# Dynamic Mechanical Properties of Poly(ethylene terephthalate)/Poly(ethylene 2,6-naphthalate) Blends

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ABSTRACT: Blends of poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN) with various compositions were prepared using a mixer at 290 °C and 100 rpm for various times. The transesterification level $f_{TEN}$ and the average chain lengths $L_{PET}$ and $L_{PEN}$ were determined using $^1$H NMR. The dynamic mechanical properties of PET/PEN blends were studied as functions of blend composition and transesterification level. This technique was found to be sufficiently sensitive to observe the change in the physical state and the molecular motions of PET/PEN blends in the glass transition and the subsequent cold-crystallization regions. For the PET/PEN blends having $f_{TEN}$ of above 10%, all the blends quenched from molten state exhibited the same dynamic mechanical behavior in the glass transition region showing a single glass transition temperature $T_g$. $T_g$ of the blend was a linear function of the blend composition and independent of $f_{TEN}$. For the PET/PEN blends having $f_{TEN}$ of about 5%, PET/PEN = 75/25 and 25/75 blends formed a one-phase system, while 40/60, 50/50, and 60/40 blends formed a two-phase system. On the other hand, the cold-crystallization behavior detected by abrupt increase in storage modulus $E'$ was observed in the temperature range from $T_g$ to $T_m$ (melting temperature) and dramatically influenced by the average chain length. Cold crystallization was observed for the samples having $L_{PET}$ or $L_{PEN}$ larger than 5, while lost for both $L_{PET}$ and $L_{PEN} \leq 5$. The effect of blend composition on miscibility has also been discussed.

## Introduction

Poly(ethylene terephthalate) (PET) has been widely used as one of the important polymers for fibers, films, and food packaging materials because of its high glass transition temperature $T_g$ and high melting temperature $T_m$. However, its thermal performance and gas (including water vapor) barrier properties are not enough to meet requirements for some particular applications such as hot-fill packaging and soft drink containers. Poly(ethylene 2,6-naphthalate) (PEN) is known to possess a higher glass transition temperature (about 50 °C higher than that of PET) and superior oxygen and carbon dioxide barrier properties as compared to the case of PET. The oxygen permeability of PEN is approximately one-quarter to one-fifth that of PET. PEN can be a good candidate for hot-fill and high barrier packaging applications, but the high cost of PEN has limited its direct applications as a common packaging material. Recently, considerable attention has been paid to blends of PET and PEN, from which one would expect to make potential packaging materials.

It has been known that PET/PEN blends including PET/PENT blends, where PENT indicates PEN−PET random copolymer, are useful for producing packages with improved thermal and barrier properties.[1−3] A number of patents have been focused on how to produce useful and high-performance packaging materials from PET/PEN blends.[3,4] There are several reports concerning fundamental studies of PET/PEN blends, such as miscibility due to transesterification.[5−10] It has been reported that PET and PEN were immiscible if there is no transesterification between PET and PEN molecules. Due to the similarity in chemical structure for both polymers, however, transesterification occurs easily during an industrial process such as extrusion for making a blend. Then, PET and PEN can become miscible by transesterification occurring in melt processing.[5] The transesterification reaction leads to formation of block and random copolyesters to enhance the miscibility.

Stewart et al.[5] have observed that the degree of transesterification was primarily controlled by the blending time and temperature rather than composition. The higher the temperature was, the faster the transesterification reaction became. The transesterification was a function of blending time: for example, the transesterification in a PET/PEN = 50/50 blend increased from 5.8% for 1.5 min to 21.3% for 4.5 min at 295 °C. They also reported that about 10% of transesterification was required to produce transparent samples and led to the formation of a single amorphous phase. On the other hand, to avoid transesterification during blend preparation, Andresen and Zachmann,[7] Ihm et al.,[8] and Lee et al.[10] prepared the PET/PEN blends of various compositions using solution precipitation at room temperature and then annealed at high temperatures. Andresen and Zachmann[7] reported that two glass transition temperatures $T_g$ were observed for short annealing times and single $T_g$ was observed for longer than 2 min by means of dynamic mechanical analysis. Ihm et al.[8] determined $T_g$ by DSC and transesterification by NMR for the annealed samples. They found that the physical (untransesterified) blends were immiscible by showing two $T_g$s, and when the transesterification reached 50%, the blends are not crystallizable and show a single $T_g$ implying formation of a miscible blend.

In general, miscibility and phase behavior of polymer blends were studied using DSC measurement. The DSC

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**Table 1. Molecular Characteristics of PET and PEN before and after the Melt Blending (290 °C for 20 min) in a Mixer**

| polymer | $M_n/10^3$ | $M_w/M_n$ | origin |
|---|---|---|---|
| PET | 15.3 | 2.98 | as received |
| PET | 11.3 | 3.45 | after blending |
| PEN | 17.5 | 2.80 | as received |
| PEN | 12.4 | 2.81 | after blending |

measurement limits the resolution of the $T_g$s because of a lack of sensitivity, as pointed out previously by Brostow et al.[11,12] for studying phase diagrams in polymer liquid-crystal systems. However, no detailed reports have been seen on the relation between the dynamic mechanical properties and the transesterification level of PET/PEN blends, although this technique is considered to be very sensitive to measure the physical properties of glass transition region. In this work, we prepared the PET/PEN blends with a broad range of compositions by melt blending and then determined the degree of transesterification of these blends using $^1$H NMR. We carried out dynamic mechanical measurements of the blends. On the basis of our experimental results, we report the feature of the dynamic mechanical behavior of the PET/PEN blends and also discuss the misciblity and cold crystallization of the PET/PEN blends as a function of the degree of transesterification and the blend composition.

## Experimental Section

**Polymers and Blending.** Poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN) used in this work were commercial polymers manufactured by Mitsubishi Chemical Corp., Japan. The polymers were used without any purification. The molecular weights before and after the blending treatment at 290 °C for 20 min in a mixer as described below were determined by GPC. A mixture of HFIP/$CHCl_3$ (5/95) was used as solvent and polystyrene as standard for the GPC measurements. The molecular characteristics of the polymers obtained are given in Table 1. The GPC results in Table 1 show that the molecular weights of the polymers decreased by about 30% while the molecular weight distribution kept the same for the PEN or became wider for the PET after the blending treatment.

Prior to blending, all polymers were dried at 100 °C in a vacuum oven for more than 15 h. The PET/PEN blends were prepared at 290 °C using a mixer (Labo-Plastomil, Toyo Seiki, Japan). The blending process comprised two steps: premixing (30 rpm for 1 min) and primary mixing (100 rpm for a desired time). The samples prepared in each run were naturally cooled to room temperature and then smashed mechanically using a grinder. The blend samples in this work are given in Table 2.

All samples for the dynamic mechanical measurements were prepared by compression molding at 290 °C through the following procedure. The smashed sample in a sheet mold was preheated in a "hot" (290 °C) laboratory press for 5 min and then pressed under a pressure of 100 MPa for 4 min to form about 1 mm thick films. The film was quenched by quickly transferring from the hot press to a "cold" (circulated by cold water) press under a press of 12 MPa to avoid crystallization as much as possible. The cooling rate reached above 20 °C/s. These quenched samples were amorphous, because they were transparent and no X-ray diffraction from crystallites was observed.

**Dynamic Mechanical Measurements.** The films prepared by compression molding were cut into size about 4.5 mm × 4.5 cm, and the edges of each film were carefully smoothed using a fine sandpaper for the dynamic mechanical measurements. The viscoelastic spectrometer VES-HF3 (Iwamoto Seisakusho, Japan) was used to determine storage modulus $E'$, loss modulus $E''$, and loss tangent tan $\delta$ in a temperature range from −120 °C to the temperature above which the storage modulus of the sample was too low to be measured by the instrument. The final temperature was defined as the "flow temperature". Since the crystallization behavior of each sample was strongly dependent on its composition and blending time, the flow temperature varied from about 160 to 270 °C. All measurements were carried out at a frequency of 10 Hz and a heating rate of 2 °C/min. The liquid nitrogen was used to attain the low temperatures.

**Table 2. PET/PEN Blends Prepared at 290 °C Using a Mixer**

| sample code | composition (PET/PEN in wt %) | PEN mol % | blending time (min) |
|---|---|---|---|
| PET-20 | 100/0 | 0 | 20 |
| 9010-20 | 90/10 | 8.1 | 20 |
| 7525-20 | 75/25 | 20.9 | 20 |
| 6040-20 | 60/40 | 34.6 | 20 |
| 5050-20 | 50/50 | 44.2 | 20 |
| 4060-20 | 40/60 | 54.3 | 20 |
| 2575-20 | 25/75 | 70.4 | 20 |
| 1090-20 | 10/90 | 87.7 | 20 |
| PEN-20 | 0/100 | 100 | 20 |
| 7525-0 | 75/25 | 20.9 | 0 |
| 7525-5 | 75/25 | 20.9 | 5 |
| 7525-10 | 75/25 | 20.9 | 10 |
| 7525-15 | 75/25 | 20.9 | 15 |
| 6040-0 | 60/40 | 34.6 | 0 |
| 5050-0 | 50/50 | 44.2 | 0 |
| 5050-5 | 50/50 | 44.2 | 5 |
| 5050-10 | 50/50 | 44.2 | 10 |
| 5050-15 | 50/50 | 44.2 | 15 |
| 4060-0 | 40/60 | 54.3 | 0 |
| 2575-0 | 25/75 | 70.4 | 0 |
| 2575-5 | 25/75 | 70.4 | 5 |
| 2575-10 | 25/75 | 70.4 | 10 |
| 2575-15 | 25/75 | 70.4 | 15 |

**Determination of Transesterification.** The transesterification in the blends prepared by compression molding was determined using a $^1$H NMR technique. The $^1$H NMR experiments were performed on specimens prepared by dissolving the blends in a 1:3 (by volume) mixture of deuterated trifluoroacetic acid and deuterated chloroform. Solution concentration was about 2 wt %. This technique measures the $^1$H NMR spectrum corresponding to ethylenic protons in the polyesters. While the ethylene peaks for N−E−N links between naphthalate (N) groups and for T−E−T links between two terephthalate (T) groups appear at approximately 4.9 and 4.8 ppm, respectively, the peak for the T−E−N links appears between 4.9 and 4.8 ppm. By measuring the integrated intensity of each resonance peak,[5,8] one can calculate the fraction of transesterification, $f_{TEN}$, using the equation

$$f_{TEN} = I_{TEN}/(I_{TET} + I_{TEN} + I_{NEN}) \tag{1}$$

where $I_{TET}$, $I_{TEN}$, and $I_{NEN}$ are the integrated intensities of the resonance peaks corresponding to the T−E−T, T−E−N, and N−E−N links, respectively.

If $P_{NT}$ is the probability of finding a T unit next to a N unit and $P_{TN}$ is the probability of finding a N unit next to a T unit, the degree of randomness $B$ is defined as[8]

$$B = P_{NT} + P_{TN} \tag{2}$$

for the transesterification. Here, $P_{NT}$ and $P_{TN}$ are calculated by

$$P_{NT} = (I_{TEN}/2)/((I_{TEN}/2) + I_{NEN}) \tag{3}$$

$$P_{TN} = (I_{TEN}/2)/((I_{TEN}/2) + I_{TET}) \tag{4}$$

$B$ is used to describe the randomness of a PET−PEN copolymer as $B = 1$ for a random copolymer, $B = 2$ for an alternative copolymer, and $B = 0$ for a block copolymer or a physical blend without transesterification between PET and PEN. Like the calculation of molecular weight during polymerization of

**Table 3. Glass Transition Temperature $T_g$, Fraction of Transesterification $f_{TEN}$, Degree of Randomness $B$, Number-Average Chain Length $L_{PEN}$ and $L_{PET}$, and Cold Crystallization for the PET/PEN Blends Given in Table 2**

| code | $T_g$, °C | $f_{TEN}$ | $B$ | $L_{PEN}$ | $L_{PET}$ | cryst[a] |
|---|---|---|---|---|---|---|
| PET-20 | 88.4 | NA | NA | NA | 58.9 | ○ |
| 9010-20 | 93.4 | 0.097 | 0.677 | 1.6 | 19.1 | ○ |
| 7525-20 | 101.4 | 0.205 | 0.639 | 2.0 | 7.8 | ○ |
| 6040-20 | 109.2 | 0.208 | 0.461 | 3.3 | 6.3 | ○ |
| 5050-20 | 111.7 | 0.313 | 0.638 | 2.7 | 3.7 | × |
| 4060-20 | 116.6 | 0.239 | 0.478 | 4.4 | 4.0 | × |
| 2575-20 | 124.6 | 0.268 | 0.602 | 5.0 | 2.5 | × |
| 1090-20 | 132.5 | 0.155 | 0.616 | 11.0 | 1.9 | ○ |
| PEN-20 | 137.5 | NA | NA | 51.7 | NA | ○ |
| 7525-0 | 98.5 | 0.030 | 0.151 | 7.5 | 59.8 | ○ |
| 7525-5 | 101.4 | 0.102 | 0.313 | 4.0 | 15.5 | ○ |
| 7525-10 | 101.3 | 0.143 | 0.450 | 2.8 | 11.2 | ○ |
| 7525-15 | 98.5 | 0.166 | 0.512 | 2.5 | 9.6 | ○ |
| 6040-0 | 106.6 (broad) | 0.060 | 0.141 | 10.2 | 23.4 | ○ |
| 5050-0 | 98.5, 122.2 | 0.048 | 0.096 | 21.0 | 20.6 | ○ |
| 5050-5 | 114.3 | 0.110 | 0.225 | 7.7 | 10.6 | ○ |
| 5050-10 | 114.3 | 0.175 | 0.358 | 4.9 | 6.6 | × |
| 5050-15 | 114.3 | 0.221 | 0.450 | 3.9 | 5.2 | × |
| 4060-0 | 96.1, 137.5 | 0.029 | 0.057 | 40.7 | 30.7 | ○ |
| 2575-0 | 124.6 | 0.056 | 0.133 | 24.8 | 10.8 | ○ |
| 2575-5 | 124.6 | 0.163 | 0.370 | 8.3 | 4.0 | ○ |
| 2575-10 | 124.6 | 0.198 | 0.445 | 6.7 | 3.4 | ○ |
| 2575-15 | 124.6 | 0.260 | 0.577 | 5.1 | 2.6 | ○ |

[a] The symbols ○ and × indicate cold crystallization and no cold crystallization, respectively.

copolymers, the number-average chain lengths $L_{PET}$ of PET and $L_{PEN}$ of PEN are simply calculated from $P_{NT}$ and $P_{TN}$.[8]

$$L_{PET} = 1/P_{NT}; \quad L_{PEN} = 1/P_{TN} \qquad (5)$$

## Results and Discussion

**Transesterification of PET/PEN Blends.** The fraction of tansesterification $f_{TEN}$, degree of randomness $B$, and number-average chain length $L_{PET}$ and $L_{PEN}$ for the PET/PEN blends are presented in Table 3. Both $f_{TEN}$ and $B$ increase with an increase in blending time. On the other hand, $L_{PET}$ and $L_{PEN}$ decrease with an increase in blending time. The fraction of transesterification $f_{TEN}$ ranged from about 0.1 at 10 wt % of PEN to the maximum of about 0.3 at the composition of 50 wt % PEN. The degree of randomness $B$ for the blends prepared at 290 °C for 20 min takes values between 0.46 and 0.68 and is almost independent of the blend composition, implying that a similar level of randomness of transesterification has been reached. The number-average chain length $L$ ($L_{PET}$ and $L_{PEN}$) obtained using eq 5 is also shown in Table 3. Here, the values of $L$ for the PET and PEN were calculated from their $M_n$ values in Table 1. $L_{PET}$ or $L_{PEN}$, independent of the polymer type, decreases in a similar pattern with increasing content of the partner polymer. The maximum effect of transesterification on the chain length is observed at the blend composition of 1:1 mole where both polymers become the same chain length of about 3.5. The reduction of chain length is symmetrical against the blend composition, suggesting that the transesterification is related to the contact probability between PET and PEN. These data agreed essentially with previous ones by Stewart et al.[5]

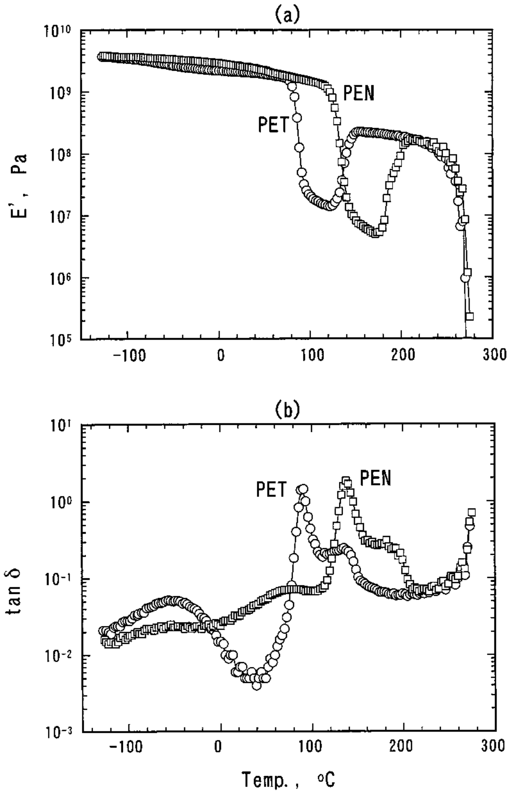

**Figure 1.** Storage modulus $E'$ (a) and loss tangent tan $\delta$ (b) as a function of temperature for the PET (○) and PEN (□) at 10 Hz and a heating rate of 2 °C/min.

**Dynamic Mechanical Properties of PET/PEN Blends.** Before studying PET/PEN blends, it is necessary to know characteristics of each component. Figure 1 shows the storage modulus $E'$ and loss tangent tan $\delta$ as a function of temperature for the quenched samples of PET and PEN, measured at 10 Hz and 2 °C/min. The PEN exhibits a similar glass modulus to the PET, which persists until about 120 °C that is about 50 °C higher than that of PET. The glass transition temperature $T_g$, defined as the temperature corresponding to the peak of tan $\delta$ in the glass transition region, is 88 °C for the PET and 137 °C for the PEN. These $T_g$ values are about 10 °C higher than those obtained from DSC measurements.[5] After passing through the glass transition, the PET began to crystallize at about 115 °C by showing a rapid increase in $E'$, while the PEN did from about 175 °C. The crystallization led the PET to show a second peak of tan $\delta$ after $T_g$, while the PEN exhibited a

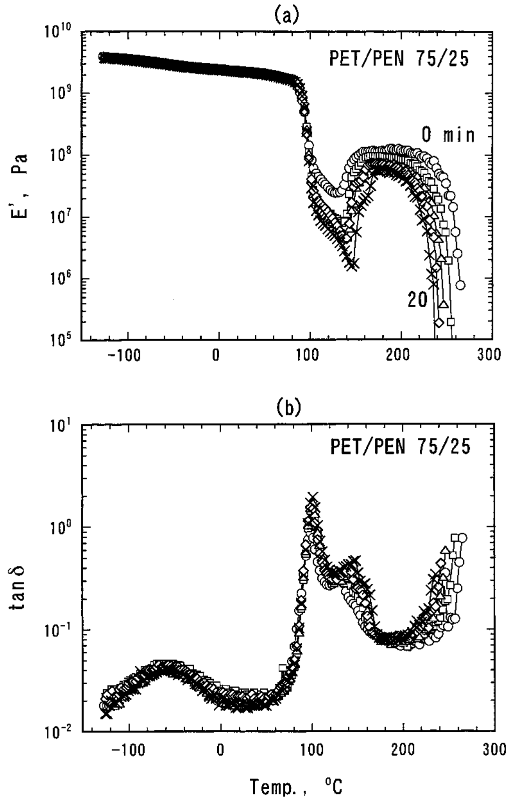

**Figure 2.** Storage modulus $E'$ (a) and loss tangent tan $\delta$ (b) as a function of temperature for the PET/PEN = 75/25 blends prepared at 290 °C and 100 rpm for 0 (○), 5 (□), 10 (△), 15 (◇), and 20 (×) min at 10 Hz and a heating rate of 2 °C/min.

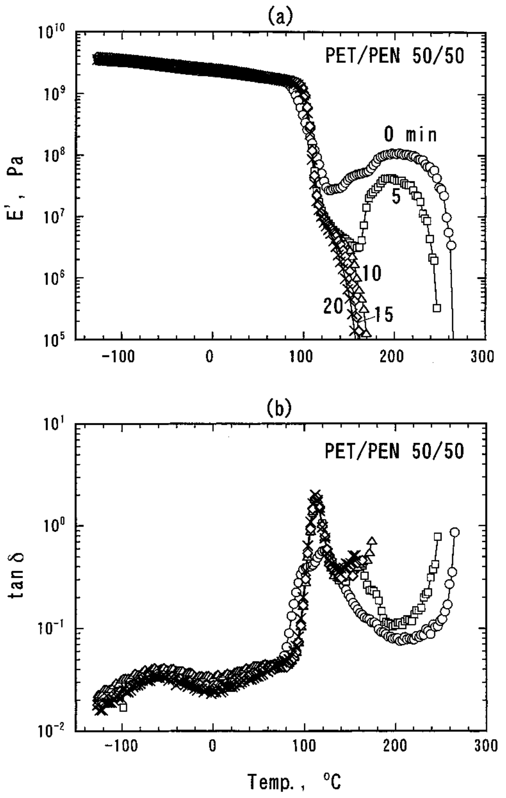

**Figure 3.** Storage modulus $E'$ (a) and loss tangent tan $\delta$ (b) as a function of temperature for the PET/PEN = 50/50 blends prepared at 290 °C and 100 rpm for 0 (○), 5 (□), 10 (△), 15 (◇), and 20 (×) min at 10 Hz and a heating rate of 2 °C/min.

plateau of tan $\delta$ during the crystallization. The PET showed a broad $E'$ plateau from 135 °C until the melting temperature. On the other hand, the PEN reached the same level of $E'$ at about 205 °C and then behaved similarly with the PET. Although $T_g$ of the PEN is about 50 °C higher than that of the PET, the melting points of PET and PEN are almost the same (265−270 °C).

Figure 2 shows the storage modulus $E'$ and the loss tangent tan $\delta$ as a function of temperature for the PET/PEN = 75/25 blends. The blending time varied from 0 to 20 min by a step of 5 min. The “0” min in the present paper means that the sample was prepared just under the “premixing” condition, as described in the Experimental Section. We observe here that both $E'$ and tan $\delta$ from the glassy state to glass transition region are the same values independent of blending time. A single peak in the tan $\delta$ curves, independent of the blending time, is observed in the glass transition region. This fact indicates that the blends are miscible state. On the contrary, the dynamic mechanical behavior above the glass transition region is strongly dependent on the blending time even though all samples were crystallizable. There are several features observed from Figure 2. (1) The beginning temperature of cold crystallization (we define it as $T_c$, the temperature at which the $E'$ began to increase by crystallization) shifts to the high-temperature side as the blending time increased. (2) The height of the $E'$ plateau due to cold crystallization is significantly reduced with increasing the blending time. (3) The melting temperature $T_m$ drops dramatically from 265 °C for the blending time of 0 min to 235 °C for the 20 min blending.

Since the blend composition of PET/PEN = 50/50 would be expected to give the maximum probability for the transesterification, one may observe the greatest effects of transesterification on the glass transition and crystallization behavior as compared to other composition. Figure 3 shows that, except for the blend 5050-0 prepared by the “premixing” condition, the other blends exhibit the same glass transition where a single tan $\delta$ peak appears at about 112 °C, independent of the blending time, as same as for the 75/25 blends. The specific behavior is observed in the blend 5050-0, which we will discuss later. The blend 5050-5 remained the cold crystallization to show the increase in modulus, while the longer blending time caused the blend to lose its cold crystallization. The effects of blending time are much stronger in the 50/50 blend than in other compositions of the blends probably because the higher degree of transesterification is reached in the 50/50 blend.

It would also be interesting to investigate the blend PET/PEN = 25/75, the opposite composition of the blend 75/25 described previously. However, it should be noted that the numerals used to represent the blend composition are the weight percentage of the component polymers. The mole percentage of PEN component in the blend, PEN mole percent, is 20.9 for PET/PEN = 75/25 and 70.4 for 25/75, as given in Table 2 for the reader's convenience. Similar to the blend 75/25 in Figure 2, the blend 25/75 shown in Figure 4 also exhibits a blending time-independent glass transition where $T_g$ is related only to the blend composition, indicating that the blends have been in one phase state. On the other hand, the particular crystallization behavior is observed in the temperature range beyond $T_g$. The blends prepared for the blending time of 0−15 min were crystallizable while the longer time (20 min) of blending made the blend uncrystallizable. The starting temperature for cold crystallization of the blend 25/75 was about 166 °C for

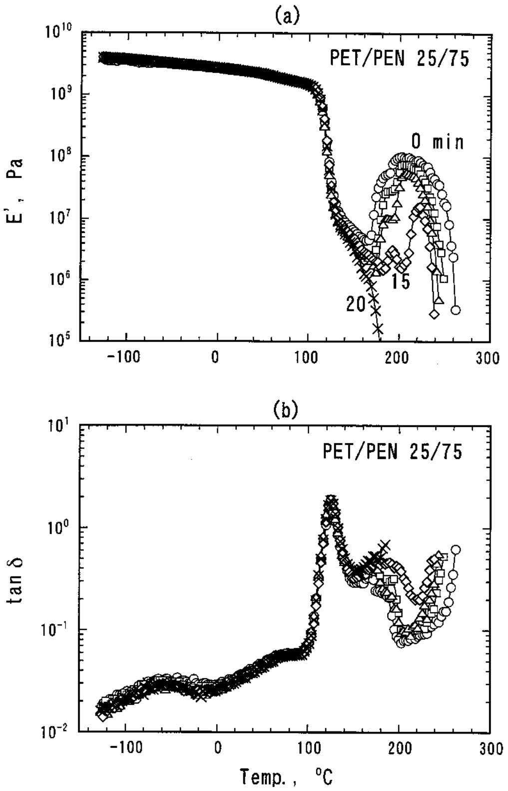

**Figure 4.** Storage modulus $E'$ (a) and loss tangent tan $\delta$ (b) as a function of temperature for the PET/PEN = 25/75 blends prepared at 290 °C and 100 rpm for 0 (○), 5 (□), 10 (△), 15 (◇), and 20 (×) min at 10 Hz and a heating rate of 2 °C/min.

0 min, 172 °C for 5 min, 175 °C for 10 min, and 183 °C for 15 min of the blending time. The maximum modulus due to cold crystallization significantly dropped with increasing the blending time.

The further experiments were carried out by focusing on how the composition affects dynamic mechanical behavior of the PET/PEN blend prepared under the same conditions (290 °C for 20 min). Parts a and b of Figure 5 represent the storage modulus $E'$ and loss tangent tan $\delta$ of the PET/PEN blends, respectively, with the composition ranging from 100/0 to 0/100 as a function of temperature. As shown in the figures, the following characteristics are observed for the blends:

(1) The modulus in the glassy state region is almost independent of the composition.

(2) The glass transition temperature shifts to higher temperatures with increasing PEN content.

(3) In the temperature range of cold crystallization, the blends 9010-20 and 1090-20 show a similar behavior to PET and PEN, respectively. But the modulus of the blends due to cold crystallization is significantly lower than those of pure components, and the melting point of the blends becomes about 237 °C, almost 20 °C lower than that of each component polymer.

(4) The blend 7525-20 was crystallizable by showing a lower plateau of $E'$ as compared to either the blend 9010-20 or the blend 1090-20, while the blend 2575-20 was uncrystallizable.

(5) As the maximum degree of transesterification can be expected for the blends 4060-20 or 5050-20, the blends completely lost the crystallization capability to result in a flow. However, the blend 6040-20 still remained crystallizable, indicating a lower degree of transesterification in the blend than that in the opposite composition of 40/60.

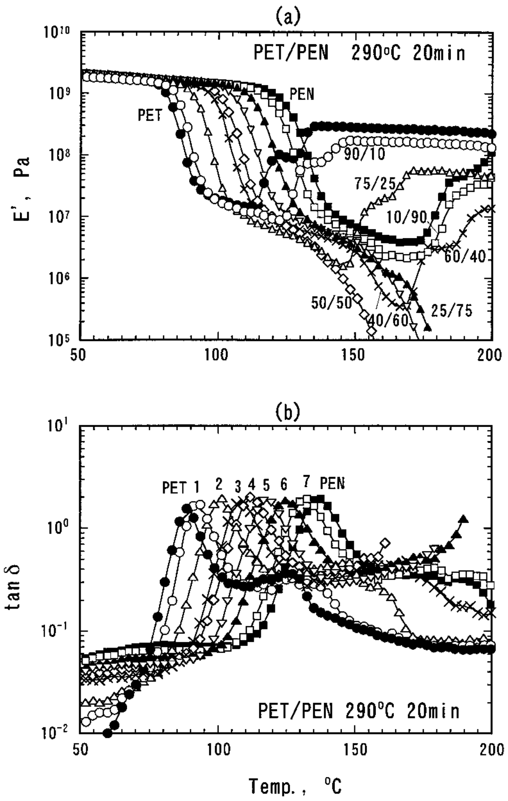

**Figure 5.** Storage modulus $E'$ (a) and loss tangent tan $\delta$ (b) as a function of temperature for the PET/PEN blends prepared using a mixer at 290 °C and 100 rpm. The blend composition (PET/PEN in weight) is 100/0 (●), 90/10 (○), 75/25 (△), 60/40 (×), 50/50 (◇), 40/60 (▽), 25/75 (▲), 10/90 (□), and 0/100 (■).

**Glass Transition Temperature and Cold Crystallization of PET/PEN Blends.** A single peak of tan $\delta$ appears in the glass transition region of each blend, suggesting that the blend has become miscible. Note that the peaks observed above the glass transition temperature region are due to the cold crystallization and are not related to the glass transition of PEN. It should be emphasized here that although all the blends were miscible by showing a single $T_g$, their crystallization behavior varied significantly as a function of blend composition. The results can be explained in terms of transesterification occurring in the blends. The difference in the crystallization behavior reflects variance of molecular structure in the blend as different degrees of transesterification were achieved in different compositions of the blends.

The glass transition temperature $T_g$ defined by the temperature corresponding to the peak of the tan $\delta$ curve in the glass transition region for all samples is listed in Table 3 and plotted as a function of PEN mole percent in Figure 6. Although some papers[1,8] reported that the Fox equation[13] holds well for PET/PEN blends, we observed a linear relationship between $T_g$ and PEN mole percent in the blends and can describe it by the following relation

$$T_g = m_1 T_{g1} + m_2 T_{g2} \qquad (6)$$

where $m_i$ indicates the mole fraction of each component. When $m_i$ is replaced with $w_i$, the weight fraction, eq 6, is still a good fit to the data. Our results in Figure 6 do no agree with prior ones.[1,8] We believe that our data are correct and suppose that this discrepancy is due to

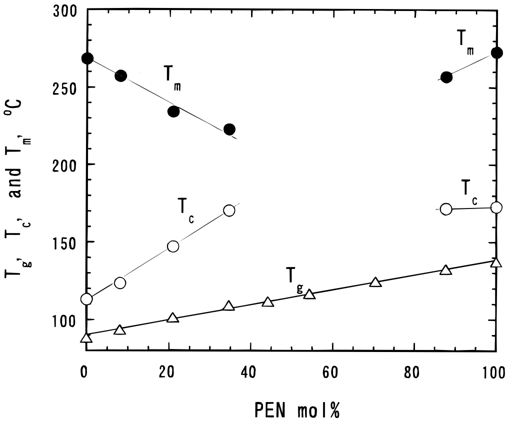

**Figure 6.** Dependence of glass transition temperature $T_g$ (△), cold-crystallization temperature $T_c$ (○), and melting temperature $T_m$ (●) on the blend composition for the PET/PEN blends.

the determination methods of $T_g$. Dynamic mechanical analysis has advantages as compared to DSC in the location of the $T_g$: large peaks in the tan $\delta$ are observed, as compared to small steps in the DSC curve around $T_g$, as already pointed out by Brostow et al.[11]

Po et al.[2] proposed that the $T_g$ of PENT random copolymers exhibits an almost linear variation with mole content of PEN and is almost independent of randomness. These facts show that $T_g$ of PET/PEN blends is not changed by the degree of esterification.

For the crystallizable blends of PET/PEN, we define the cold-crystallization temperature $T_c$ and the melting temperature $T_m$ as follows. $T_c$ is the temperature at which the blend begins to crystallize to show an increase in $E'$ during a temperature sweep at a heating rate of 2 °C/min from an originally amorphous state. $T_m$ is the temperature at which the blend achieves an $E'$ of $10^6$ Pa from the crystallization plateau as temperature rises. Although the crystallizable blends showed various patterns of crystallization, one may find a similarity that the crystallization developed by two steps. This phenomenon became more clear as the blending time was increased and would be probably due to a combination of two contributions: One is the crystallization of PET and the other that of PEN. As reported, the crystallization temperature of PET is lower than that of PEN.[2] Therefore, one may consider that the first step crystallization was attributed to the PET component (including PET-rich molecules) while the second step crystallization was attributed to the PEN component (including PEN-rich molecules). Furthermore, a phase separation due to the different crystallites between PET and PEN may be also considered in the blends. Except for the case where the individual crystallization of PET or PEN can be clearly observed like the blend 2575-15, however, it would be difficult to separate the contributions for two components only through the viscoelastic measurements.

An important feature we have to point out here is that the crystallization behavior of the blend is controlled not only by the value of $f_{TEN}$ but also by the composition. For example, at a blending time of 15 min (see Table 3), although the blend 5050-15 achieved a transesterification level of 0.22, lower than that (0.26) for the blend 2575-15, the former became uncrystallizable while the latter was still crystallizable. This reflects the variance in molecular structure, caused by the transesterification occurring differently in the different compositions of blends.

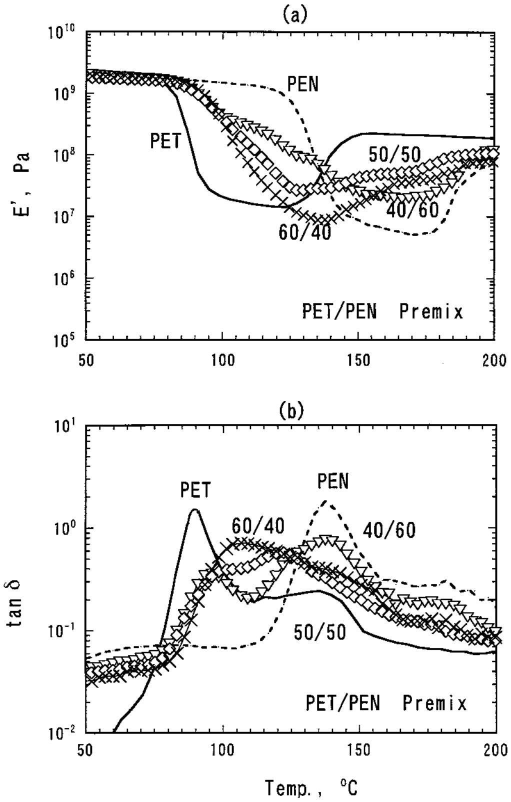

**Figure 7.** Storage modulus $E'$ (a) and loss tangent tan $\delta$ at 10 Hz and a heating rate of 2 °C/min for three PET/PEN blends (PET/PEN = 60/40, ×; 50/50, ◇; 40/60, ▽) prepared at 290 °C and 30 rpm for 1 min. For comparison, $E'$ and tan $\delta$ curves of PET (solid line) and PEN (dashed line) are given in the same range of temperatures.

Po et al.[2] reported that the blends with monomer average sequence lengths of 5−6 are able to crystallize. We also judge crystallization of the blend using the number-average chain length $L$ ($L_{PET}$ and $L_{PEN}$). By comparing the crystallization of each blend given in Table 3, we can found that (1) the blend was crystallizable when one of the polymers (PET or PEN) had an average chain length of larger than 5 and (2) the blend became uncrystallizable when both chain lengths ($L_{PET}$ and $L_{PEN}$) were less than 5. The blends 5050-10 and 5050-15 exhibited a weak deviation from the above rule. This may suggest that the other molecular information such as molecular weight distribution of polymers caused by transesterification has to be taken into account.

**Miscibility of PET and PEN.** It has been reported that PET and PEN are immiscible in the absence of some transesterified polymers.[1,7,8] Two glass transition temperatures were observed in the PET/PEN blends that were prepared by solution precipitation and then melt-pressed or annealed for a short period of time,[7,8] indicating that two phases, a PET-rich phase and a PEN-rich phase, were present in the blend. The further thermal treatment such as melt blending or annealing for a longer period of time can easily make the blend to show a single glass transition temperature, meaning the generation of one-phase state.

Figure 7 shows the storage modulus (a) and the loss tangent tan $\delta$ (b) plotted against temperature for the blends of PET/PEN = 60/40, 50/50, and 40/60 prepared by the premixing condition. These blends had a transesterification of less than 6%. The tan $\delta$ curves of the

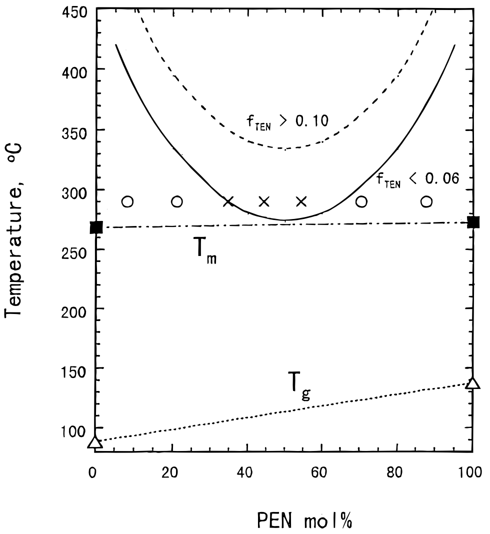

**Figure 8.** Schematic view of phase diagram for PET/PEN blends. The circles and crosses represent miscible and immiscible, respectively, at 290 °C.

PET and PEN are also given in the figure for comparison. We can clearly observe two $T_g$s for the blend 40/60, which are considered to be attributed to the two phases: the PET-rich phase and the PEN-rich phase. The two-$T_g$ behavior of the blend 5050-0 is not observed as clearly as in the blend 4060-0, but the broad peak with a shoulder and a hill in the temperature range from about 75 to 135 °C is doubtless evidence of the phase separation in the blend. In the case of the blend 6040-0, it seems that two $T_g$s contribute to the broad peak of tan $\delta$. It should be noted here that the temperature range for the appearance of two-$T_g$ behavior does not cover that for crystallization, so that one may simply judge the miscibility by checking whether there are two glass transition temperatures or not. It should also be noted that in the present work all samples prepared by the melt blending passed a second thermal process, the thermal compression molding (290 °C for 4 min). Since the transesterification was also possible in the second thermal process, an immiscible blend prepared by melt blending for a short period of time would be able to become miscible during the thermal compression molding. Ihm et al.[8] reported that PET/PEN blends show a single $T_g$, when the degree of randomness is greater than about 0.50. Our present results disagree with the results by Ihm et al. but agree with the results by Stewart et al.[5]

On the basis of the results that the blends 4060-0, 5050-0, and 6040-0 exhibited two $T_g$s although the blends 7525-0 and 2575-0 did a single $T_g$, we can draw a schematic view of the phase diagram for PET/PEN blends with low transesterification level as described in Figure 8. Here, the lower critical solution temperature (LCST) is assumed according to Okamoto and Kotaka.[9] The circles and crosses represent miscible and immiscible, respectively, at 290 °C. Since the discussion of phase separation without considering crystallization is not available in the temperature region between $T_g$ and $T_m$ for a crystallizable blend, we confine our discussion of phase behavior for the blends in the molten state. Since our samples were prepared by quenching from 290 °C and the viscoelastic measurements were performed from −120 °C, the miscibility described by the glass transition behavior represents that at 290 °C. By comparing the fractions of transesterification with the viscoelastic properties of the PET/PEN blends, we found that when the transesterification exceeded a level of $f_{TEN} = 0.10$, the blend was in the one-phase state by showng a single glass transition temperature $T_g$. This fact shows that increasing $f_{TEN}$ makes the LCST curve shift to higher temperatures. The cloud point curve (solid line) is expected to shift to the dashed line due to the increase in transesterification, which results in an extension of the miscible area. The viscoelastic results indicate that PET/PEN = 75/25 and 25/75 blends are miscible for very low transesterification. We can guess that PET/PEN = 90/10 or 10/90 blend is miscible for no esterification. This may be the reason why the transesterification rate of these blends is very high.

## Conclusions

We have studied the dynamic mechanical properties of the blends of poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN) as a function of blend composition as well as the blending time. These blends were prepared by melt blending at 290 °C in a mixer. The results are as follows. (1) The blends of PET/PEN = 40/60 to 60/40 were immiscible for a transesterification level of less than 6%, while the other blends (10/90, 25/75, 75/25, 90/10) showed one-phase behavior at the same level of transesterification (below 6%). (2) All the blends having a transesterification level of above 10% were in the one-phase state by showing a single glass transition temperature $T_g$. $T_g$ of the blend was a linear function of the blend composition, independent of the blending time. The blending time did not significantly affect the dynamic mechanical behavior in glass transition region but dramatically changed the behavior of the blends in the cold-crystallization region as a function of blend composition. (3) The measurements of transesterification by $^1$H NMR have provided us with information about the fraction of transesterification as well as the average chain length. The cold-crystallization behavior of a PET/PEN blend was able to be judged by the average chain lengths $L_{PET}$ and $L_{PEN}$: the cold crystallization remained until $L_{PET}$ or $L_{PEN}$ was larger than 5 while the cold crystallization disappeared for both $L_{PET}$ and $L_{PEN} \leq 5$.

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