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Uniaxial orientation and tensile properties of poly(ethylene terephthalate)/poly(ethylene-2,6-naphthalate) blends

Masayoshi Ito[a,*], Mizuho Takahashi[a], Tetsuo Kanamoto[b]

[a]*Department of Chemistry, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*
[b]*Department of Applied Chemistry, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*

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Abstract

Amorphous films of poly(ethylene terephthalate)/poly(ethylene-2,6-naphthalate) (PET/PEN) blends with different blend ratios were uniaxially drawn by solid-state coextrusion and the structure development during solid state deformation was studied. As-prepared blends showed two T_gs. The lower T_g was ~72 °C, independent of the blend ratio. In contrast, the higher T_g increased with increasing PEN content. Thus, the coextrusion was carried out around the higher T_g of the sample. At a given draw ratio of 5, which was close to the achievable maximum draw ratio, the tensile strength of the drawn samples from the initially amorphous state increased gradually with increasing PEN content. On the other hand, the tensile modulus was found to decrease initially, reaching a minimum at 40–60 wt% PEN, and then increased as the PEN content increased. The results indicate that we can get the drawn films with a moderate tensile modulus and a high tensile strength. The drawn samples from the blends containing 40–60 wt% of PEN showed a maximum elongation at break, and a maximum thermal shrinkage around 100 °C. Also, the degree of stress-induced crystallinity showed a broad minimum around the blend ratio of 50% of PEN. These morphological characteristics explained well the effects of blend ratio on the tensile modulus and strength of drawn PET/PEN blend films. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate)/poly(ethylene-2,6-naphthalate) blends; Crystallization; Tensile properties

1. Introduction

Blending of poly(ethylene terephthalate) (PET) with poly(ethylene-2,6-naphthalate) (PEN) has been attracting increasing interest from both industrial and scientific viewpoints, because it combines the superior properties of PEN with the economy of PET [1–5].

PET and PEN are basically immiscible independent of the blend compositions [6]. The transesterification in melt blending of PET and PEN leads to the formation of block copolymers first and then of random copolymers, which enhances the miscibility of the blend [1]. Santa Cruz et al. [7] studied the crystalline structure of random copolymers of PET and PEN. For the samples containing 0–30 mol% of PEN, the PET sequences crystallize while PEN segments remain in the amorphous regions. In contrast, for the samples containing >80 mol% PEN component, the PEN sequences crystallize in the α-form and the PET segments are excluded in the non-crystalline regions. Kyotani et al. reported [4] that for the PET/PEN blend of 50 wt% PEN content was most difficult to crystallize relative to the other blends under identical crystallization conditions. Such crystallization behaviors are interesting and important from the viewpoints of structure development during solid-state deformation of semicrystalline polymers, which involves a strain-induced crystallization.

In this study, uniaxial drawing was carried out on amorphous films of PET/PEN blends. The tensile modulus and strength of the resultant drawn films were correlated to the structure development during the solid-state deformation.

2. Experimental

2.1. Samples

Commercially available PET (IV = 0.63 dl/g) and PEN (IV = 0.65 dl/g) pellets were used. The blending of PET with PEN was done in two stages. In the first stage, pellets of each homopolymer were dissolved individually in a mixed solvent of trifluoro acetic acid and dichloromethane (50/50, v/v) at room temperature. A desired volume of PET solution (3 wt%) was mixed with a desired volume of PEN

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* Corresponding author. Tel.: +81-3-5228-8275; fax: +81-3-3235-2214.
E-mail address: maito@ch.kagu.sut.ac.jp (M. Ito).

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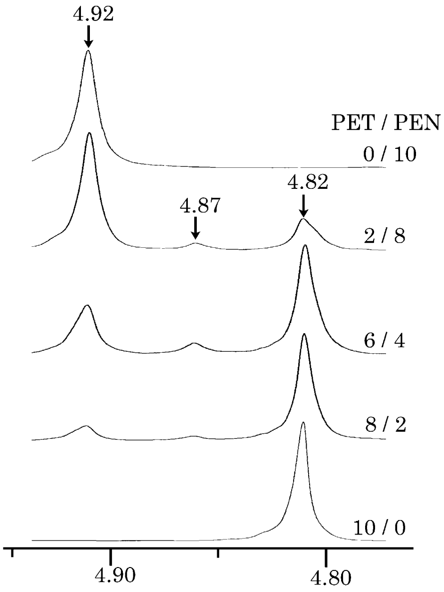

Fig. 1. ^{1}H NMR spectra of ethylene unit region for PET, PEN and their blends.

solution (3 wt%). The mixture containing requisite amounts of PET and PEN components was poured into methanol to get polymer precipitates. In the second stage, the dried precipitates were molded at 290 °C for 5 min under pressure, followed by quenching in ice water. The films of the pure components were molded under similar conditions used for the preparation of blend films. The blend ratio was expressed by a weight ratio of the two components, PET/PEN, g/g.

As-prepared blends showed two glass transition temperatures (T_g). The lower T_g was ~72 °C, independent of the blend ratio. In contrast, the higher T_g increased with increasing PEN content. Thus, uniaxial drawing was carried out by solid-state coextrusion near the higher T_g for each blend. The extrusion draw ratio (EDR) of each sample was fixed to be 5.

2.2. Measurements

The extent of transesterification of the PET/PEN blends was estimated by using the ^{1}H NMR spectra corresponding to the ethylene moiety [8]. The samples for the NMR measurements were prepared by dissolving the blends in a mixture of trifluoroacetic acid/deuterated chloroform (10/20, v/v). The measurements were carried out at 25 °C on a JEOL JNM-LA 400 at a field strength of 400 MHz for the proton observations. The chemical shift was referenciated by TMS.

The thermal behavior of the samples was examined with a Seiko Instrument differential scanning calorimeter (DSC) model SSC-5200 in a dry nitrogen atmosphere at a heating rate of 10 °C/min. In this work, the T_g was determined by an inflection point method which was easily found in the differential DSC thermogram as a peak.

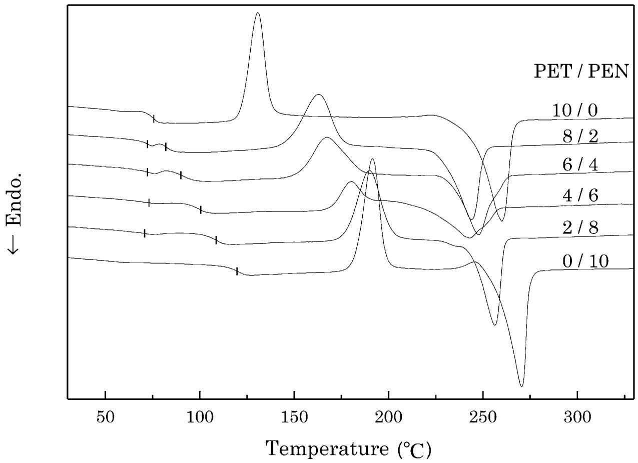

Fig. 2. DSC thermograms for PET, PEN and their blends.

Wide-angle X-ray diffraction (WAXD) patterns of the samples were obtained at room temperature with Cu Kα radiation generated at 40 kV and 25 mA on a Rigaku Gigerflex RAD-IIIA and monochromatized with a graphite crystal.

The tensile modulus and strength on the fiber axis of the samples were measured at strain rates of 10^{-3} and 10^{-2} s^{-1}, respectively, at room temperature. The modulus was determined from the initial slope of the stress–strain curve at a low strain (<0.1%). The gauge length for all samples was adjusted to 5 cm. The cross-sectional area of a sample was determined by the combination of optical microscope and micrometer measurements.

3. Results and discussion

3.1. Characterization of pre-drawn films

The ^{1}H NMR spectra of the homopolymers and their blends in the ethylene unit region are shown in Fig. 1. The peaks at 4.82 and 4.92 ppm are attributed to the ethylene units of PET and PEN, respectively, and the one at 4.87 ppm is attributed to those that exist between terephthalic and naphthalic groups in the polymer backbone [1]. These three peaks were used to determine the extent of transesterification. The details were described in the literature by Shi and Jabarin [8]. The results showed that the percentage transesterification was 7–10 mol%, almost independent of blend composition. Previous works of PET/PEN blends revealed that the major effects on the transesterification could be attributed to blending temperature and blending time and the composition had little effect on transesterification of the blends [1,2,8].

Fig. 2 shows DSC thermograms for PET, PEN and their blends. Both PET and PEN showed a single glass transition

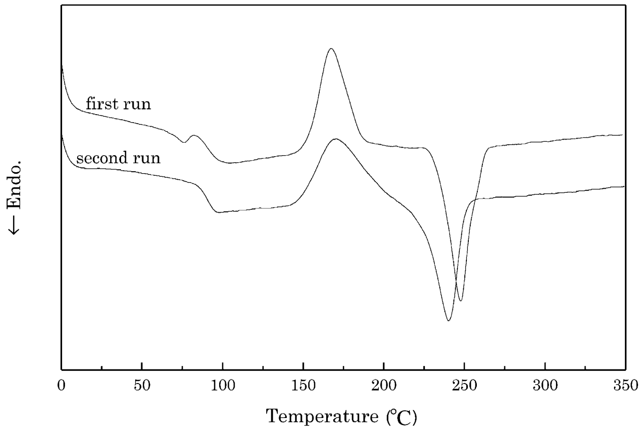

Fig. 3. DSC thermograms for the blend (PET/PEN, 6/4) at the first and second heating runs.

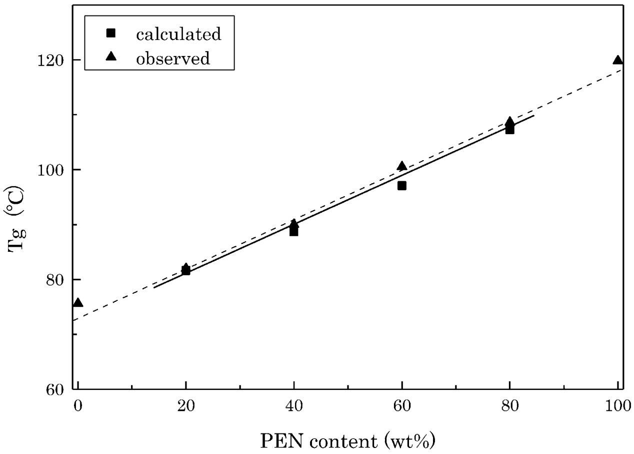

Fig. 4. T_g of blends as a function of PEN content.

temperature (T_g) around 75 and 120 °C, respectively. On the other hand, all the blends showed two T_gs. The lower T_g was ~72 °C, independent of the blend ratio. This value is comparable to that for the PET homopolymer. In contrast, the higher T_g increased with increasing PEN content. These results suggest that the blends are composed of PET phase and miscible or random copolymer phase. According to the normal blend theory, all the blends should have a PET rich phase, PEN rich phase and the miscible phase. The missing of the T_g for the PEN rich phase is less understandable. Thus, the following DSC measurements were carried out to understand the results shown in Fig. 2. The blends were heated up to the desired temperature which was chosen between lower T_g and 160 °C, holding for 1 min, followed by a rapid cooling to 0 °C. Then the second heating run was carried out. The DSC thermograms at the first and second heating runs for the blend (PET/PEN, 6/4) are shown in Fig. 3. It is clear that the lower T_g disappeared at the second heating run. But, the higher T_g still existed at the same temperature which was observed at the first heating run. Such annealing effects were almost independent of holding temperature and blend composition. These results suggest that the as-prepared blends are in a thermodynamically metastable state. During the heating run, thermodynamically unstable and immiscible system might change quickly into stable and miscible one. This means that above T_g of the PET, all the blends are miscible. This is confirmed by the results shown in Fig. 4 in which the T_g observed at the second heating run is plotted as a function of PEN content. In the case of miscible blends of polymers or random copolymers, the T_g of the blends or copolymer can be expressed by the empirical Fox equation [9]. The T_gs of the blends were calculated by Fox equation and the results are also shown in Fig. 4. The Fox equation gives good fits to the experimentally obtained T_g values, indicating the formation of miscible blends or random copolymers of PET and PEN. In this work, uniaxial drawing was carried out around the higher T_g of the blends. This means that the drawing was done under a miscible state of the blends. Kyotani et al. [4] suggested that at a low level of transesterification, both PET and PEN rich phases existed in the blends. In contrast, Shi and Jabarin reported [10] that although the blends with low level of transesterification were translucent, suggesting the existence of multiphases, most of the blends showed only one T_g even at very low transesterification levels.

As described in Section 2, the technique used for the preparation of our blends was different from the widely used mechanical mixing. In our work, the precipitates from PET and PEN solutions were molded at 290 °C under a high pressure (~200 kg/cm^2), followed by quenching in ice water. Thus, the whole series of PET/PEN blends was completely amorphous as revealed by WAXD patterns (data not shown). Our DSC results obtained at the second run were similar to those reported by Shi and Jabarin [10]. This implies that the mixing capability utilized in this work is similar to that for widely used mechanical mixing.

As it can be seen in Fig. 2, all the blends were capable of crystallizing during the heating run, resulting in the appearance of melting behavior of the crystals which were developed during the DSC scan. It is well known that the DSC melting behavior of semicrystalline polymers are greatly affected by some factors including crystalline morphology, crystalline form, crystalline perfection and heating rate of DSC scan. Thus, we cannot get any definitive information on the crystalline phase of the blends from DSC thermograms shown in Fig. 2.

Fig. 5 shows the WAXD patterns of the annealed blends with different blend ratios. The annealing was carried out at 180 °C for 4 h under a reduced pressure, followed by a quenching in liquid nitrogen. It is clear that for the blends with a low PET content (0/10–4/6), the PEN crystallized preferentially into the α-form [11], but the PET was not. On the other hand, the PET component crystallized for the blends with a low PEN content (6/4–10/0). In this case, the crystallization of the PEN was less.

Fig. 6 shows the heat of fusion (ΔH_m) of the annealed homopolymers and their blends calculated from the endothermic regions of the DSC curves on heating run as

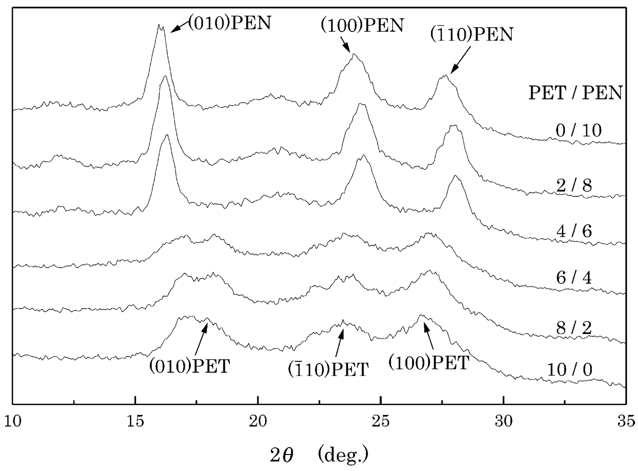

Fig. 5. WAXD patterns for the annealed blends.

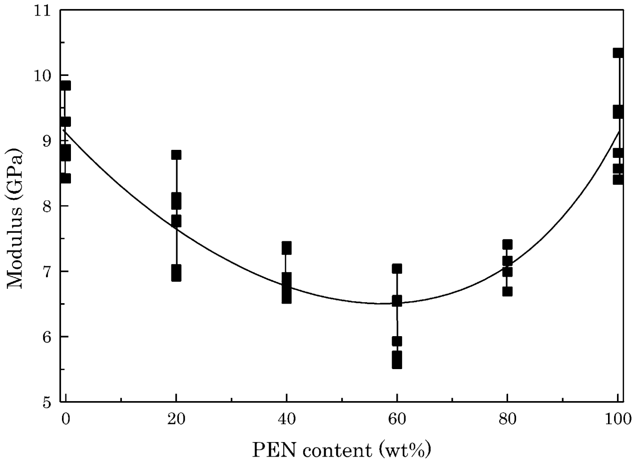

Fig. 7. Tensile modulus of the drawn blends as a function of PEN content.

a function of PEN content. It should be noted that the ΔH_m exhibits a minimum for blends with 40–60 wt% PEN. The heat of fusion of the PET and PEN crystals are 130 J/g [12] and 103 J/g [13], respectively. Thus, the combination of the results in Figs. 5 and 6 shows that the crystallinity of the blends with 40–60 wt% PEN is only about 15–23 wt%, and lowest among the blends. This means that the blends with 40–60 wt% PEN are more difficult to crystallize than the other blends under a similar crystallization condition.

There are a few reports on the crystallization behavior of PET/PEN blends [14,15] and copolymers of PET and PEN [16]. Shi and Jabarin [15] reported that the Avrami exponent is different for PET, PEN and the blends, indicating different crystallization mechanisms for the blends from those for pure PET and PEN. Lu and Windle [16] studied the crystallization behavior of random copolymers of PET and PEN and found that the crystallinity of the copolymers showed a minimum at an intermediate PEN composition. Further, in the composition range of 0–60 mol% PET, the WAXD patterns were quite similar to that for the PEN homopolymers, whereas the patterns for the copolymers with 80–100 mol% PET units were similar to the patterns of PET, but distinct from those in the 0–60 mol% PET range. Santa Cruz et al. [7] studied the crystalline structure of random copolymers of PET and PEN and distinguished the regions in which PET or PEN blocks crystallized, while the other component was ejected into the amorphous phase. The present results shown in Figs. 5 and 6 were quite similar to the crystallization behavior of copolymers of PET and PEN. The crystallization behavior of miscible blends has attracted interest for many years [17,18]. However, the PET/PEN blends are usually composed of multi phases (copolymers of PET and PEN, miscible phase of PET and PEN and each homopolymer in some cases), which might make it difficult to understand the crystallization behavior of the blends.

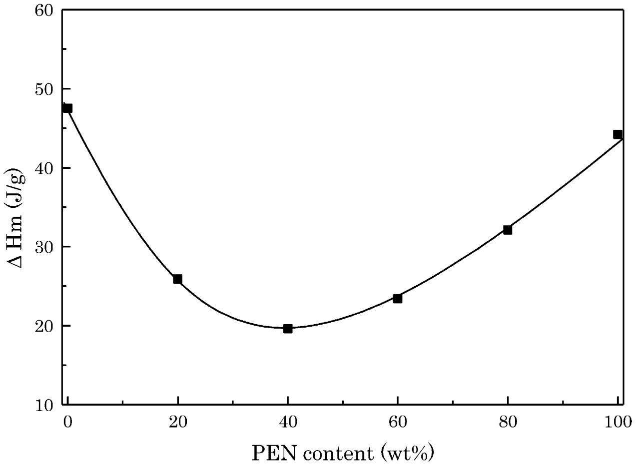

Fig. 6. Heat of fusion (ΔH_m) of the annealed blends as a function of PEN content.

3.2. Tensile properties

The tensile modulus and strength of drawn samples with an EDR of 5 from PET/PEN blends are shown as a function of PEN content in Figs. 7 and 8. The EDR 5 was close to the achievable maximum EDR. The tensile modulus of the samples was found to decrease with increasing PEN content and reached a minimum at 40–60 wt% PEN, then increased as the PEN content increased further. On the other hand, the tensile strength gradually increased with increasing PEN content. It is noted that the modulus/PEN content relation is different from that found in the strength/PEN content.

The deformation behavior and the tensile properties of the resultant drawn materials of PET and PEN have been extensively investigated for a long time. When initially amorphous films of PET or PEN are drawn around the T_g of the sample, strain-induced crystallization occurs, which enhances the tensile modulus and strength of the resultant drawn materials. We have shown that both the tensile modulus and the strength of drawn PET and PEN at a given deformation ratio (draw efficiency) are much affected by

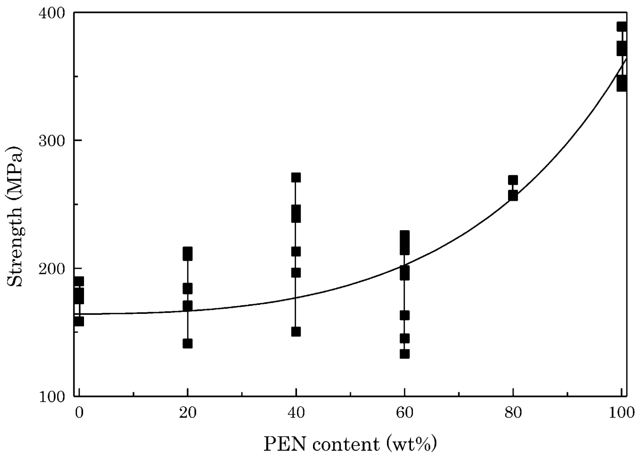

Fig. 8. Tensile strength of the drawn blends as a function of PEN content.

the draw conditions, molecular weight of the polymer, predrawn morphology and sample geometry [19–24]. Further, the value of tensile strength has a close relation with that of tensile modulus; the higher the tensile modulus, the higher is the tensile strength that can be achieved. That is, the draw efficiency evaluated from the tensile modulus for a given sample is quite similar to that of the tensile strength.

The crystal modulus of PEN along the chain direction has been determined to be 145 GPa by the WAXD method [25], which is about 40% higher than that of PET (108 GPa) [26]. Thus, the tensile modulus of drawn samples might be expected to increase with increasing PEN content if similar levels of chain extension, orientation and crystallization are achieved in both PET and PEN molecules. However, this is different from the experimental results shown in Fig. 7.

Fig. 9 shows the WAXD profiles on the equator of the drawn samples with a constant EDR of 5. The profiles were diffuse and broad compared with those in Fig. 5. This is reasonable since the deformation temperature (80–110 °C) was far below the annealing temperature of 180 °C. For the blends with a low PET content (0/10–4/6), the WAXD patterns were quite similar to that of PEN, whereas, the patterns for the samples with a low PEN content (10/0–6/4) were similar to that of PET. The effects of PEN content on the strain-induced crystallization behavior was quite similar to the case of thermal crystallization behavior as shown in Fig. 5.

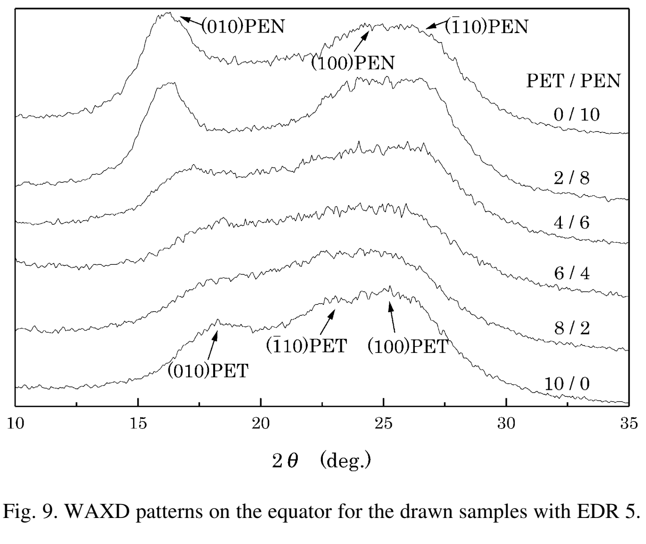

Fig. 9. WAXD patterns on the equator for the drawn samples with EDR 5.

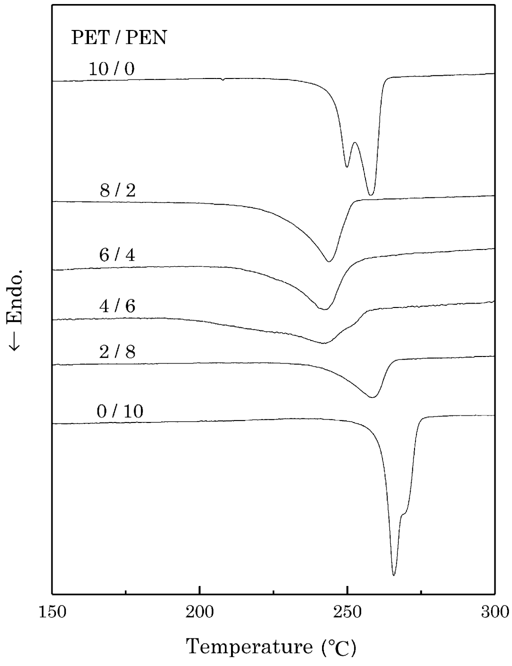

Fig. 10. DSC thermograms of drawn samples with EDR 5.

Fig. 10 shows the DSC thermograms of the drawn samples with a constant EDR of 5. All the samples showed endothermic peaks due to the melting of stress-induced crystals. The drawn samples from homopolymers (PET and PEN) showed double melting peaks. On the other hand, most of the melting peaks for the blends were single. As described, the melting behavior of semicrystalline polymers is greatly affected by some factors, thus, we cannot find any evidence for the coexistence of PET and PEN crystals from the results shown in Fig. 10. The drawing was carried out around the higher T_g of the blends where all the blends were in miscible state. Such phase structure might influence the stress-induced crystallization behavior.

Fig. 11 shows the heat of fusion (ΔH_m) of the drawn samples with a constant EDR of 5 as a function of PEN content. The relation between ΔH_m of annealed samples and PEN content (already shown in Fig. 6) is also shown by a dotted line in the same figure for the comparison. At a given PEN content, the ΔH_m for the drawn sample is larger than that for annealed one although the WAXD patterns for the former are more diffuse than those for the latter (see Figs. 5 and 9). The reason is not clear at present and is currently studied. However, one possibility might be related to the structural difference between drawn and annealed samples. As described, the deformation temperature was far below the annealing temperature. Thus, the crystal

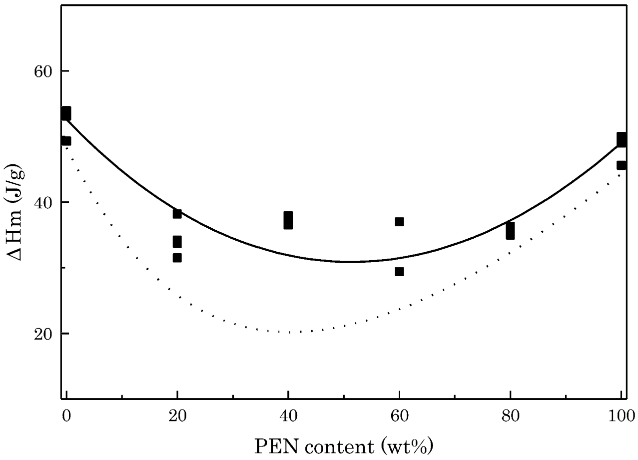

Fig. 11. Heat of fusion (ΔH_m) of the drawn samples with EDR 5 as a function of PEN content.

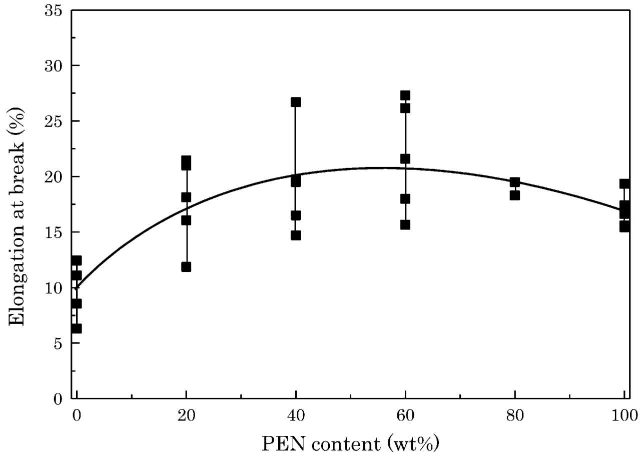

Fig. 13. Elongation at break of the drawn samples with EDR 5 as a function of PEN content.

perfection of annealed samples is higher than the stress-induced crystals as seen in Figs. 5 and 9. On the other hand, there exists extended non-crystalline molecules in the drawn samples, which might contribute to the endotherms of drawn samples.

The crystallinities of the drawn samples were evaluated from DSC thermograms assuming that the crystals developed in the samples with a PEN content of 0–40 wt% were PET crystals, and the crystals for the ones with a PEN content of 60–100 wt% were PEN crystals as shown in Figs. 5 and 9, which showed a minimum at 40–60 wt% PEN (data not shown), where the tensile modulus also showed a minimum (see Fig. 7). The extent of strain-induced crystallization depends on the degree of chain extension/orientation achieved upon drawing and the crystallization rate. As discussed in Section 3.1 (Figs. 5 and 6), the blends with 40–60 wt% PEN are more difficult to crystallize relative to the other blends under a similar thermal condition. A similar situation was found in the strain-induced crystallization as shown in Figs. 9–11. The thermal shrinkage shown in Fig. 12 is primarily ascribed to the relaxation of the oriented chains in the amorphous regions. Around 100 °C, all the samples showed a stepwise increase of shrinkage on the heating process with this tendency more prominent in the drawn samples with a lower crystallinity (blend ratios; 6/4 and 4/6). These suggest that the crystalline phase of the drawn samples might act as net points of extended non-crystalline molecules, which suppress the thermal shrinkage on heating. As it was described the drawing was carried out around the T_g of the blends where extended non-crystalline molecules might be able to relax. That is, the tensile modulus of drawn samples is greatly affected by the strain-induced crystallinity which is a function of the PEN content of the blends.

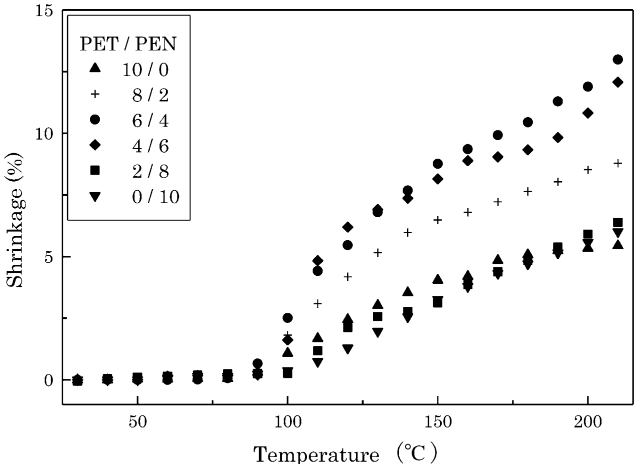

Fig. 12. Shrinkage of the drawn samples with EDR 5 as a function of temperature.

As described, the tensile strength/PEN content relation is quite different from that found in the tensile modulus/PEN content. The tensile modulus was determined from the initial slope of stress–strain curve at a low strain (<0.1%). Thus, the structural changes in the samples during measurements might be negligibly small. On the other hand, for the measurements of tensile strength, a large structural change sometimes takes place, especially for a sample of a low crystallinity. In fact, we observed a large value of elongation at break, which was dependent on the PEN content, in other word sample crystallinity. Fig. 13 shows the elongation at break (Eb) of the drawn samples as a function of PEN content. The Eb showed a maximum around 40–60 wt% PEN where the sample crystallinity showed a minimum (Fig. 11). This fact suggests that the elongation of an oriented sample proceeds through the deformation of amorphous regions although the amorphous chains are significantly oriented as suggested by the thermal shrinkage data.

The crystallinity of the drawn samples was dependent on the PEN content, which influenced the chain extension in the non-crystalline phase of the drawn samples (EDR = 5). That is, the structure development upon the solid-state deformation is greatly affected by the blend ratio, leading to the appearance of the different relations between modulus/PEN content and strength/PEN content. The drawn film with moderate tensile modulus and high tensile strength will be of much use for the practical application such as packaging materials.

4. Conclusions

The structure and tensile properties of PET/PEN blends with different blend ratios were studied in relation to the structure development upon solid-state deformation around the T_g of the blends, and the following conclusions were derived from the experimental results.

1. The strain-induced crystallization behavior of PET/PEN blends was quite similar to the thermally induced one. That is, the blends with 40–60 wt% PEN were more difficult to crystallize relative to the other blends. Further, in the samples containing 0–40 wt% PET, the PEN component crystallized into the α-form. On the other hand, the PET component crystallized for the blends containing 60–100 wt% PET.
2. At a given draw ratio of 5, which was close to the achievable maximum draw ratio, the tensile strength of the drawn samples from an initially amorphous state increased gradually with increasing PEN content. On the other hand, the tensile modulus was found to decrease with increasing PEN content, reaching a minimum at 40–60 wt% PEN, and then increased as the PEN content increased. The drawn samples from the blends containing 40–60 wt% PEN showed a minimum degree of stress-induced crystallinity, a maximum elongation at break, and a maximum thermal shrinkage around the T_g. For the drawn samples with a low crystallinity, a part of the extended non-crystalline molecules might be partly relaxed during the drawing, which leads to a lower tensile modulus. Such partly relaxed chain molecules are forced to extend during the measurements of tensile strength, leading to the increase of the tensile strength of the samples with a low crystallinity and hence, a low modulus.

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