

On the miscibility and transesterification of poly(butylene naphthalate) with a novel phosphorus containing polyester

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Abstract

Blends of a novel phosphorus containing PEN copolyester (PENP2) and poly(butylene naphthalate) (PBN) have been studied before and after transesterification. According to DSC results, the physical blend exhibits complete miscibility when the content of PBN is less than 40% or higher than 90% by weight and exhibits partial miscibility outside these ranges. Transesterified blends were obtained by holding the physical blend at 260–280°C. The transesterified systems show a single T_g and exhibit a marked melting point depression. ^{31}P and ^1H NMR and wide-angle X-ray diffraction were also performed in this article. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Phosphorus; Copolyester; Differential scanning calorimetry

1. Introduction

Poly(butylene terephthalate) (PBT) is a fast crystallizable thermoplastic polyester with a high melting point and excellent solvent resistance, but its low T_g induces a noticeable deficiency in some mechanical properties, such as tensile and flexural modulus. Poly(butylene naphthalate) (PBN), with a naphthalene group in the repeating structure, provides higher rigidity, thermal properties and mechanical properties than that of PBT. Although PBN exhibits higher thermal resistance and flame retardancy than that of PBT, like other polyesters, the flame retardancy of PBN is not good enough.

Polymer blending provides a fast and useful way for the development of new polymeric materials. If the two blending polymers contain either ester or carbonate group, interchange reaction may take place during melting state, for example: the blending of polyester–polyester [1–6], polyester–polycarbonate [7–10] and polyester–polyester–carbonate [11,12]. In our previous paper [13], we have reported on the preparation and characterization of a series of phosphorus-containing PEN copolyesters, which are thermally more stable and flame retardant than PEN. V-0 grade for UL-94 vertical test can be achieved if phosphorus content in the copolyester is larger than 0.5 wt%. However, incorporating a bulky phosphorus group into PEN has

resulted in amorphous copolyesters, which limit their applications as high performance polymers.

Since PBN is a highly crystallizable polymer with excellent mechanical, thermal and electrical properties, PBN should be a suitable candidate to blend with the phosphorus containing PEN copolyester to yield a new flame retardant and crystallize polymer. The miscibility and transesterification between these two polyesters were studied by DSC and NMR.

2. Experimental

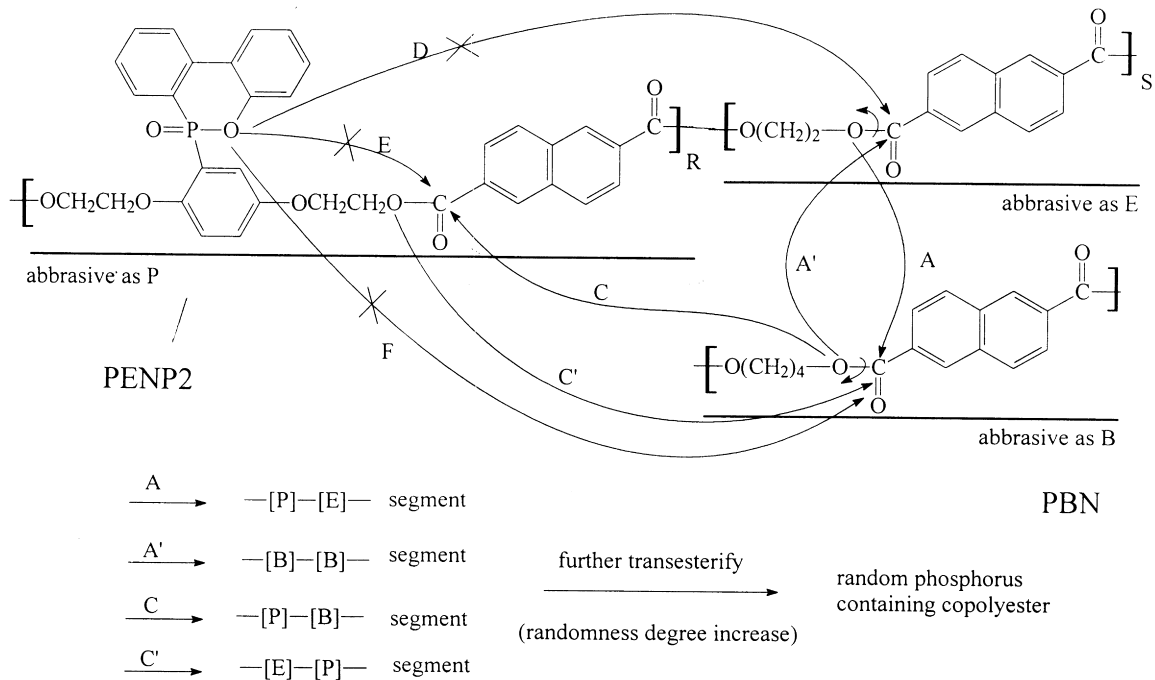
2.1. Materials

Among the phosphorus containing PEN copolyesters, we choose the copolyester with phosphorus content of 2.0 wt% as starting material. Its viscosity is 0.57 dl/g (measured at 30°C at a concentration of 0.5 g/dl in tetrachloroethane/phenol (2/3, w/w)). Its structure is shown in Scheme 1 and named as PENP2. It is an amorphous and random copolyester. PBN with a viscosity of 0.63 dl/g was kindly provided by CCP in Taiwan. Dichloroacetic acid was purchased from Acros and was used without further purification.

2.2. Measurement

DSC was performed by using a Perkin–Elmer DSC 7 operating in nitrogen atmosphere. Temperature calibration was carried out using pure samples of In and Zn. The

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Scheme 1.

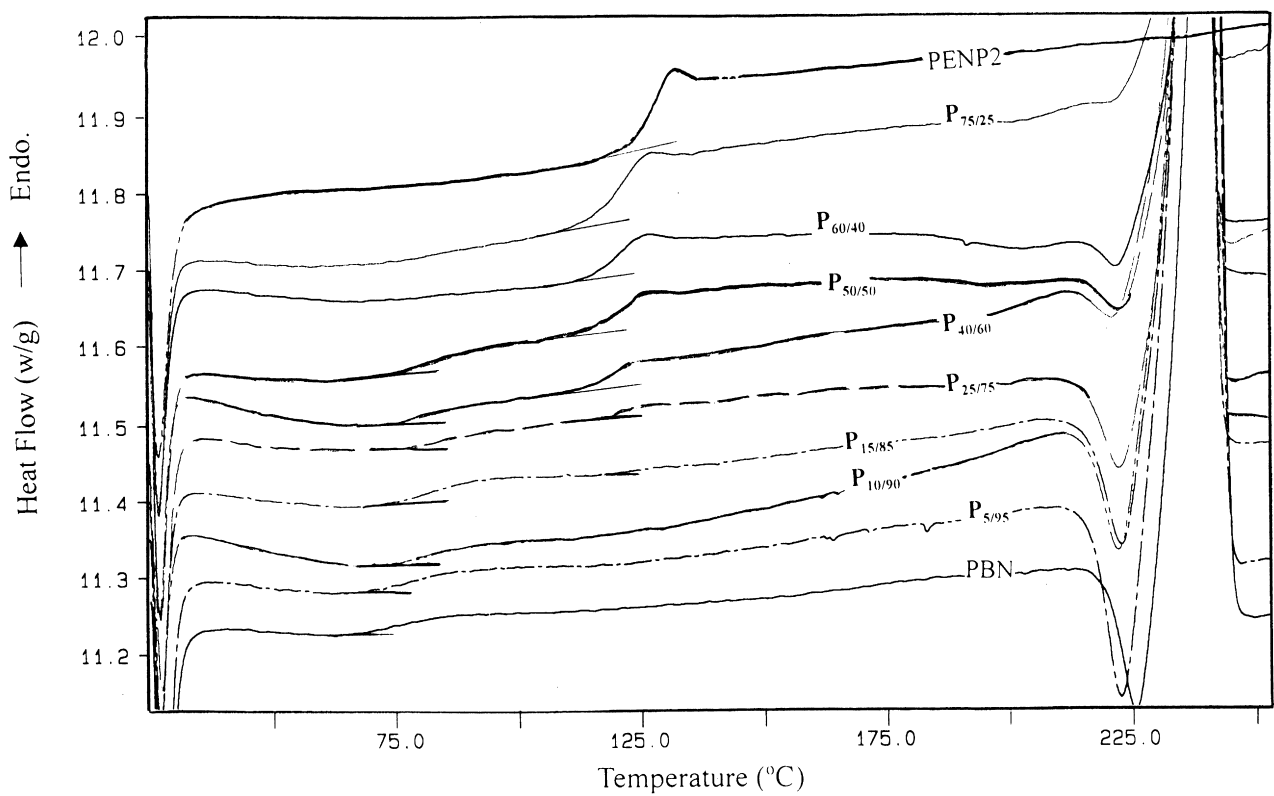


Fig. 1. DSC heating scans of various PENP2/PBN blends after melt at 250°C for 2 min, then quenched (200°C/min) to room temperature.

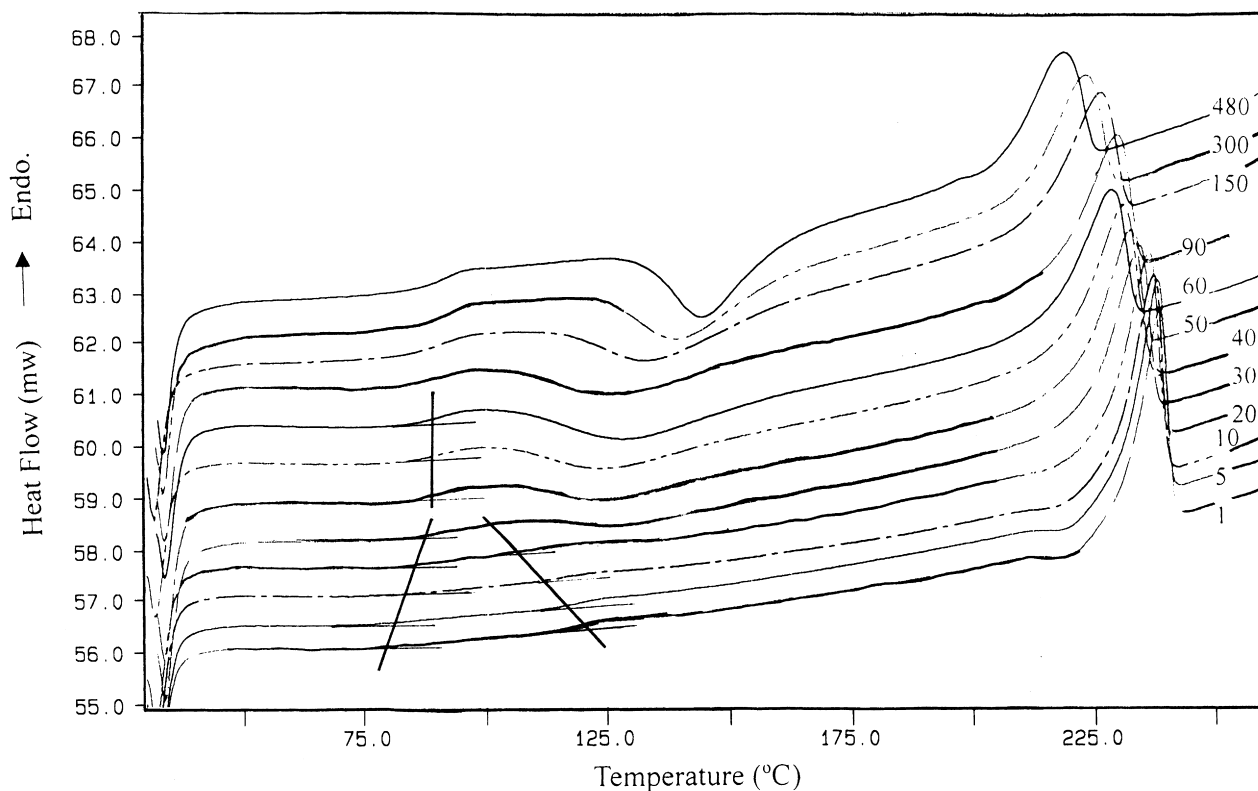


Fig. 2. DSC heating scans of $P_{40/60}$ after annealing at 260°C for 1–480 min. The annealing time is marked on the figure.

apparent enthalpies were determined using the conventional method, comparing the areas under the DSC curve with the corresponding areas of a standard sample of indium, taking $\Delta H_f = 28.45 \text{ J/g}$. ^1H NMR and ^{31}P NMR spectra were obtained with a Bruker AMX-400 using $\text{DMSO-}d_6$ as a solvent using TMS and H_3PO_4 as internal standard, respectively. The wide-angle X-ray diffraction measurements were performed at room temperature with a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni filtered Cu K_α radiation. The scanning rate was $4^\circ/\text{min}$. TGA was performed by using Perkin–Elmer TGA7 at a heating rate of $20^\circ\text{C}/\text{min}$ in an air atmosphere from 30 to 700°C .

2.3. Blending method

To prevent transesterification reaction between PENP2 and PBN, the blending was performed in solution. Blends of PENP2/PBN in various weight ratios (PENP2: 100/0, $P_{75/25}$: 75/25, $P_{60/40}$: 60/40, $P_{50/50}$: 50/50, $P_{40/60}$: 40/60, $P_{25/75}$: 25/75, $P_{15/85}$: 15/85, $P_{10/90}$: 10/90, $P_{5/95}$: 5/95 and PBN 0/100, w/w) were prepared by dissolving the component polymers in dichloroacetic acid completely and then poured into a large excess of methanol. The precipitated blends were filtered and washed by excess methanol four times to ensure that no dichloroacetic acid exists in the blends. After that, they are dried in a vacuum oven at 60°C for 2 days. Transesterification was carried out in a DSC aluminum pan under

a nitrogen atmosphere at $260\text{--}280^\circ\text{C}$ and annealing at that temperature for various times.

3. Results and discussion

3.1. Solution blend

Fig. 1 shows DSC heating scans of PENP2/PBN blends after melt at 250°C for 2 min, then quenched ($200^\circ\text{C}/\text{min}$) to room temperature. Since little transesterification occurred in this short time, we take this data as physical blend. The pure PBN shows a T_g of 69°C and the pure PENP2 has a T_g of 124°C . Single T_g is observed for blends $P_{5/95}$, $P_{10/90}$ and $P_{60/40}$, $P_{75/25}$ implying that they are miscible blends. Two T_g s are observed for other compositions suggesting that they are partially miscible.

While Yoon et al. [14] have reported that blends of PEN/PBN have been found to be immiscible except when the PBN content exceeds 80 wt%. In our system, PENP2/PBN was miscible at PBN less than 40% or higher than 90%. Obviously, incorporation of bulky phosphorus containing group into PEN changes its miscibility window when it was blended with PBN.

3.2. Transesterification

It is well known that polyesters can have acidolysis by an acid-end group, alcoholysis by a hydroxy-end group, and

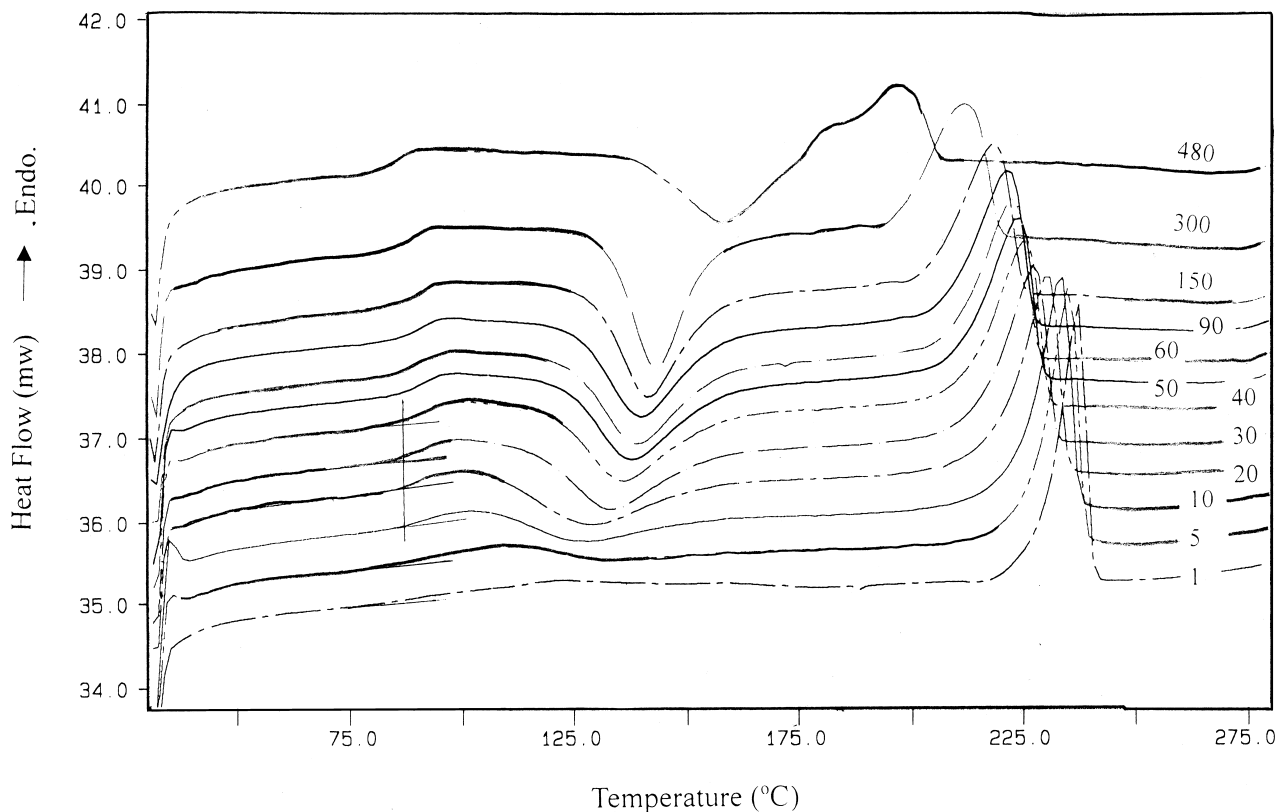


Fig. 3. DSC heating scans of $P_{40/60}$ annealed at 280°C for 1–480 min. The annealing time is marked on the figure.

midchain ester–ester interchange (transesterification) with itself or with other polymers at high temperature. For high molecular weight polyesters and their blends, the probability of transesterification occurring is much higher than

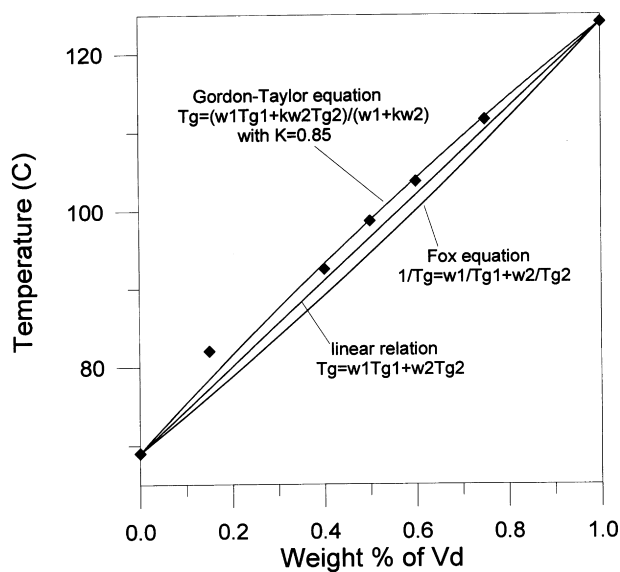


Fig. 4. T_g versus composition of the PENP2/PBN blends after annealing at 280°C for 60 min.

that of acidolysis or alcoholysis occurring, because of relatively low end-group concentrations. Therefore, transesterification usually dominates the reaction process. Since the I.V. of our starting material was 0.57 and 0.63 dl/g, respectively, the major reaction between two polyesters blend is the transesterification. The acidolysis and alcoholysis were neglected in this system. Since the structure and sequence distribution of blends will change with the trans-reaction, changes in melting and glass transition temperatures are useful indication of transesterification reaction. Fig. 2 presents DSC heating scans of $P_{40/60}$ after annealing at 260°C for 1–480 min. As the annealing time increases, the two T_g s start to merge and a single T_g at about 92.4°C was observed at time = 40 min. As annealing time increases, the melting point decreases and a cold crystallization peak appears. The decrease of melting point can be explained as the length of homo segments in polymer chain decreases and crystal formation is disturbed due to irregularity of the structure with the progress of the transesterification. The increase of cold crystallization temperature suggests that this blend becomes more difficult to crystallize during heating scans. This also can be explained from the irregularity of the structure causing difficulty in crystallization, which is consistent with the depression of melting point. Similar results were observed when they were annealed at 280°C (Fig. 3), except a single T_g which was observed beyond annealing over 10 min.

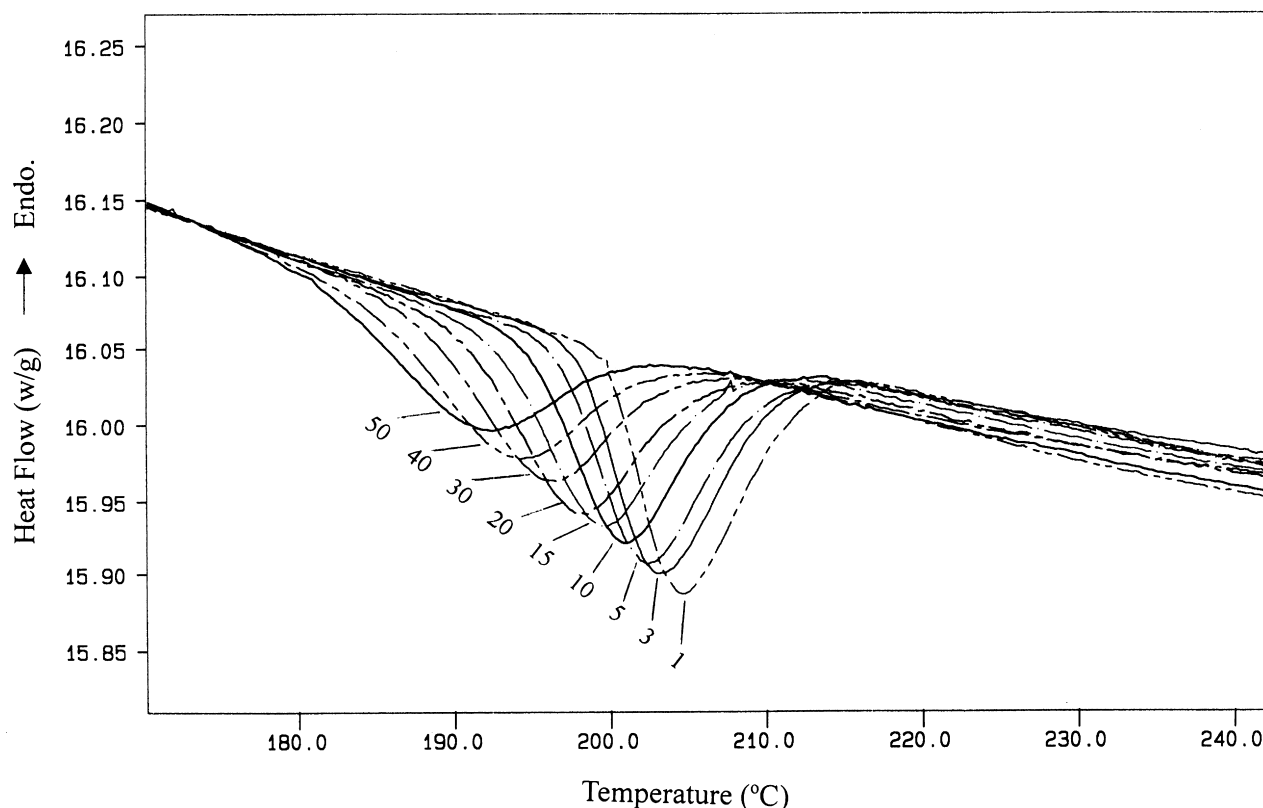


Fig. 5. DSC cooling scan (5°C/min) of P_{50/50} after annealing at 250°C for various times. The annealing time is marked on the figure.

3.3. T_g after transesterification

To quantitatively describe the T_g –composition relationships for PENP2/PBN blend, the experimental T_g data were compared with the known theories, such as Fox equation

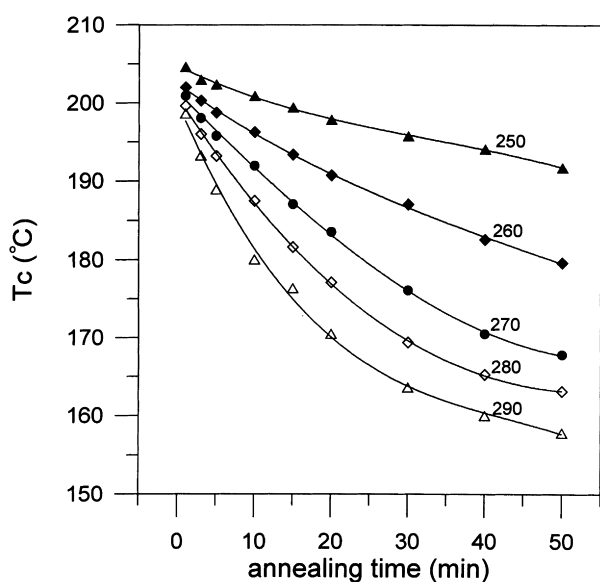


Fig. 6. The plot of T_c versus annealing time at various temperatures for P_{50/50}. The annealing temperature is marked on the figure.

and Gordon–Taylor equation [15]. Fig. 4 shows the T_g versus composition of the PENP2/PBN blends after annealing at 280°C for 60 min. The Gordon–Taylor equation with an adjustable parameter $k = 0.85$ seems to describe the T_g data best. A positive deviation from Fox equation and linear relationship were observed in Fig. 4. However, deviation of the experimental data from the Fox equation does not indicate the lack of miscibility in the blend. Robeson and Furtek [16] have reported a similar positive deviation in T_g for poly(butylene terephthalate)/poly(hydroxy ether of bisphenol-A) blend after annealing at 150°C. Woo and coworkers [17] have also reported the positive deviation for T_g –composition in epoxy/polycarbonate blends and concluded that the possible bonding through chemical reactions between the epoxy and polycarbonate. Another example for positive deviation from the mixture rule of T_g –composition was observed in our previous paper [18] on the transesterified blends of polyphosphonate/poly(ethylene terephthalate). Thus, the positive deviation from the mixture rule indicated that the interactions responsible for the miscibility occurring between PENP2/PBN are stronger than regular physical/polar force. This is reasonable in our system due to the transesterification that occurred during the annealing. A more detailed investigation on the transesterification will be discussed below.

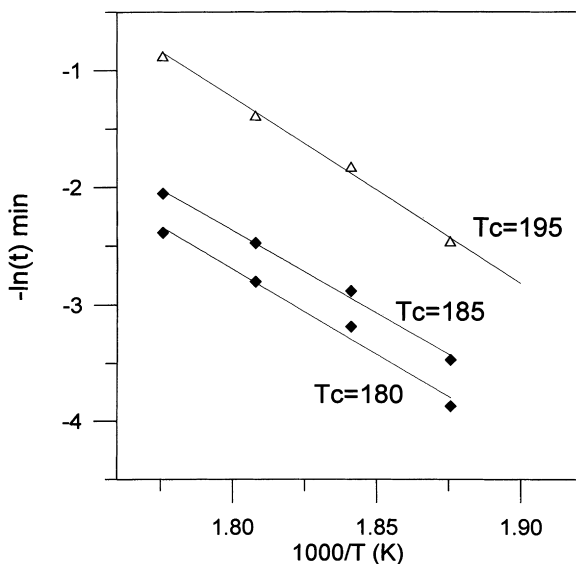


Fig. 7. The plot of $-\ln t$ versus $1/T$ for $P_{50/50}$.

3.4. Activation energy of exchange reaction

In order to assess the relative rate of ester exchange between PENP2 and PBN, sample $P_{50/50}$ was exposed to 250, 260, 270, 280 and 290°C for various time intervals followed by determination of the crystallization temperature T_c by cooling from 250°C at a cooling rate of 5°C/min. DSC was utilized to expose the sample to the predetermined time–temperature conditions. The samples were rapidly heated at 100°C/min to the exposure temperature, held at a specific time interval, cooled to 250°C at 100°C/min, and then cooled at 5°C/min to determine T_c [19]. Fig. 5 shows DSC cooling scan (5°C/min) of $P_{50/50}$ after annealing at 250°C for various times. The crystallization peak (T_c) shifts to lower temperature implying that the crystallization rate decreases with annealing times. This result suggests that transesterification occurs between PBN and PENP2 during annealing at 250°C. Fig. 6 shows the plot of T_c versus annealing time at various temperatures. As the annealing temperature increases, the shifts of T_c to lower temperature become more apparent. From a plot of T_c versus exposure time, the time required to yield a T_c value of 180, 185 and 190°C was determined. The reciprocal time required to yield $T_c = 180, 185$ and 190°C will be proportional to the ester exchange rate ($k \sim 1/t$) [19] and the Arrhenius equation can be written by the following equation:

$$k = A e^{-E/RT} \sim 1/t \quad (1)$$

and

$$\ln k = -E/RT = \ln 1/t = -\ln t \quad (2)$$

where T is the absolute temperature, E the activation energy of transesterification and t is the time required to yield a T_c of 180, 185 and 190°C. The activation energy of transesterification can be calculated by the plot of $-\ln t$ versus $1/T$

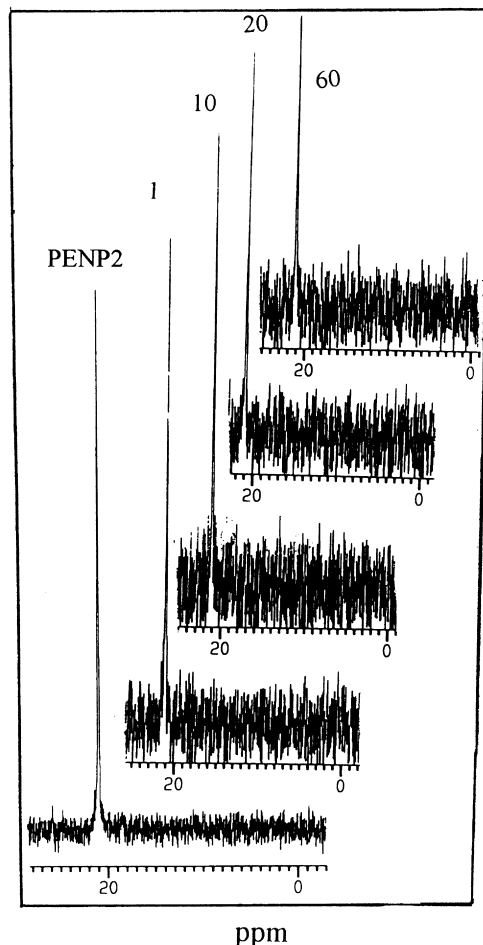


Fig. 8. ^{31}P NMR of PENP2 and $P_{50/50}$ after annealing at 260°C for 1–60 min. The annealing time for $P_{50/50}$ is marked on the figure.

(Fig. 7). The activation energy of exchange reaction is about 123 kJ/mol, which is smaller than that of polyarylate and PET. Robeson [7] has reported that the activation energy for the exchange reaction between polyarylate and PET was 154 kJ/mol. The higher activation energy for polyarylate/PET may be attributed to the higher chain rigidity of polyarylate/PET system.

3.5. NMR spectrum

Lee and coworkers [20] have reported the transesterification of poly(ethylene terephthalate) and poly(ethylene naphthalate) blend by high resolution NMR. According to the change in ^1H NMR spectrum caused by sequence distribution (such as $-\text{N}-\text{E}-\text{T}-$, $-\text{N}-\text{E}-\text{N}-$ and $-\text{T}-\text{E}-\text{T}-$, where N is naphthalate group, E ethylene group and T is terephthalate group), they can detect the degree of transesterification. Figs. 8 and 9 show ^{31}P NMR and ^1H NMR of $P_{50/50}$ after annealing at 260°C for 1–60 min. Only one single peak around 21 ppm was observed in Fig. 8 implying that the change in chemical surrounding phosphorus element is limited. There is also no obvious peak that

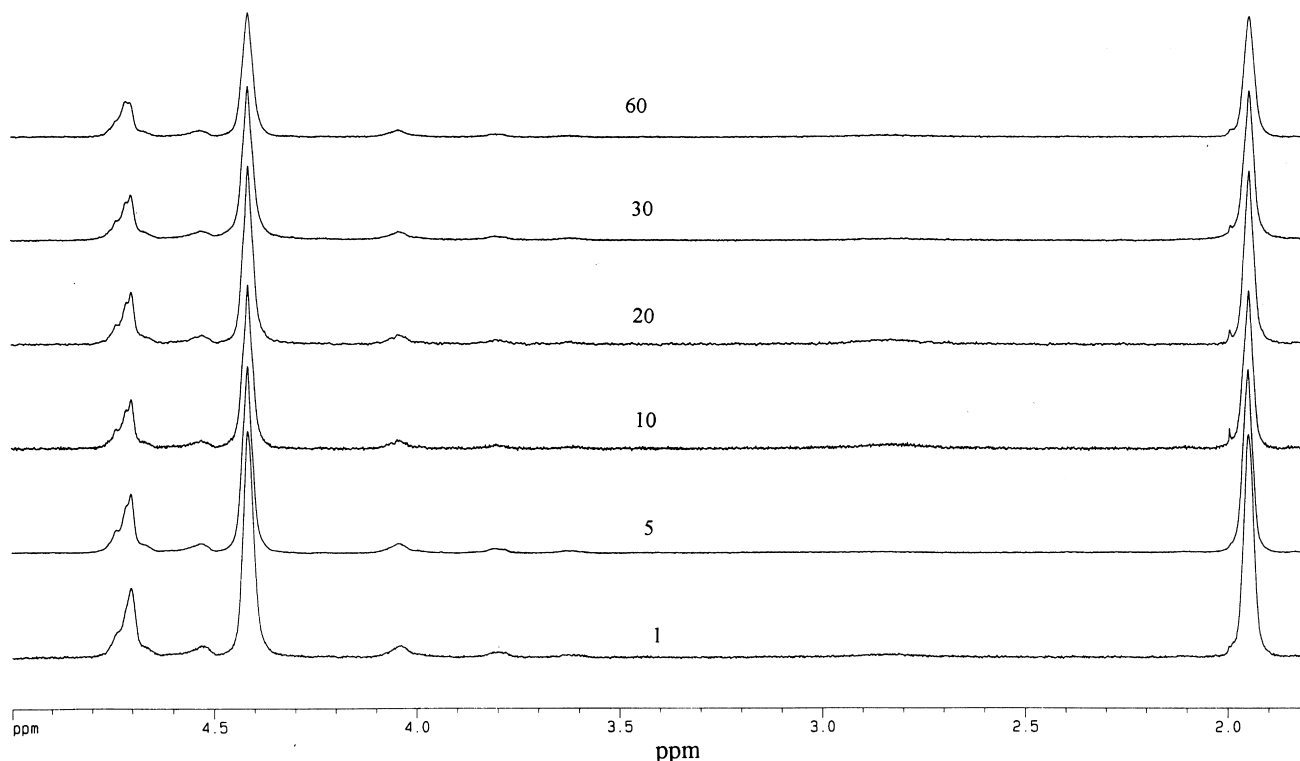


Fig. 9. ^1H NMR (for aliphatic protons) of $\text{P}_{50/50}$ after annealing at 260°C for 1–60 min. The annealing time is marked on the figure.

appears in the ^1H NMR spectra. This seems to conflict with DSC result. To explain this strange phenomenon, the chemical structure of the blend is shown in Scheme 1. According to the single and unchanged peak of ^{31}P NMR spectra, one can assume that the reaction path D, E and F did not occur in this blend. According to transesterification mechanism, the paths A, A', B and B' are the possible reaction paths.

However, path A results in $-\text{P}-[\text{E}]-$ segment, path A' results in $-\text{B}-[\text{B}]-$ segment, path C results in $-\text{B}-[\text{E}]-$ segment, path C' results in $-\text{E}-[\text{P}]-$ segment. They can further react with each other to increase their randomness. According to the results of Lee and coworkers [20], a single T_g was observed when the degree of randomness is greater than 0.5. Although the degree of randomness to achieve a single T_g may be different with different systems, they should change with the degree of transesterification. Why there is no obvious change in NMR spectra? It can be explained that the similarity in structures before and after transesterification causes the difference in chemical surrounding to be very limited and thus cannot be detected by our NMR. If one checks the peak at around 4.6–4.8 ppm carefully, he will find the change in peak shape. It is recommended that a higher resolution NMR is necessary to detect the sequence distribution.

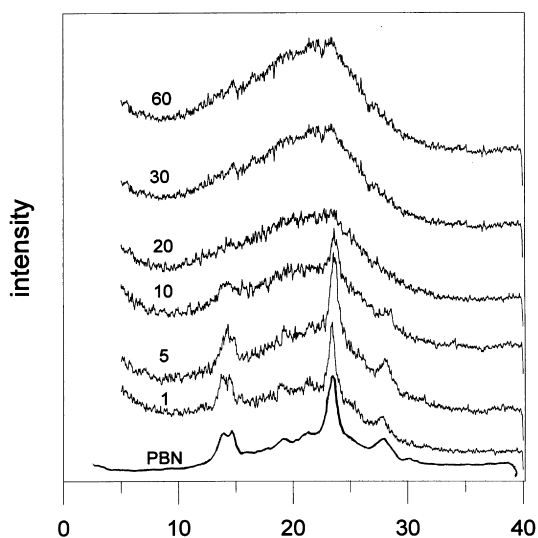


Fig. 10. Wide angle X-ray diffraction patterns of $\text{P}_{50/50}$ after annealing at 260°C for 1–60 min, then cooled to room temperature at a cooling of $20^\circ\text{C}/\text{min}$. The annealing time is marked on the figure.

3.6. X-ray diffraction

Although NMR spectra show little change before and after transesterification, wide-angle X-ray diffraction patterns show large difference. Fig. 10 shows the wide angle X-ray diffraction patterns of $\text{P}_{50/50}$ after annealing at 260°C for 1–60 min, then cooled to room temperature at a cooling rate of $20^\circ\text{C}/\text{min}$. Compared with the diffraction angles of PBN, one should notice that the diffraction angles of these blends are the same as PBN, which implies that the diffraction is derived from the PBN segment in the blends.

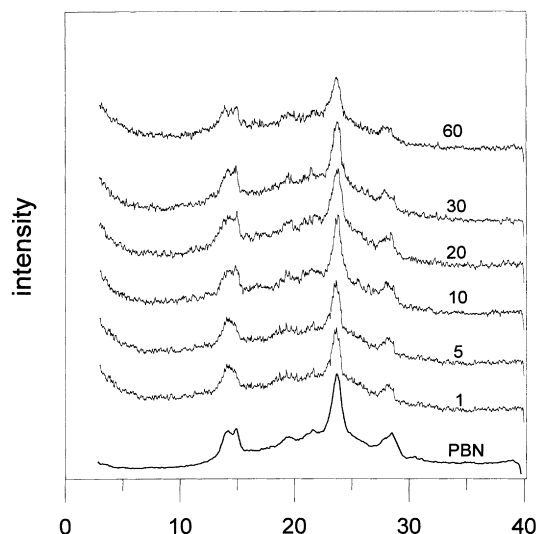


Fig. 11. Wide angle X-ray diffraction patterns of $P_{50/50}$ after annealing at 260°C for 1–60 min, then isothermal annealing at 170°C for 2 h. The annealing time is marked on the figure.

At annealing time of 10 min, the diffraction peaks become not obvious and even disappear after annealing time is longer than 20 min. This may be due to the shortening of the length of PBN segment by transesterification and the increase in irregularity of the structure, which also results in slow crystallization rate or even do not crystallize during

the cooling scan. However, the uncrystallized PBN segment will crystallize during isothermal annealing at 170°C for 2 h (Fig. 11). One should notice that the diffraction patterns are still the same as the PBN, which implies that no other diffraction patterns derived from other segments (such as PEN segment) was observed.

3.7. Thermal properties

TGA traces provide additional information regarding their thermal stability and thermal degradation behavior. Fig. 12 shows TGA thermograms of $P_{50/50}$ under air atmosphere after they are annealed at 260°C for 1–60 min. TGA traces revealed two decomposition steps because of oxidative degradation of the carbonaceous residue. In general, the incorporation of phosphorus linkage into the polymer main chain results in lower thermal stability of polymers [21–23] and their degradation temperatures were around $200\text{--}300^{\circ}\text{C}$, while the blends investigated in this paper exhibited higher thermal stability. The reasons why these phosphorus-containing copolyesters exhibit good thermal stability have been discussed in our previous paper [13]. Their 5% decomposition temperatures and char yield increase with annealing time until 10 min annealing. Over 10 min annealing, they all exhibit similar thermal behavior regardless of the annealing time. The little difference observed is due to the similarity in structures of this blend before and after transesterification. This result is consistent with the NMR results.

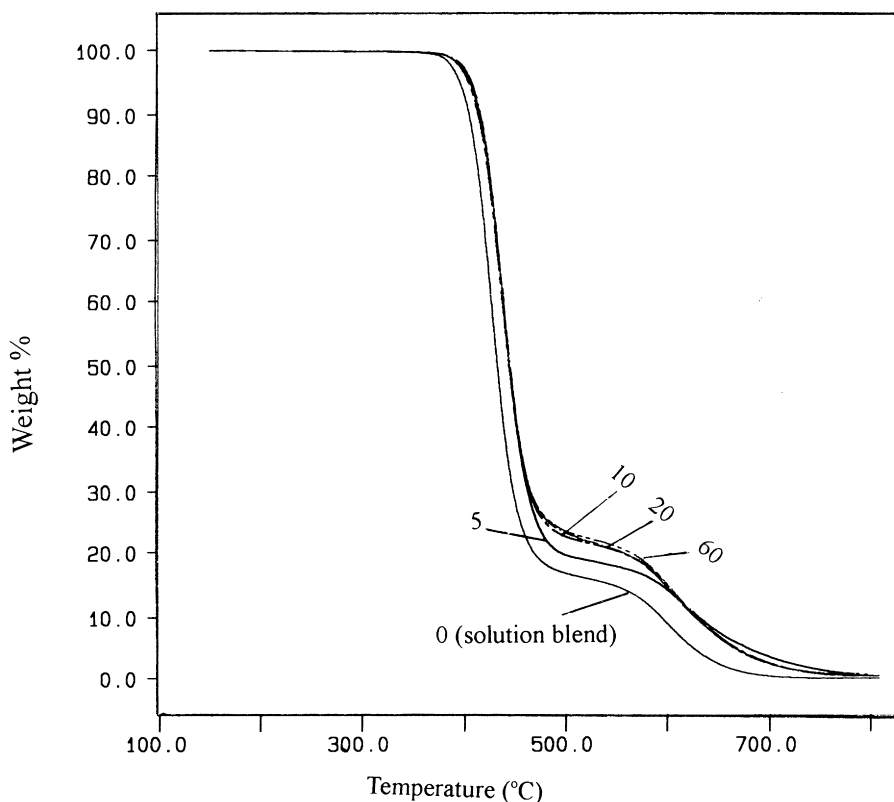


Fig. 12. TGA thermograms (under air atmosphere) of $P_{50/50}$ after annealing at 260°C for various times. The annealing time is marked on the figure.

4. Conclusion

Physical blends of PENP2 and PBN are found to be miscible if the content of PBN is less than 40% or higher than 90%. Transesterification can be induced in the physical blends at 260–280°C as monitored by merging of two T_g s and depression of melting point. The activation energy of transesterification according to Robenson's method is about 123 kJ/mol. However, no obvious chemical shift was observed for ^{31}P and ^1H NMR spectra, which may be due to the similarity in structures before and after transesterification. Wide angle X-ray diffraction patterns display that only PBN segment in these blends can crystallize after isothermally annealed at 170°C for 2 h. They exhibit good thermal stability and similar degradation behavior before and after transesterification by TGA since the transesterified blends have similar structures.

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