

# Phase behaviour and transesterification in poly(ethylene 2,6-naphthalate) and poly(ethylene terephthalate) blends

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The effect of transesterification on the phase behaviour in poly(ethylene 2,6-naphthalate) and poly(ethylene terephthalate) blends was investigated by using differential scanning calorimetry. The transesterification between the two polymers was confirmed by  $^1\text{H}$  nuclear magnetic resonance. The blend samples heat treated for up to 11 min at  $280^\circ\text{C}$  show two glass transitions, which approach closer with the increase of reaction time. After 13 min, a single glass transition is observed, and the glass transition range becomes narrow with the lapse of reaction time. From the glass transition behaviour, the phase compositions and the phase fractions were determined as functions of reaction time at  $280^\circ\text{C}$ . The composition difference between ethylene 2,6-naphthalate (EN)-rich and ethylene terephthalate (ET)-rich phases decreases as the transesterification proceeds. On the other hand, though the weight fractions of the EN-rich phase, the ET-rich one and the interfacial zone tend to change with the lapse of time, the changes are small in magnitude. © 1997 Elsevier Science Ltd.

(Keywords: transesterification; phase composition; phase fraction)

## INTRODUCTION

There has been great interest in polyester blends from the viewpoints of industrial applications and academic interest. In these blends, transesterification (such as alcoholysis, acidolysis or ester exchange) commonly occurs in the molten state, which first produces block copolymers and finally random copolymers. Many studies<sup>1-6</sup> have been focused on the miscibility and transesterification in polyester blends. Suzuki *et al.*<sup>7</sup> reported that polycarbonate (PC) and poly(ethylene terephthalate) (PET) were homogenized by transesterification at  $270^\circ\text{C}$ . They observed double glass transitions, reflecting an inhomogeneous phase, for the samples with a short melt processing time. However, a single glass transition was observed after sufficient time of melt processing. Porter and Kimura<sup>8,9</sup> studied the phase behaviour and transesterification for a PC and polyarylate (PAr) blend. For up to 1 h of transesterification at  $250^\circ\text{C}$ , the blend showed a new copolymer phase in addition to the PC phase and the PAr-rich phase. After 4 h at  $250^\circ\text{C}$ , a single glass transition was observed, reflecting a homogeneous phase.

Poly(ethylene 2,6-naphthalate) (PEN) is quite useful for many packaging applications, due to good mechanical properties, low permeability of oxygen and carbon

dioxide, and good thermal properties (high-melting and high glass transition temperatures). However, PEN exhibits a high melt viscosity and is also expensive. One way to overcome these limitations is to mix PEN with PET. PEN is known to be immiscible with PET<sup>10</sup>. Therefore, in order to achieve compatibility in the PEN and PET blend, it is necessary to induce and control the transesterification between the two polymers. Recently, Stewart *et al.*<sup>11</sup> reported that the primary factors controlling the transesterification in PEN and PET blend were the blending time and temperature, while the composition of the blend and residual polyester catalysts had little effect on the transesterification. In addition, the transesterification led to the formation of a single phase. In this study, during the transition process from the heterogeneous phase to the homogeneous one by the transesterification in PEN and PET blends, the phase behaviour (such as the compositions of the PEN-rich and PET-rich phases, and the weight fractions of the PEN-rich phase, the PET-rich one and the interfacial zone) was investigated by d.s.c.

## EXPERIMENTAL

### Polymers

PEN was prepared from dimethyl naphthalate and ethylene glycol by melt polycondensation, which is

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described in detail elsewhere<sup>12</sup>. PET was supplied by Kolon Ind. The weight-average molecular weights of PEN and PET, measured by the laser light-scattering method, were  $2.03 \times 10^4$  and  $3.93 \times 10^4$  g mol<sup>-1</sup>, respectively.

#### Sample preparation

The blends were prepared by dissolving the component polymers in a mixed solvent of phenol/*o*-dichlorobenzene (6/4, v/v). The polymer solutions were poured into a large excess of acetone. The precipitate was a solid blend of the two polymers, which was recovered by filtration and dried in a vacuum oven at 60°C for 24 h. Heat treatment for the transesterification was carried out on a du Pont 910 differential scanning calorimeter under a dry nitrogen atmosphere. Samples were heated rapidly from room temperature to 280°C, maintained at that temperature for various time intervals, and quenched into dry ice powder.

#### Analysis

<sup>1</sup>H n.m.r. spectra were obtained by using a Bruker AMX-500 FT-NMR spectrometer (500 MHz) on solutions in deuterated trifluoroacetic acid/chloroform (7/3, v/v). Thermal analysis was performed on a du Pont 910 differential scanning calorimeter, and all scans were conducted at 20°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

#### Confirmation of transesterification

Figure 1 shows <sup>1</sup>H n.m.r. spectra in the range from 4.7 to 5.2 ppm, for PEN/PET (50/50, wt/wt) blend samples with various reaction times at 280°C. In the spectrum of the sample which was not heat treated at 280°C, two peaks are observed at 4.98 and 4.90 ppm, consistent with proton signals of the ethylene unit in PEN and PET homopolymers, respectively. For the samples heat

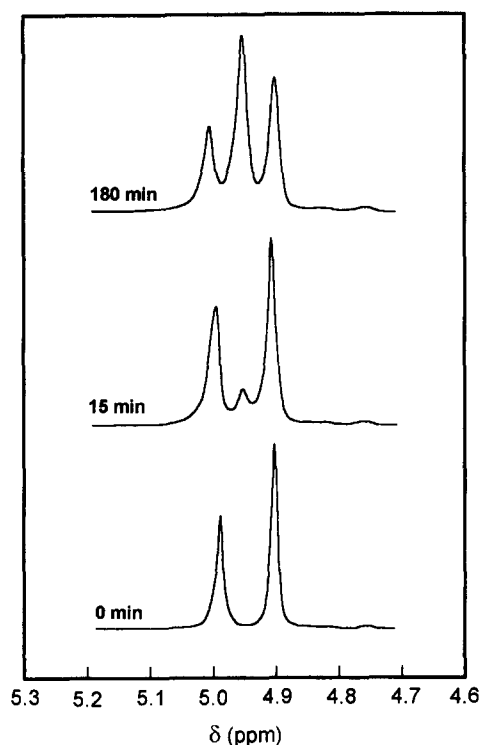


Figure 1 <sup>1</sup>H n.m.r. spectra for the PEN/PET (50/50) blend. The curve indicates the reaction time at 280°C

treated at 280°C, a new peak appears at 4.95 ppm, and the intensity increases as a function of the reaction time. This peak is assigned to protons of the ethylene unit bonded between 2,6-naphthalate and terephthalate, formed by transesterification<sup>11</sup>. Hence, the relative peak areas of the three signals at 4.98, 4.95, and 4.90 ppm are proportional to the concentrations of ethylene 2,6-naphthalate–ethylene 2,6-naphthalate (EN–EN), ethylene 2,6-naphthalate–ethylene terephthalate (EN–ET), and ethylene terephthalate–ethylene terephthalate (ET–ET) dyad sequences in the reacted blend system, respectively. The number-average sequence lengths of EN ( $\langle L_{EN} \rangle$ ) and ET ( $\langle L_{ET} \rangle$ ), and the degree of randomness ( $B$ ) are defined as

$$\langle L_{EN} \rangle = \frac{2x_{EN}}{x_{EN-ET}} \quad (1)$$

$$\langle L_{ET} \rangle = \frac{2x_{ET}}{x_{EN-ET}} \quad (2)$$

$$B = \frac{x_{EN-ET}}{2x_{EN}x_{ET}} \quad (3)$$

where  $x_{EN}$  is the mole fraction of EN,  $x_{ET}$  is the mole fraction of ET, and  $x_{EN-ET}$  is the mole fraction of the EN–ET dyad. As shown in Figures 2 and 3, the number-average sequence lengths decrease with the

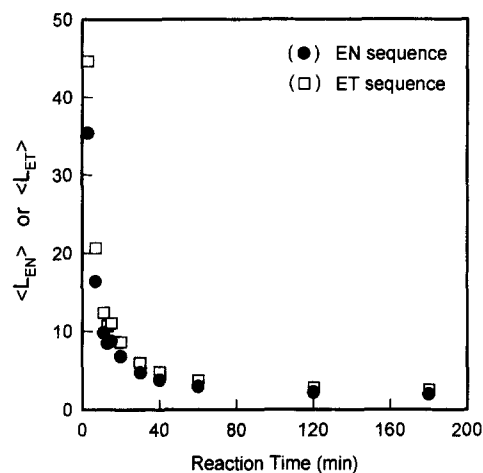


Figure 2 Change of the number-average sequence length with the reaction time at 280°C for the PEN/PET (50/50) blend

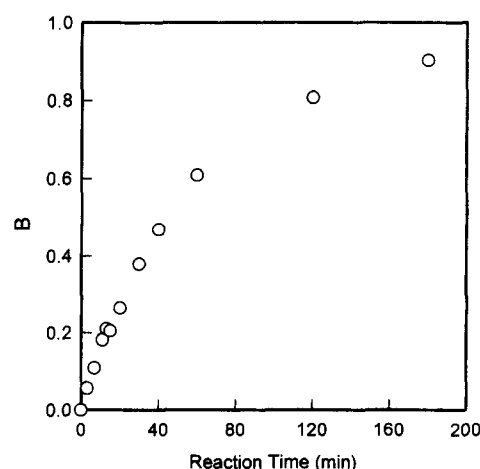


Figure 3 Change of randomness with the reaction time at 280°C for the PEN/PET (50/50) blend

increase of reaction time, and the randomness increases with the increase of reaction time. From these behaviours it is obvious that the transesterification between PEN and PET takes place at 280°C, and that the blend system becomes randomized as the transesterification progresses.

#### Phase behaviour

Figure 4 shows the d.s.c. curves obtained on heating the quenched samples after melting at 280°C for 3 min. All the blend samples have double glass transitions, double cold-crystallization exotherms, and double melting endotherms. This indicates that the mixtures are immiscible. The transition temperatures of the blends are slightly different to those of the component homopolymers, because the transesterification occurred when the samples were melted at 280°C for 3 min. Figure 5 shows

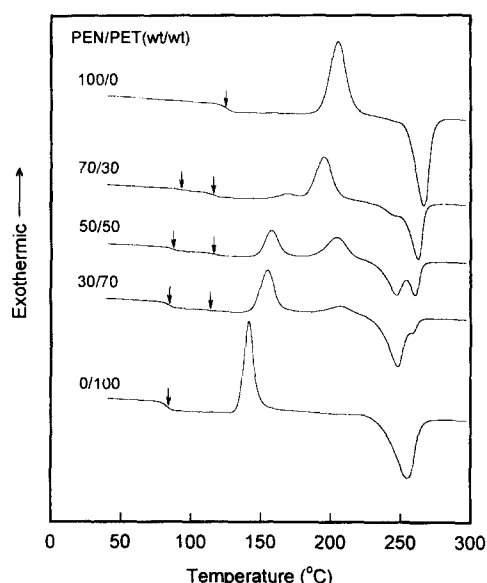


Figure 4 D.s.c. curves for the PEN/PET blends. The arrow indicates the position of the glass transition temperature

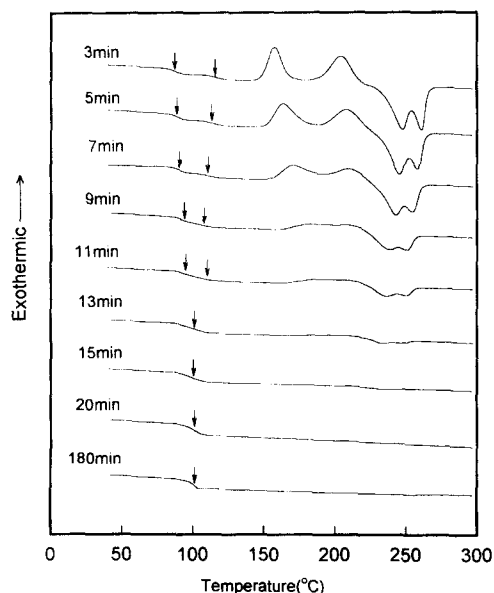


Figure 5 D.s.c. curves for the PEN/PET (50/50) blend. The curve indicates the reaction time at 280°C

the d.s.c. curves for PEN/PET (50/50) blend samples, which were isothermally maintained at 280°C for different time intervals. The heats of double cold-crystallization and melting peaks reduce with the increase of reaction time, respectively. In addition, the cold-crystallization temperatures increase and the melting temperatures decrease. These thermal behaviours suggest that crystallization is hindered, due to the disruption of the chain periodicity as a consequence of transesterification. For the blends heat treated for 20 min or more, the cold-crystallization and melting were not observed. Recalling  $\langle L_{EN} \rangle = 6.8$  and  $\langle L_{ET} \rangle = 8.6$  for the blend reacted for 20 min, the minimum value of the average sequence length necessary to form the crystallites is approximately 7–8.

The effect of reaction time on the glass transition behaviour for the PEN/PET (50/50) blend is shown in Figure 6. The glass transition temperature ( $T_g$ ) was taken as the inflection point of the heat capacity change, and the glass transition range was taken as the temperature range between the two onset points of the low-temperature and high-temperature baselines. Until 11 min, the blend shows double glass transitions, which approach closer with the increase of reaction time. The higher  $T_g$  is attributable to the EN-rich phase, and the lower to the ET-rich phase. After 13 min, a single glass transition is observed, and the glass transition range becomes narrow with the lapse of reaction time, reflecting that the transesterification enhances the miscibility. In the early stage of transesterification, the EN-rich phase coexists with the ET-rich one, and the composition of each phase varies with the degree of transesterification. The composition of the two phases can be estimated, if we know the dependence of the glass transition temperature on the composition for a one-phase system. Hence, the glass transition temperatures were measured for blend samples maintained at 280°C for 180 min. As shown in Figure 7, the  $T_g$  behaviour satisfies the following linear relation:

$$T_g = w_1 T_{g1}^0 + w_2 T_{g2}^0 \quad (4)$$

where  $T_{gi}^0$  is the glass transition temperature of homopolymer  $i$  and  $w_i$  is the weight fraction of component  $i$ . The EN and ET units are designated as 1 and 2, respectively. In Figure 6, the glass transition temperature

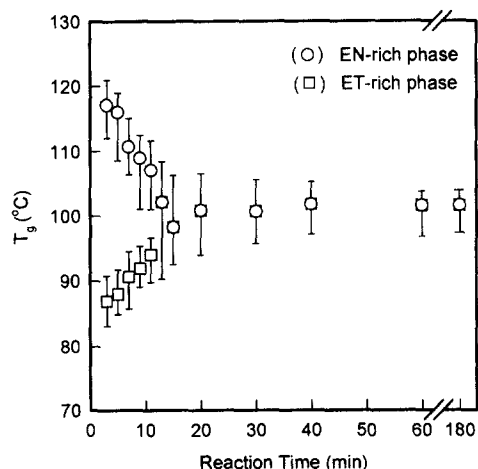


Figure 6 Change of the glass transition behaviour with the reaction time at 280°C for the PEN/PET (50/50) blend

after 13 min is almost invariant of reaction time, even though the glass transition temperature range becomes narrow. This means that the glass transition temperature is independent of the sequence lengths of EN and ET units. As an extreme case, the glass transition temperature of PEN/PET blend with no transesterification (if this blend forms a single phase) may be equal to that of the random copolymer. Therefore, the compositions of EN-rich and ET-rich phases can be estimated from equations (5) and (6), respectively,

$$T_{gU} = w_{1U}T_{g1}^0 + w_{2U}T_{g2}^0 \quad (5)$$

$$T_{gL} = w_{1L}T_{g1}^0 + w_{2L}T_{g2}^0 \quad (6)$$

where the subscripts U and L correspond to the EN-rich phase and the ET-rich one, respectively. As the transesterification proceeds, the difference in composition between the EN-rich phase and the ET-rich one lessens (Figure 8). This result can be explained as follows. The unreacted blends of PEN and PET are known to be immiscible, and the polymer-polymer interaction parameter is a small positive value (0.015 at 280°C)<sup>13</sup>. Therefore, in the first step of transesterification, the reaction must take place at the interface between the EN (or PEN) phase and the ET (or PET) one, and produce

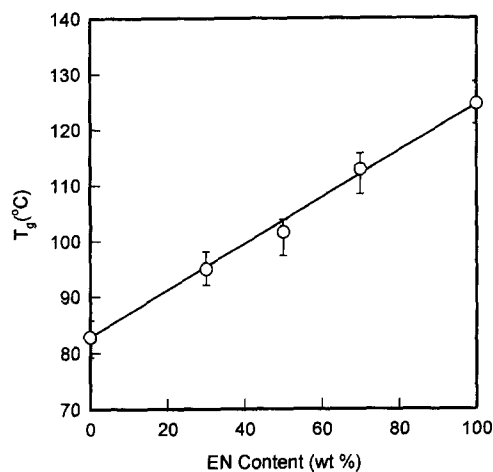


Figure 7 Glass transition temperatures of the EN/ET copolymers prepared by heat treating of PEN/PET blends at 280°C for 180 min. The solid line follows the additive rule

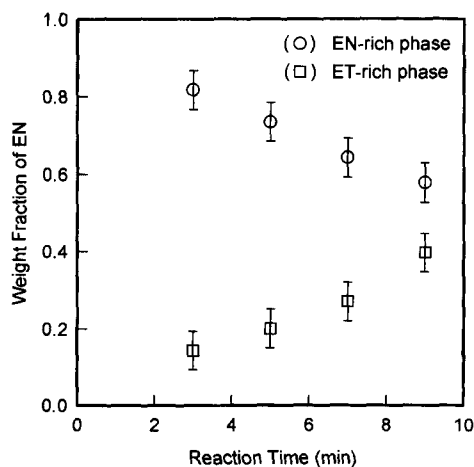


Figure 8 Change of the coexisting phase compositions with the reaction time at 280°C for the PEN/PET (50/50) blend

block copolymers, even though the kinetics of the transesterification will be characteristic of the blend structure generated during precipitation. In the second step, some block copolymers, containing the EN unit as a major component, may penetrate into the EN phase. Similarly, other block copolymers with the ET unit as a major component can diffuse into the ET phase. This mutual solubility, i.e. partial miscibility, results in a reduction in the composition difference of both phases.

For a partially miscible blend, the fractions of two co-existing phases and the interfacial zone can be estimated by a similar method, postulated by Beckman *et al.*<sup>14</sup>. In this method, the only essential data are the heat capacity changes at the glass transition temperatures of the partially miscible blend ( $\Delta C_{pS}$ ) and the pure homopolymers ( $\Delta C_{pS}^0$ ). Assuming that the  $\Delta C_{pS}$  vary linearly with mass fractions and  $\Delta C_{pS}^0$ ,

$$\Delta C_{pU} = \Delta C_{p1}^0 \left( \frac{m_{1U}}{m_T} \right) + \Delta C_{p2}^0 \left( \frac{m_{2U}}{m_T} \right) \quad (7)$$

$$\Delta C_{pL} = \Delta C_{p1}^0 \left( \frac{m_{1L}}{m_T} \right) + \Delta C_{p2}^0 \left( \frac{m_{2L}}{m_T} \right) \quad (8)$$

where  $m_{iU}$  and  $m_{iL}$  are the masses of component  $i$  in the EN-rich and ET-rich phases, and  $m_T$  is the total mass of the system. From equations (5)–(8), the weight fractions of the EN-rich phase ( $w_U$ ), the ET-rich phase ( $w_L$ ), and the interfacial zone ( $w_I$ ) can be expressed as

$$w_U = \frac{\Delta C_{pU}(T_{g2}^0 - T_{g1}^0)}{\Delta C_{p1}^0(T_{g2}^0 - T_{gU}) + \Delta C_{p2}^0(T_{gU} - T_{g1}^0)} \quad (9)$$

$$w_L = \frac{\Delta C_{pL}(T_{g2}^0 - T_{g1}^0)}{\Delta C_{p1}^0(T_{g2}^0 - T_{gL}) + \Delta C_{p2}^0(T_{gL} - T_{g1}^0)} \quad (10)$$

$$w_I = 1 - w_U - w_L \quad (11)$$

From the d.s.c. curves in the glass transition region,  $\Delta C_{pU}$  and  $\Delta C_{pL}$  were determined schematically by using tangential lines, as shown in Figure 9. The influence of the reaction time on the phase fractions is shown in Figure 10. The fractions of the EN-rich and ET-rich phases tend to decrease slightly with increasing reaction time, which results in the increment change of the

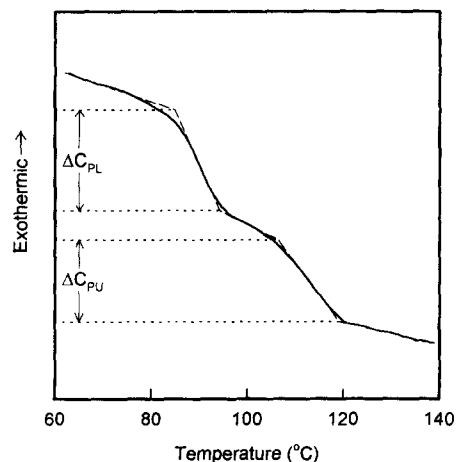
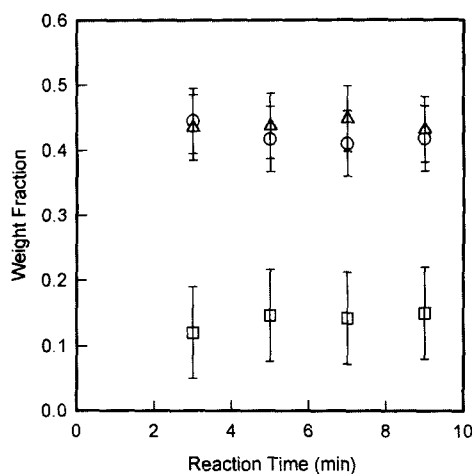


Figure 9 Typical d.s.c. curve in the glass transition region to determine the heat capacity changes at the glass transitions for the PEN/PET (50/50) blend maintained at 280°C for 5 min. Dashed lines are tangential lines



**Figure 10** Change of the phase fractions with the reaction time at 280°C for the PEN/PET (50/50) blend: ○, EN-rich phase; △, ET-rich phase; □, interfacial zone

interfacial fraction. This seems to be attributed to the increase in the number of block copolymers as the transesterification proceeds. However, the magnitudes of the changes in the three fractions are smaller than those of the composition changes in the EN-rich phase and the ET-rich one during the homogenization process. Consequently, as the transesterification proceeds, the initial heterogeneous system becomes a single phase through a diminishment in composition difference between the EN-rich phase and the ET-rich one, without large changes to the phase fractions.

## CONCLUSIONS

Transesterification in PEN/PET blends takes place in the molten state, which was confirmed by  $^1\text{H}$  n.m.r. Three kinds of dyad sequences could be determined from the proton peaks in the n.m.r. spectra of the reacted blends. The number-average sequence lengths and the randomness were determined from the relative peak areas of the three dyad sequences. As the reaction time is prolonged, the number-average sequence lengths decrease, resulting in an increase of randomness. The dependence of the phase behaviour on the transesterification was investigated by d.s.c. For the PEN/PET (50/50) blend samples heat treated at 280°C for 20 min or

more, cold crystallization and melting were not observed, which is attributable to the disruption of the chain periodicity as a consequence of transesterification. In the early stage of transesterification, two glass transitions appear, which approach mutually closer with the increase of reaction time. This indicates that the composition difference in two coexisting phases decreases, as the transesterification proceeds. The weight fractions of the two coexisting phases and the interfacial zone were estimated by measuring the heat capacity changes at the glass transition temperatures of the blends and the pure homopolymers. Though the three fractions tend to change with the lapse of reaction time, the changes are relatively small in magnitude. Therefore, it is considered that the initial heterogeneous system becomes a single phase through diminishment in the composition difference between the EN-rich phase and the ET-rich one, without large changes to the phase fractions.

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