenization of the blends. Takeda and Paul¹¹ studied the effect of physical interactions, which could be directly related to the size of interfacial area on the extent of interchange reactions for polyamide blends, and reported that the magnitude of the physical polymer–polymer interaction energy influenced the extent of reaction and the time to achieve phase homogenization of the polyamide blends. We studied the effect of PET–PEN random copolymer on the phase behavior of PET/PEN blends in the molten state and reported¹² that the addition of copolymer enhanced the homogenization of PET/PEN blends in the molten state; however, the extent of transesterification reactions between PET and PEN was not directly related to the homogenization. That is, the extent of transesterification reactions under the given conditions was lower for the ternary blends of PET/PEN/copolymer than for the binary blends of PET/PEN.

Transesterification reactions in PET/PEN system primarily occur as a direct ester–ester exchange reaction and can be described as a second-order reversible reaction.^{13,14} In this case, terephthalate-ethylene-naphthalate (TEN) sequences are produced by the consumption of terephthalate-ethylene-terephthalate

Correspondence to: M. Ito (itma56@rs.kagu.tus.ac.jp).

(TET) sequences and naphthalate-ethylene-naphthalate (NEN) sequences in PET and PEN. The rates of consumption of TET and NEN units depend on the concentrations of PET and PEN. It is generally accepted that the transesterification reactions first lead to the formation of block copolymers and then of random copolymers, which enhances the homogenization of polyester blends. This means that the concentrations of TET and NEN in the copolymer produced by the reaction decrease, and simultaneously the concentration of TEN sequences increases with the progress of the reaction. Thus, the changes in the concentrations of TET and NEN units with the reaction time during the transesterification reactions in PET/PEN blends are complex, which affect the transesterification level in PET/PEN blends. Also, the level might depend on the molecular weight of reacting species.

In this study, the effects of degree of randomness of copolymer and molecular weight, on the extent of transesterification reactions for the binary blends of PET/PEN and ternary blends of PET/PEN/PET-PEN copolymer, were examined by differential scanning calorimeter (DSC) and NMR to evaluate the factor affecting the extent of transesterification reaction at a given temperature and time for PET/PEN blends.

EXPERIMENTAL

Synthesis of P(ET-co-EN)

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

P(ET-co-EN) random copolymer (P(ET-ran-EN))

The esterification reaction was carried out using zinc acetate [0.03 mol %/(ET+EN)] for the blend of ET, EN, and EG (blend ratio; 1/1/2, mol/mol/mol) by agitating the reactant at 230°C for 2 h in the atmosphere, followed by the polycondensation reaction at 285°C for 2 h under a reduced pressure using antimony (III) oxide [0.1 mol %/(ET+EN)] as a catalyst and trimethoxyphosphate as a stabilizer. The product was dissolved in a mixed solvent of trifluoroacetic acid (TFA) and dichloromethane (DM) (30/70, v/v) at room temperature. The solution was poured into methanol to purify the product. The precipitate was dried at room temperature under a reduced pressure for 24 h.

P(ET-co-EN) block copolymer (P(ET-block-EN))

First of all, low-molecular-weight poly(ethylene terephthalate) (L-PET) and low-molecular-weight poly(ethylene-2,6-naphthalate) (L-PEN) were synthesized.

The L-PET was synthesized by esterification reaction at 220°C by using ET, EG, and zinc acetate [0.03 mol %/(ET)], followed by a solid-state polymerization (SSP) at 240°C by using antimony (III) oxide [0.1 mol %/(ET)] as a catalyst and trimethoxy phosphate as a stabilizer.

The L-PEN was synthesized by the similar procedure to that for L-PET. The temperatures for esterification reaction and for SSP were 230 and 260°C, respectively.

The synthesis of P(ET-block-EN) was carried out by the SSP for the mixture of L-PET and L-PEN (blend ratio: 1/1, g/g) at 240°C for 30 min under a reduced pressure. The product was purified by the reprecipitation similar to the P(ET-ran-EN).

Synthesis of high-molecular-weight PET and PEN

High-molecular-weight PET and PEN (H-PET and H-PEN) were obtained by a SSP of L-PET and L-PEN at 240°C under a reduced pressure. Details of the conditions for the SSP were described elsewhere.¹⁵ The intrinsic viscosities (IVs) of H-PET and H-PEN were 3.0 and 2.9 dL/g, respectively.

Preparation of blend samples

Commercial grade of PET (IV = 0.63 dL/g) and PEN (IV = 0.65 dL/g) as well as P(ET-co-EN), L- and H-homopolymers of PET and PEN synthesized in this study were used as the starting materials.

All blends were prepared by a solution blending to prevent the transesterification reactions 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 solution (3 wt %) and PEN solution (3 wt %). Then, the mixed solution was poured into methanol to obtain polymer precipitates. The precipitates were dried at room temperature under a reduced pressure for 24 h.

Measurements

The IVs of the samples were measured in a mixed solvent of TFA/DM (50/50, v/v) with an Ubbelohde viscometer at 25°C. The IV values for PET were used for the calculation of number-average molecular weight (M_n) by using the IV~ M_n relation reported by Huang et al.¹⁶ For PEN, in our knowledge, a reliable IV~ M_n relation has not been reported. Thus, the IV~ M_n relation for PET was also used for the calculation of M_n for PEN. The results are shown in Table I.

¹H-NMR measurements were carried out by using JEOL JNM-LA 500 at 25°C. The solvent used was a

TABLE I
The Number-Average Molecular Weight (M_n) for PET and PEN Samples

Sample	M_n (g/mol)	Sample	M_n (g/mol)
L-PET	15000	L-PEN	15000
PET	32000	PEN	32000
H-PET	190000	H-PEN	185000

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.⁴ The calculation was carried out by using the 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, DSC). The measurements were carried out in a dry nitrogen atmosphere at a heating rate of 10°C/min. The thermal history of the samples used for the measurements was as follows: the as-prepared blends were inserted into preheated compression molding machine and they were held at 280°C for a constant time in the range of 1–30 min, followed by a rapid quenching into an ice water to preserve the phase structure of molten state. These were termed as MQ samples.

The transparency of the samples in the 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 used for the observation was as follows: the as-prepared blends were inserted into the hot stage, in which the temperature was controlled at 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)s

Figure 1 shows the ¹H-NMR spectra of P(ET-*ran*-EN) and P(ET-*block*-EN) in the ethylene unit region. The observed peaks at 4.77 and 4.87 ppm are attributed to ethylene units of PET and PEN homopolymers, respectively.^{4,12} The observed peak at 4.82 ppm is due to the ethylene unit that exists between terephthalic and naphthalic groups in the polymer backbone.^{4,12} The degree of randomness (B) and block length for PET (L_{PET}) and PEN (L_{PEN}) were calculated using the peak intensities of the spectra according to the report by Yamadera and Murano.¹⁷ The B values were 2, 1, and 0 for alternative copolymer, random copolymer, and block copolymer or physical blends, respectively.

For P(ET-*ran*-EN), the values of B , L_{PET} and L_{PEN} were 1.01, 2.03, and 1.93, respectively, indicating a random copolymer. For P(ET-*block*-EN), the values of B , L_{PET} , and L_{PEN} were 0.18, 12.99, and 9.90, respectively. These results indicate that P(ET-*block*-EN) is a block copolymer. These were summarized together with the IV data in Table II. The DSC thermograms on the heating process of MQ samples of

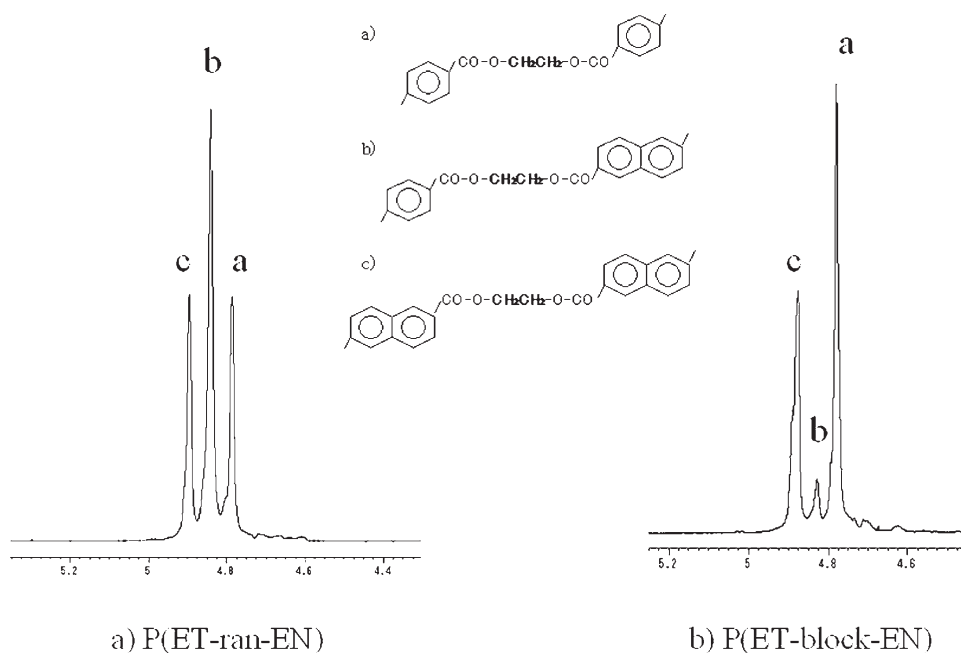


Figure 1 ¹H-NMR spectra of the ethylene unit region for P(ET-*ran*-EN) and P(ET-*block*-EN).

TABLE II
Characterization of P(ET-co-EN)s

	L_{PET}	L_{PEN}	B	IV (dL/g)
P(ET- <i>ran</i> -EN)	2.03	1.93	1.01	0.30
P(ET- <i>block</i> -EN)	12.99	9.90	0.18	0.30

L_{PET} = averaged block length of PET;
 L_{PEN} = averaged block length of PEN;
 B = degree of randomness.

P(ET-*block*-EN) and P(ET-*ran*-EN) are shown in Figure 2. The two MQ samples had the same thermal history of 280°C for 3 min followed by quenching in ice water.

P(ET-*ran*-EN) showed a single T_g around 90°C. No noticeable exothermic peak during the heating process of P(ET-*ran*-EN) corresponding to the cold crystallization was observed. Details of the DSC results were explained in our previous article.¹²

Block copolymers often form the microdomain structures, depending on the block length and composition ratio.¹⁸ When the size of microdomain structure is large enough, the block copolymer may show multiple T_g s corresponding to each domain.¹⁹ However, the P(ET-*block*-EN) showed a single T_g around 85°C, suggesting that the domain sizes of PET and PEN components are not large enough to show an individual T_g probably due to low molecular weight of copolymer.

P(ET-*block*-EN) showed an exothermic peak around 150°C because of the cold crystallization. The values of L_{PET} and L_{PEN} for P(ET-*block*-EN) were larger than 3 (see Table II), which was a minimum length for the crystallization of PET and PEN,²⁰ resulting in the thermal crystallization during the heating process of DSC scan.

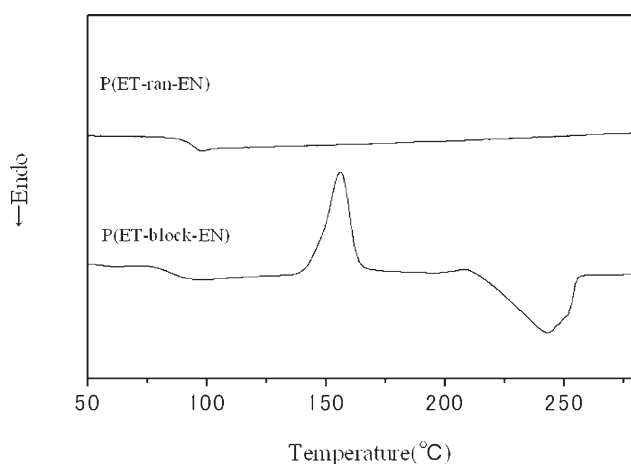


Figure 2 DSC thermograms on the heating process of MQ samples of P(ET-*ran*-EN) and P(ET-*block*-EN).

Changes of reaction level

When PET/PEN blends are heat-treated in the molten state, transesterification reactions often occur at the interface between PET and PEN phases. Further, the inhomogeneous phase structure in the molten state of the blends changes to homogeneous one (immiscible to miscible) with the progress of the reaction. Thus, the interfacial area and the thickness of the interface change with the progress of transesterification reactions in the blends. In this study, the transesterification reactions were carried out at 280°C. Therefore, the information on the phase behavior of the blends as a function of time is necessary to discuss on the extent of transesterification reaction.

We reported¹² the phase behavior for PET/PEN/P(ET-*ran*-EN) blends at 280°C as a function of time using DSC results and optical microscope observations. In this work, similar techniques were used to get information on the phase behavior for PET/PEN/P(ET-*block*-EN) blends.

Figure 3 shows DSC thermograms of MQ samples of PET/PEN/P(ET-*block*-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_g s of PET and PEN indicating that PET and PEN are in the immiscible state. On the other hand, the blend treated for 5 min showed only one T_g around 85°C, apparently, miscible state.

Optical microscope observations during the heat treatments were carried out for the ternary blends. It was found that at a given temperature of 280°C, an opacity–transparency transition happened at the treatment time of 3 min. The quenched sample from the opaque state showed two T_g s in the DSC

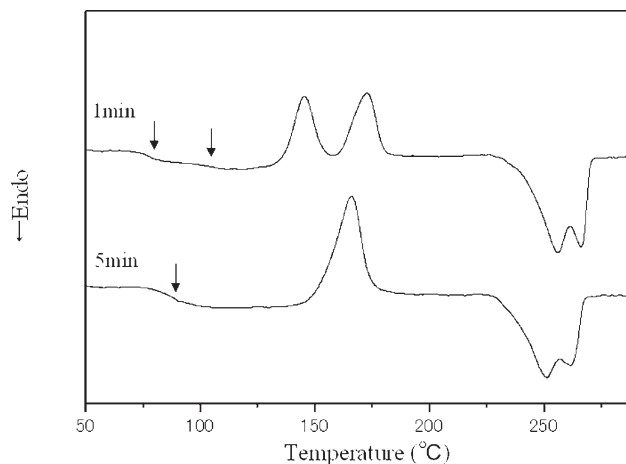


Figure 3 DSC thermograms on the heating process of MQ samples of PET/PEN/P(ET-*block*-EN) (1/1/1, g/g/g) blends annealed at 280°C for 1 and 5 min.

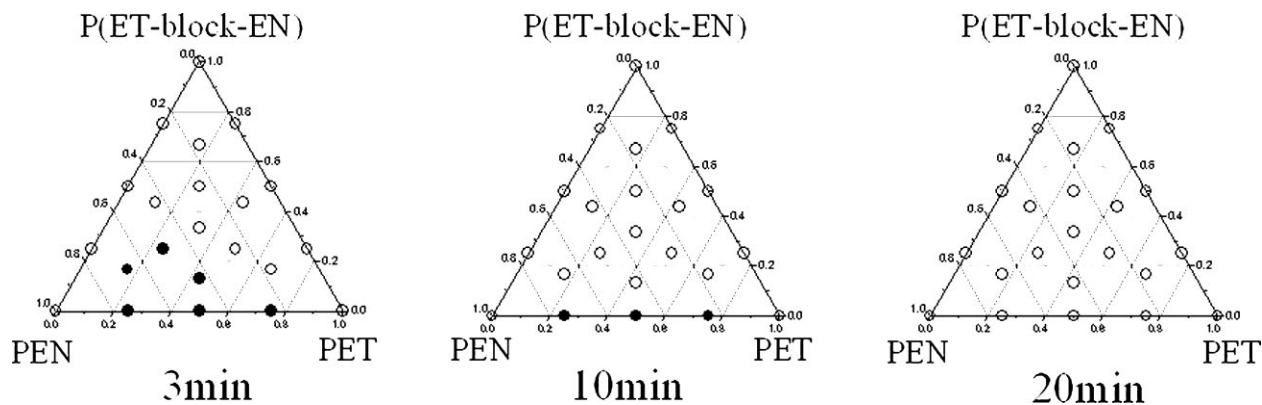


Figure 4 The phase diagrams in the molten state of PET/PEN/P(ET-*block*-EN) at 280°C for the treatment times of 3, 10, and 20 min. ○: homogeneous; ●: inhomogeneous.

thermogram. On the other hand, the quenched sample from the transparent state showed only one T_g around 85°C. These results indicate that the opacity to transparency transition corresponds to the immiscible to miscible phase transition of PET and PEN domains in the molten state of PET/PEN/P(ET-*block*-EN) blends.

On the basis of opacity–transparency transition obtained by the optical microscope observations, the phase diagrams at 280°C for the ternary blends of PET/PEN/P(ET-*co*-EN) were constructed as a function of blend ratio for different treatment times, and the results are shown in Figures 4 and 5. Details of the construction of the phase diagrams were described in our previous article.¹² It is seen that the phase of the binary blends of PET/P(ET-*co*-EN) and PEN/P(ET-*co*-EN) was homogeneous in any case (composition, treatment time). On the other hand, the binary blends of PET/PEN were inhomogeneous in any compositions when the treatment time was less than 10 min; although the phase became homogeneous after a prolonged treatment time of 20 min. The phases of ternary blends of PET/PEN/P(ET-*co*-EN) were homogeneous in a wide range of composi-

tions. Also, a noticeable difference was not observed in the phase diagrams between PET/PEN/P(ET-*block*-EN) and PET/PEN/P(ET-*ran*-EN) blends. As will be shown, the transesterification level at the treatment time of 3 min was negligibly small. These results indicate that the P(ET-*co*-EN) worked as a compatibilizer for the PET/PEN blends, and the degree of randomness of P(ET-*co*-EN) had little effect on the phase behavior of the ternary blends of PET/PEN/P(ET-*co*-EN).

The transesterification level was evaluated from the increase of TEN sequences (mol %) by using NMR data, which could play a key role in homogenizing the PET/PEN blends.

First of all, the relation between transesterification level and treatment time was examined for the four binary blends of PET/P(ET-*block*-EN), PET/P(ET-*ran*-EN), PEN/P(ET-*block*-EN), and PEN/P(ET-*ran*-EN). The blend ratios for all samples were fixed to be 1/1 (g/g). These blends were appropriate to minimize the effect of inhomogeneous–homogeneous transition on the reaction level. Because, the transition for the four blends was attained within a short treatment time of 3 min (see Figs. 4 and 5).

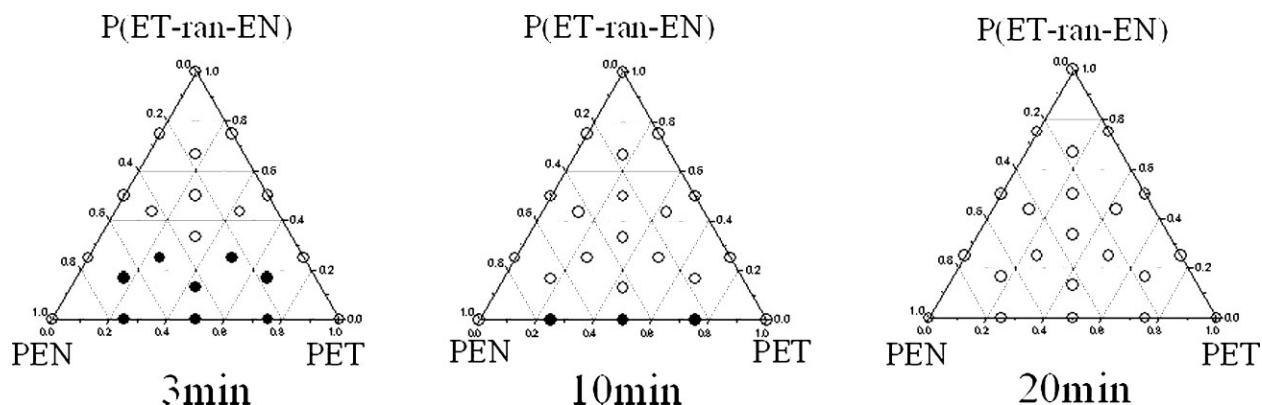


Figure 5 The phase diagrams in the molten state of PET/PEN/P(ET-*ran*-EN) at 280°C for the treatment times of 3, 10, and 20 min. ○: homogeneous; ●: inhomogeneous.

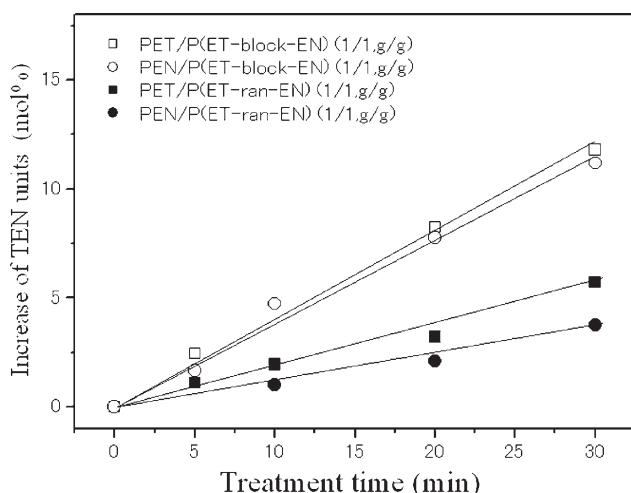


Figure 6 The increase of TEN units for the binary blends as a function of treatment time at 280°C.

In Figure 6, the increase of TEN (mol %) was plotted against the treatment time at 280°C for the four systems. The increased TEN units (mol %) were obtained by the subtraction of TEN units (mol %) in the as-prepared blends from that in the heat-treated one. It is seen that the number of TEN units for all blends increased with increasing the treatment time. At a given time, the increase of TEN unit was larger for both PET/P(ET-block-EN) and PEN/P(ET-block-EN) than for both PET/P(ET-ran-EN) and PEN/P(ET-ran-EN). The TEN units were produced by consuming ethylene units in both PET (TET) and PEN (NEN) in homopolymers and copolymers. As shown, the original P(ET-ran-EN) itself had a large number of TEN unit when compared with P(ET-block-EN). This means that the numbers of TET and NEN units in the copolymer available for the production of TEN units are smaller for P(ET-ran-EN) than for P(ET-block-EN). Therefore, the net rise of TEN unit is smaller for homopolymer/P(ET-ran-EN) than for homopolymer/P(ET-block-EN), in accordance with the experimental results.

The rise of TEN unit was slightly larger for PET/P(ET-ran-EN) than for PEN/P(ET-ran-EN). At present, the reason is not clear. One possible explanation is the difference of melt viscosity between PET and PEN, and the viscosity is higher for PEN than PET at a given molecular weight.²¹ The degree of transesterification reac-

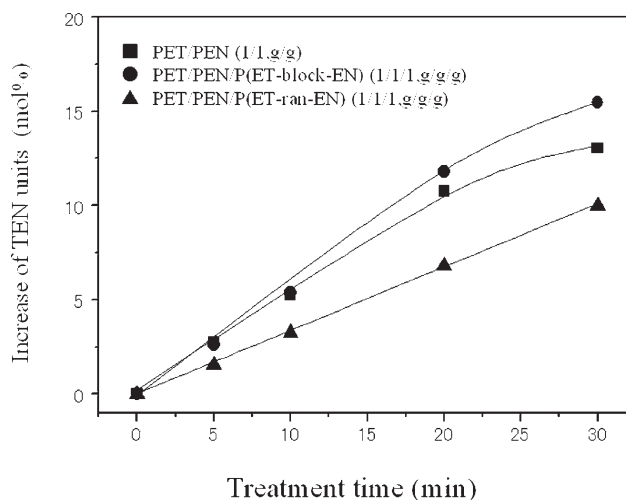


Figure 7 The increase of TEN units for the binary and ternary blends as a function of treatment time at 280°C.

tions might be affected by the molecular mobility in the molten state, which is a function of melt viscosity.

In Figure 7, the increase of TEN unit (mol %) was plotted as a function of heat treatment time at 280°C for ternary blends of PET/PEN/P(ET-ran-EN) and PET/PEN/P(ET-block-EN) with the blend ratios of 1,1,1, g/g/g. The results for the binary blends of PET/PEN (blend ratio: 1/1, g/g) were also shown in the same figure.

By increasing the treatment time, the number of TEN units for all blends increased. At the beginning of the heat treatment at 280°C, all blends were inhomogeneous states. As seen in Figures 4 and 5, the phase of the two ternary blends was homogeneous at the treatment time of 3 min. That is, an inhomogeneous to homogeneous transition occurred within a short treatment time of 3 min. For the binary blends of PET/PEN, such change was observed around the treatment time of 10 min. However, a smooth rise of TEN units during the heat treatment (see Fig. 7) suggests that the transesterification reaction was not affected by the phase homogenization of the blends in the molten state, which is different from the results for the polyamide blends.¹¹ For the polyamide blends, direct chemical couplings between the component polyamides enhance the phase homogenization of the blends.²² On the other hand, for the PET/PEN blends, the homogeneous state can be obtained by using compatibilizer as shown in our

TABLE III
The Molar Fractions of TET, TEN, and NEN in the As-Prepared Blends

Sample	TET in PET (mol %)	TET in copolymer (mol %)	NEN in PEN (mol %)	NEN in copolymer (mol %)	NET in copolymer (mol %)
PET/PEN (1/1, g/g)	56.8	–	43.2	–	–
PET/PEN/P(ET-block-EN) (1/1/1, g/g/g)	39.4	12.0	29.9	16.1	2.6
PET/PEN/P(ET-ran-EN) (1/1/1, g/g/g)	37.7	8.5	28.3	8.5	17.0

previous work.¹² Taking these into consideration, it can be speculated that in the inhomogeneous state, the domain size formed by the component polymer is smaller for PET/PEN blends than for polyamide blends. In this case, the change of domain size at the inhomogeneous to homogeneous transition is not large enough to produce the large difference of interfacial area. The details are currently studied.

At a given treatment time, the rise of TEN units was in the order of PET/PEN/P(ET-*block*-EN) > PET/PEN > PET/PEN/P(ET-*ran*-EN).

As described earlier, the increase of TEN units was dependent on the concentrations of TET and NEN in the system. Thus, the concentrations before the heat treatment were roughly estimated from NMR data. The concentration was expressed by the mole % per gram of blend, and the values are shown in Table III. The molar fractions of TET and NEN for the PET/PEN/P(ET-*ran*-EN) were the lowest among the blends used. This is reasonable because the increase of TEN units at a given treatment time for the PET/PEN/P(ET-*ran*-EN) was the smallest among the blends. On the other hand, the increase of TEN units was larger for the PET/PEN/P(ET-*block*-EN) than for the PET/PEN; although the concentrations of TET and NEN units were lower for the former than the latter. At the prolonged treatment time, degree of randomness (*B*) of P(ET-*block*-EN) was enhanced, and simultaneously both L_{PET} and L_{PEN} decreased. The results are shown in Figure 8, which indicate that the chemical structure of P(ET-*block*-EN) approaches that of P(ET-*ran*-EN) at the prolonged treatment time. In this case, the concentrations of TET and NEN units in the copolymer should reduce with time, leading to the decrease of production rate of TEN units. However, the mol % of TEN units increased steadily with time.

As seen in Table II, the IV of copolymer was quite low, almost half of the homopolymer. Thus, the

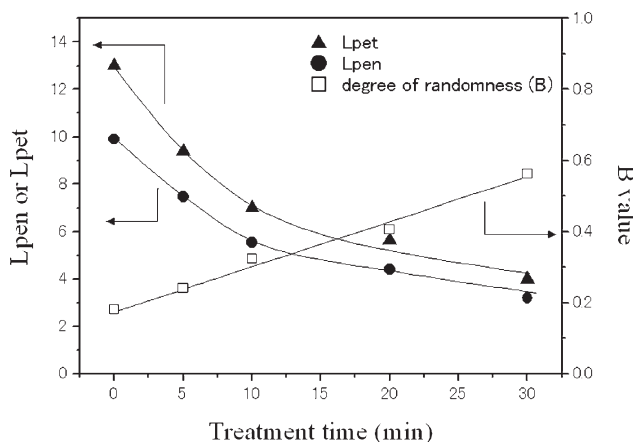


Figure 8 The changes of *B*, L_{PET} , and L_{PEN} as a function of treatment time at 280°C.

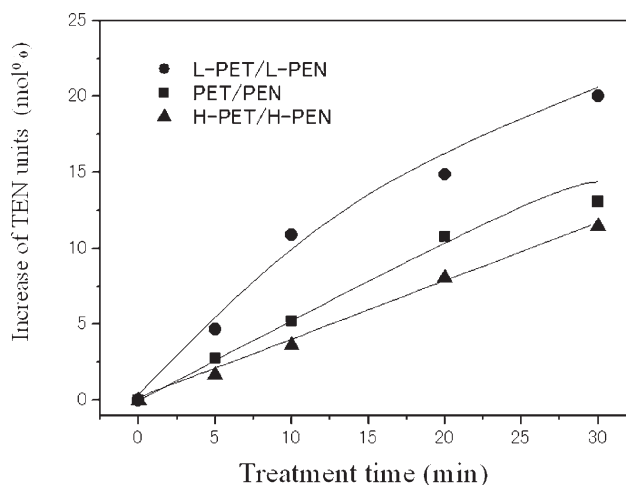


Figure 9 The increase of TEN units as a function of treatment time at 280°C for the binary blends of PET/PEN with different molecular weights.

mobility of TET and NEN units in the copolymer might be higher than those in homopolymers. The reaction level may enhance by increasing the mobility of reacting species. For the ternary blends, about 30% of TET and NEN units in the blends belong to copolymer. Thus, the effects of molecular weight on the reaction level was investigated to explain the high level of transesterification in PET/PEN/P(ET-*block*-EN) blends shown in Figure 7.

In Figure 9, the increase of TEN units by the transesterification reactions was plotted as a function of heat treatment time at 280°C for the binary blends of PET/PEN (1/1, g/g) with different molecular weights. For all blends, ET/EN = 56/44 (mol %) was confirmed by NMR data.

It is clearly seen that the TEN units increased with treatment time with this tendency more prominent

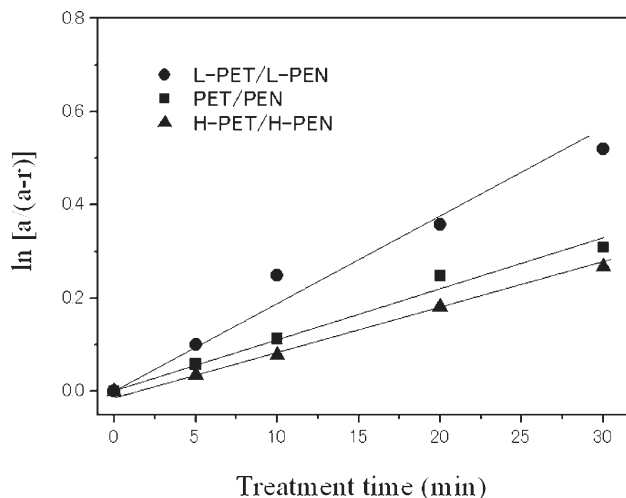


Figure 10 Plot of $\ln[a/(a-r)]$ against *t* for the blends of various molecular weights.

TABLE IV
Rate Constants of the Transesterification for PET/PEN Blends with Different Molecular Weights at 280°

Samples	k (10^{-2} min^{-1})	R^2
L-PET/L-PEN	1.80	0.97
PET/PEN	1.10	0.98
H-PET/H-PEN	0.88	0.99

in the blends with the lowest molecular weight. Attempts had been made to investigate the effects of molecular weight on the transesterification kinetics of PET/PEN blends by using eq. (1), which was given by Devaux et al.²³

$$\ln[a/(a-r)] = kt \quad (1)$$

where a is the initial molar fraction of PET, r is equal to x/b , x is the half molar fraction of TEN at time t , b is the initial molar fraction of PEN, and k is the reaction rate. The values of a and r were calculated by using NMR data.

In Figure 10, the $\ln[a/(a-r)]$ was plotted against the treatment time at 280°C. A clear linear dependence on time is seen for all samples, indicating that the transesterification kinetics of PET/PEN blends with different molecular weights can be analyzed with the reversible second-order reaction.

The rate constant of the reaction (k) was calculated for the blends by using the data shown in Figure 10, and the results are shown in Table IV. It is clearly seen that the k values increased with the decrease in the molecular weight. These results support our consideration that the higher level of transesterification in the PET/PEN/P(ET-*block*-EN) is due to the effects of molecular weight when compared with PET/PEN.

CONCLUSIONS

The extent of transesterification in PET/PEN blends with the addition of PET-PEN copolymer were examined by DSC and ¹H-NMR to evaluate the factor affecting the reaction level at a given temperature and time. The following conclusions were derived from the experimental results:

1. The degree of randomness of PET-PEN copolymer had almost no effect on the phase homogenization in the molten state of PET/PEN blends.

2. During the heat treatment at 280°C, an inhomogeneous to homogeneous phase transition occurred in the blends; however, the reaction level of transesterification was less affected by the phase transition.
3. At a given temperature and time, the level of transesterification in the PET/PEN blends was primarily determined by the concentrations of TET and NEN units and the molecular weight of reacting species in the blends.

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