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Structural development and mechanical properties of polyethylene naphthalate/polyethylene terephthalate blends during uniaxial drawing

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Abstract

The blends of poly(ethylene naphthalate) (PEN) and poly(ethylene terephthalate) (PET) were obtained by melt blending at 310°C for 2 min and quenching into an ice water. Mechanical properties and structural formation of unoriented amorphous PEN/PET blend films during drawing at 85, 100 and 130°C were studied by tensile tests and in situ X-ray measurements. The results obtained were compared with the pure PEN and PET.

The PET film could not be drawn due to partial melt at above 100°C and a lower drawing rate but the film blended with PEN was possible to be drawn. The crystallization of PEN/PET blend during drawing proceeded gradually due to the effect of PET at 100°C though the crystalline reflections in the crystallization of pure PEN appeared suddenly by necking. This was evidenced by the formation of α-form crystalline reflections of PEN as detected by in situ X-ray measurements. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: PEN/PET blend film; Oriented crystallization; In situ WAXD measurement

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1. Introduction

Poly(ethylene 2,6-naphthalate) (PEN) has naphthalene rings in its main chain in place of benzene rings of poly (ethylene terephthalate) (PET). Accordingly, PEN has higher modulus, melting temperature ($T_m = 270$°C) and glass transition temperature ($T_g = 113$–117°C) than PET ($T_m = 265$°C; $T_g = 69$°C) [1–3]. Thus, PEN is utilized, for example, in the production of electrical parts such as ultra-small layer tip condenser [4] and in the electrical audio-visual accessories such as base film of longplay videotape of high quality [5,6]. PEN has also a higher barrier property for oxygen and carbon dioxide which makes it more suitable for food packaging [7]. However, PEN is an expensive resin and may not be always feasible for industrial applications. Through polymer blending, the superior performance of PEN and the economics of PET are expected to be obtained. For this reason, the PEN/PET blends have attracted considerable interests among the researchers [7–18]. However, the crystallization mechanism and structural formation by drawing PEN/PET blend films are not yet fully understood.

PEN and PET have been known to be immiscible with each other as suggested by the phase separation obtained by cross-polarization/magic-angle spinning/dipolar decoupling (c.p./m.a.s./d.d.) ^{13}C NMR [19]. However, during melt blending, they undergo a transesterification reaction which provided them a certain degree of miscibility. Stewart et al. [7] reported that this reaction was dependent on the blending time and temperature while the blend composition and the residual polyester catalysts had no significant effect. The miscibility afforded improvement on the clarity and mechanical properties of the blend.

In our previous works [20,21], the structure development in the crystallization of amorphous PEN films was investigated during uniaxial drawing above the glass transition temperature. In the case of uniaxial drawing at 150°C, crystallization started to appear suddenly at about draw ratio (DR) 2.0 on the equator and at the same time appeared to be accompanied by streaks on the off-equatorial layer lines. These streaks suggested the existence of paracrystalline structure by lattice distortion to the drawing direction. Thereafter, the crystalline reflections showed the α-form of triclinic structure. This was due to the axial shift of neighboring chains along the chain axis with respect to one another.

Likewise, several authors had investigated the structural formation of PET [22,23]. Asano [23] studied the effect of the drawing rate on the structure of cold-drawn PET. The

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slowly drawn PET showed paracrystalline structure, which was transformed to triclinic structure when annealed above 100°C. Bonart [22] reported the development of different structures of PET after drawing above its T_g point from amorphous to nematic and then smectic states. Recently, Asano et al. [24] showed that amorphous cold-drawn PET films annealed at 60, 70 and above 80°C revealed the appearance of smectic order with a period of 10.7 Å, a layer structure in the scale of 110 Å and triclinic order, respectively. Mahendrasingam et al. [25,26] observed that when sheets of the polymer are drawn close to T_g, the mesophase which had a highly oriented weak transient diffraction peak occurred immediately prior to strain-induced crystallization of the polymer.

In this report, the structural changes of PEN/PET blends during uniaxial drawing at 85, 100 and 130°C were investigated using a wide-angle X-ray diffraction (WAXD) system equipped with imaging plates. The mechanical properties of the blends were correlated with the structure from the results of WAXD measurements. The final WAXD patterns and the mechanical properties of pure PEN and PET were also present to facilitate the evaluation of the WAXD patterns of the blends. These studies are essential in determining the performance of the polymer blend for application in a new product/field.

2. Experimental

2.1. Polymers and blending

PEN, PET and their blend films were kindly supplied by the Teijin. The molecular weights of PET and PEN were both 18,000. Melt blending of PEN and PET (blend ratio: 100/0, 70/30, 50/50, 30/70 and 0/100 by weight) was undertaken using a Toyoseiki Labo Plastomill Twin Screw Extruder C-type with *L/D* ratio of 25/1. The equipment was set at 310°C, screw speed at 233 rpm and residence time of 2 min. The molten film was quenched immediately into an ice water to obtain an unoriented amorphous structure of the polymer. These specimens had about 5% copolymers in blend films from ^{1}H NMR measurements and exhibited only a single T_g, and were totally transparent. Specimens were cut towards the direction of the extruder and subject to tensile and X-ray measurements.

2.2. Mechanical tests

Tensile properties of the films were determined using a Shimazu Tensile Tester model AGS-G equipped with a heating chamber (TCR2-300). The stress–strain (S–S) curves were measured at 85, 100 or 130°C and at a constant cross-head speed of 5 mm/min. The size of the samples was 30 mm (length) × 5 mm (width) × 0.6–0.7 mm (thickness).

2.3. Wide-angle X-ray diffraction

In situ WAXD measurement was carried out using a rotating-anode Rigaku X-ray generator operated at 40 kV and 240 mA. Cu Kα X-ray beams were monochromatized with a graphite monochromator and directed onto the specimen through a pinhole collimator of 0.5 mm in diameter. As an X-ray detector, the IP system (MAC Science, DIP 220) was used. The distance of the specimen to the imaging plate was 84 mm. In the drawing device, the furnace was set at 85, 100 or 130°C and the specimen was drawn after reaching the desired temperature at drawing rate of 4 mm/min. The dimension of the samples was 24 mm (length) × 5 mm (width) × 0.6–0.7 mm (thickness). The specimen temperature was controlled by blowing thermostated hot air vertically into the specimen chamber in which the specimen was drawn in the horizontal direction in order to attain a uniform distribution of temperature over the whole specimen. The specimen temperature vis-a-vis the temperature of the air in the chamber, was monitored with a chromel–alumel (C–A) thermocouple placed in the vicinity of the specimen area illuminated with the X-ray beams. The precision of temperature regulation was ±0.5°C at a specimen temperature under 250°C. Details of the in situ WAXD equipment [27–29] and the drawing device [30,31] were described.

The results of WAXD measurement were represented by two-dimensional patterns and their corresponding equatorial intensity profiles simultaneously. The DR, in this report, was defined as follows: After finishing a drawing run, the drawn specimen was cooled down to room temperature and then taken out of the drawing device. The final DR was estimated from the elongated graduation marks in the specimen area which were illuminated with the X-ray beams. Then, based on the drawing rate and the total drawing time for that run, the DR was calculated by proportional allotment.

3. Results and discussion

3.1. Mechanical properties

Fig. 1 shows the S–S curves of unoriented amorphous films of PEN, PET and their blends which were measured at 85, 100 and 130°C. At 85°C as shown in Fig. 1a, PEN and PET exhibited the highest and the lowest yield stress, respectively. When PEN was blended with PET, the stress decreased with the PET content. Necking behavior (stress drop after the yield point) was observed on PEN and on the blends containing more than 50% PEN. The S–S curves of the blends of smaller PEN contents showed very low stress value and necking behavior was not observed. This behavior is related to the results of the crystal reflections on the WAXD patterns/profiles of PEN and PET drawn above their T_gs showed the presence and absence of the neck, respectively. These will be discussed further in the next

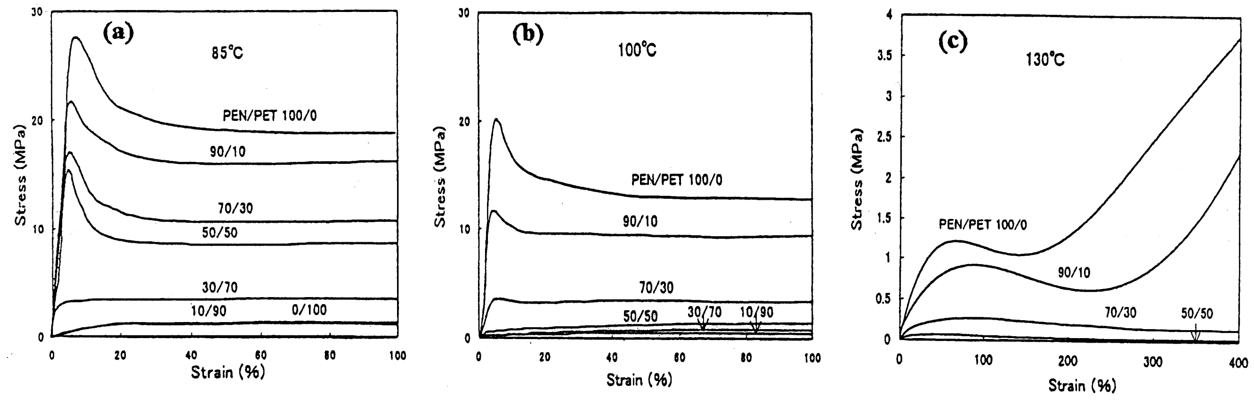

Fig. 1. Tensile S–S curves of PEN/PET blend films at (a) 85°C, (b) 100°C and (c) 130°C. Drawing speed = 5 mm/min. Stress = load/initial cross-section area.

section. Thus, two types of S–S curves were observed depending on the PEN/PET blend ratio.

The increase of the drawing temperature from 85 to 100°C decreased the stress at yield point and the stress on the plastic deformation of PEN and PEN/PET blends as revealed in Fig. 1b. At PEN/PET (70/30) blend in Fig. 1b, the stress drop by necking was very small which further decreased with the addition of PET. At PEN/PET (50/50) blend, the stress drop was no longer observed and the yield stress was very low. On the other hand, the pure PET was cut off during drawing due to the active chain mobility or movement of the molecules caused by its partial melting at 90–100°C. For this reason, the S–S curve for PET was observed only at 85°C. But in the blend film containing more than 10% PEN, the drawing was possible and consequently, the effect of blending was clearly manifested.

Drawing at 130°C of the PEN and PEN/PET blends showed a significant decrease of the stress as depicted in Fig. 1c. The curve of the pure PEN showed a yield point at 70% strain, decreased and retained up to 180% strain and then increased considerably. The latter behavior suggests the stretching of the oriented amorphous and oriented crystallized molecular chains followed by the oriented crystallization when drawn above T_g. The PEN/PET (90/10) blend showed the increase of the stress after 270% strain. Blending with 30 and 50% PET resulted in smooth curves with very low stress values.

The modulus of the blends were evaluated from Fig. 1 decreased with the increase of temperature and PET content. PEN film might not be as useful as PET film for a packaging material because of its high modulus value or high stiffness. By blending, its stiffness decreases monotonously with the increase of PET.

3.2. Wide-angle X-ray diffraction

The structural development of unoriented amorphous PEN/PET blend film (blend ratio: 100/0, 70/30, 50/50, 30/70 and 0/100) during uniaxial drawing at 85, 100 and 130°C was investigated by using in situ WAXD. Since crystallization of PEN [20] and PET [22–26] during drawing had already been reported, only the WAXD patterns of the said polymers at the final stage of drawing were presented for comparison with the PEN/PET blends (Fig. 2).

3.2.1. Drawing of PEN/PET (70/30) blend

Figs. 3 and 4 show the series of WAXD pattern and equatorial intensity profiles of PEN/PET (70/30) blend from in situ X-ray measurements during uniaxial drawings at 85, 100 and 130°C. At 85°C, the WAXD pattern at the initial stage of drawing as shown in Figs. 3a and 4a exhibited a ring-shaped broad halo while the intensity profile on the equator showed a symmetrical intensity scattering peak at about $2\theta = 20°$ indicative of the unoriented amorphous structure of the blend. Drawing to DR 3.1 led to the formation of oriented amorphous structure of PEN as shown by the concentration of the amorphous halo on the equator and the increase of asymmetrical scattering peak at about $2\theta = 24°$. Further drawing at DR 3.8–4.5 yielded 10 horizontal lines on the meridian (Fig. 3a). As shown in Fig. 2a and d, drawing of PEN at 85°C showed only eight horizontal lines while these were not observed in PET drawn under the same conditions. The 10 horizontal lines observed in the

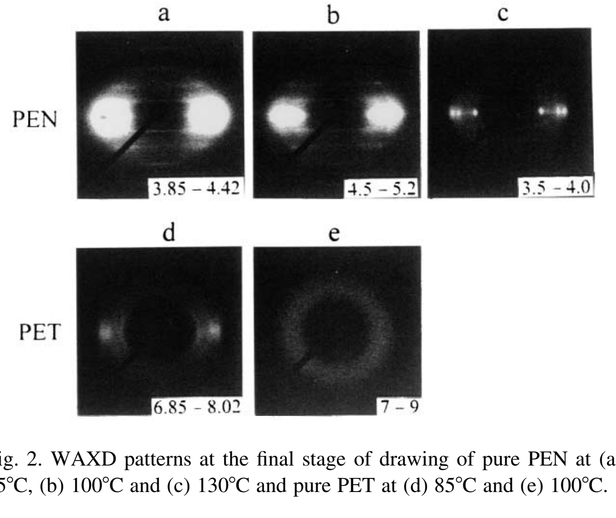

Fig. 2. WAXD patterns at the final stage of drawing of pure PEN at (a) 85°C, (b) 100°C and (c) 130°C and pure PET at (d) 85°C and (e) 100°C.

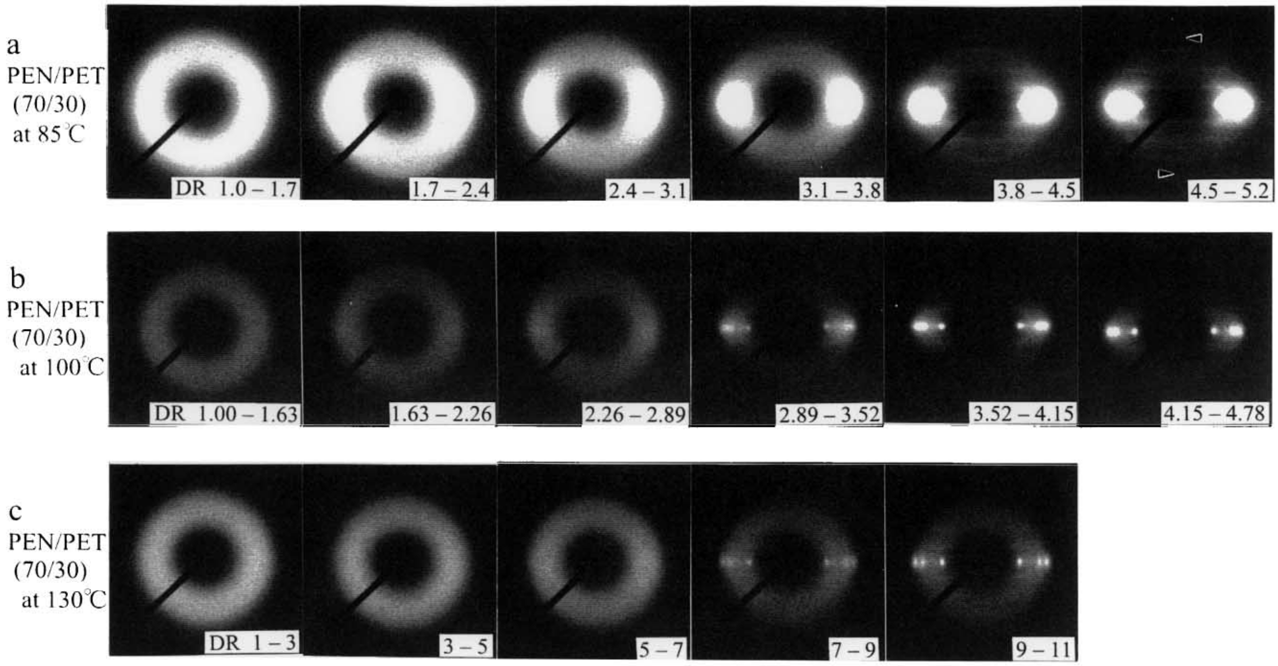

Fig. 3. Change of WAXD patterns of unoriented amorphous films of 70/30 PEN/PET blend during drawing at (a) 85°C, (b) 100°C and (c) 130°C at drawing rate of 4 mm/min.

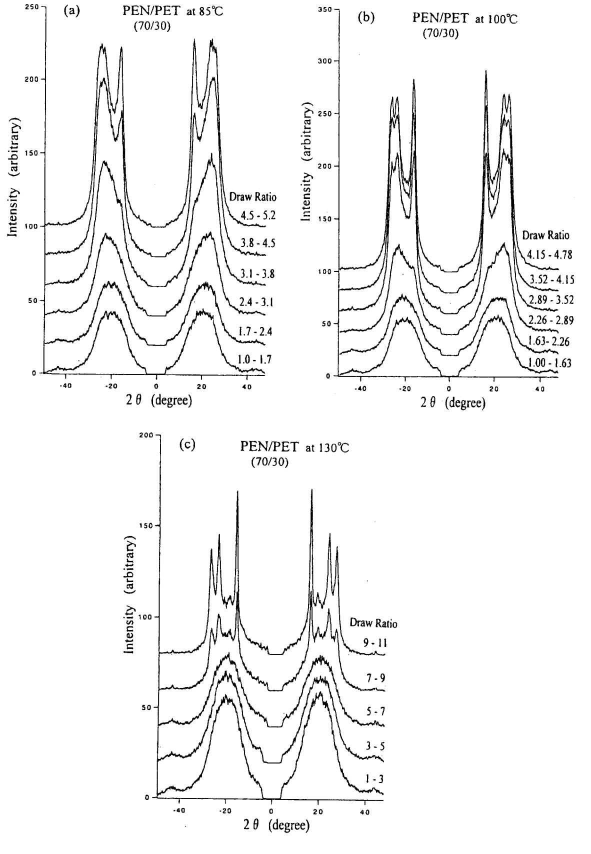

Fig. 4. Change of the intensity profiles on the equator of the WAXD patterns of Fig. 3 at (a) 85°C, (b) 100°C and (c) 130°C.

PEN/PET blend are, therefore, attributed to the paracrystalline structure of PEN and PET. This paracrystalline is a result of lattice distortion and/or the small crystallite size [32]. In this case, lattice distortion is caused by the shifting of molecular chains because the higher the layer lines, the broader the reflections. The eight streak lines on the off-equatorial layer of PEN came from the paracrystalline nature caused by the axial shift of polymer chains with respect to one another in the direction of the chain [33]. The two lines across the meridian of PET (the arrow mark in Fig. 3a) demonstrated the pair of $\bar{1}05$ and $\bar{1}\bar{1}5$ reflections [34]. The corresponding equatorial intensity profile at DR 3.8–4.5 exhibited a sharp peak of 010 plane and a broad peak at about $2\theta = 24°$ indicative of the presence of paracrystalline structure of PEN.

At 100°C, the WAXD pattern and the equatorial intensity profiles demonstrated the rapid transition from the oriented amorphous to paracrystalline structures of the blends at DR 2.26–2.89 to DR 2.89–3.52 as exhibited in Figs. 3b and 4b. At DR 2.89–3.52, the crystalline reflections showed the occurrence of six faint spots on the equator indicating a good orientation of the oriented amorphous structure. Drawing at DR 3.52–4.15 increased the sharpness of the six spots while the corresponding intensity profile exhibited strong crystalline reflections of 100 and $\bar{1}10$ in the triclinic structure of PEN. As seen in Fig. 2b and e, the drawing of pure PEN and PET at 100°C resulted in the formation of paracrystalline and amorphous unoriented structures, respectively. The formation of the triclinic structure in PEN/PET (70/30) blend is attributed to the ease of diffusion of PET in

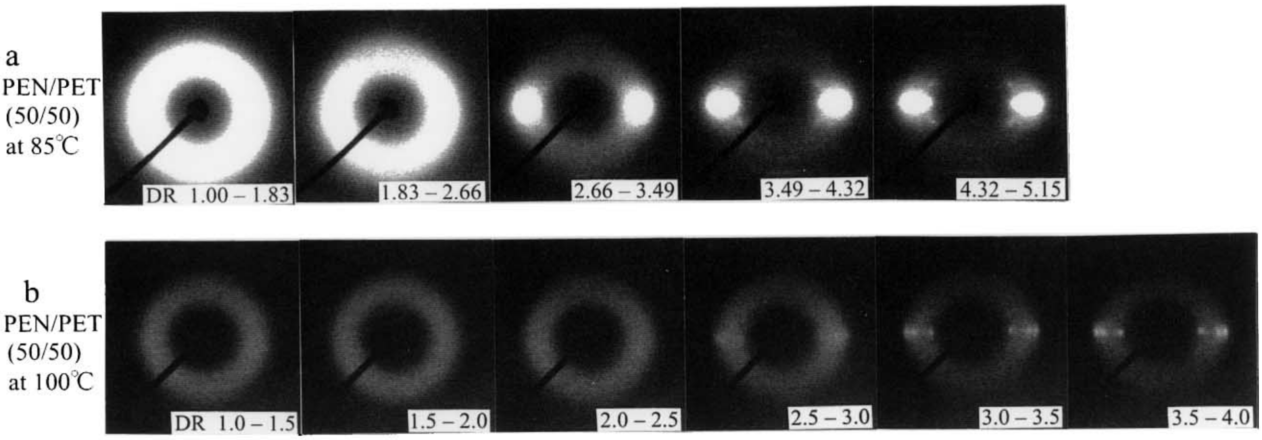

Fig. 5. Change of WAXD patterns of unoriented amorphous films of 50/50 PEN/PET blend during drawing at (a) 85°C and (b) 100°C at drawing rate of 4 mm/min.

the blend due to its low viscosity. This property resulted to the orientation and crystallization during drawing of the blend.

Drawing at 130°C of the PEN/PET (70/30) blend led to the formation of triclinic structure as expected because the drawing temperature was higher than the T_g points of both PEN and PET. At DR 5–7, a typical oriented amorphous halo of PET on the equator was observed and at DR 7–9, sharp crystalline reflections of PEN appeared on the equatorial intensity profile as shown in Figs. 3c and 4c. The small crystalline reflection of β-form of PEN was seen between 010 and 100 reflections at $2\theta = 18.7°$. At DR 9–11, the three crystalline reflections for the triclinic structure became very sharp. These indicate the increase in the size of crystallites and/or decrease of the defect in crystals. The presence of PET at 100°C had contributed to the development of better crystalline structure of rigid PEN even if the drawing is under T_g (117°C) of PEN.

3.2.2. Drawing of PEN/PET (50/50) blend

In Figs. 5a and 6a, the WAXD patterns and the equatorial intensity profiles of PEN/PET (50/50) blend uniaxially drawn at 85°C were presented. At DR 2.66–3.49, the WAXD pattern showed an oriented amorphous structure of the polymers. The crystal reflections started to appear at DR 3.49–4.32 on the intensity profiles while four $01\bar{1}$ reflections on the first layer lines, above and under the 010 reflection of the equator, were observed on the WAXD pattern. These are indicative of the presence of PET crystal in the paracrystalline phase of PEN. After DR 4.32–5.15, the sample was cut via necking which can be attributed to lower viscosity of PET and rigidity of PEN.

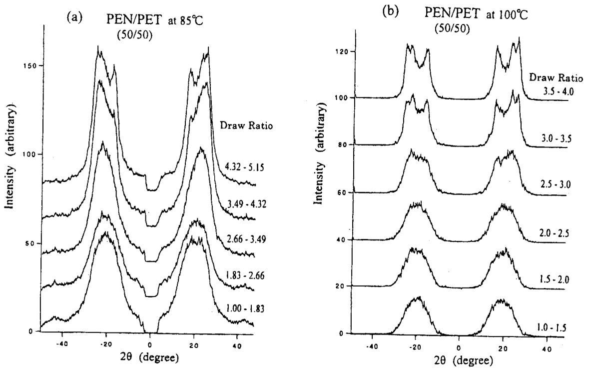

Fig. 6. Change of the intensity profiles on the equator of the WAXD patterns of Fig. 5 at (a) 85°C and (b) 100°C.

In Fig. 5b, the blend drawn at 100°C shows six spots of the crystalline reflections on the equator of the WAXD pattern at DR ratio larger than 2.5, which sharpened when DR increased. It could be observed that the equatorial intensity profile of DR 3.0–3.5 showed broad 010, $\bar{1}10$ and 010 reflections indicating the crystalline structure of both PEN and PET in Fig. 6b. The broadness of these reflections is due to the presence and/or overlapping of the PEN and PET peaks. The 100 and $\bar{1}10$ reflections of PEN drawn at 100°C were not split, but were split on blending with PET. These could be attributed to the T_g of PEN/PET blend, viz. about 93°C. After the orientation of the polymer chains, the crystallization proceeded at defined positions of the triclinic structure of PEN. As observed from WAXD patterns (Fig. 6b), the six spot-like crystal reflections of the PEN/PET (50/50) blend indicate the good orientation of PEN with gradual crystallization though the reflections in the drawing of pure PEN appeared suddenly by necking. This is interpreted as follows: The drawing of PEN/PET (50/50) blend exhibited the typical characteristic reflections of both PEN and PET, that is, the crystallization of PEN gradually occurred by PET and induced the appearance of strong reflections by PEN.

Further drawing of the blend at 130°C showed that the amorphous structure was not oriented due to the molecular fluidity during the drawing and stress relaxation. However, at DR greater than 7.4, the film became narrower and was cut due to the high PET content at high temperature and slow drawing speed (4 mm/min).

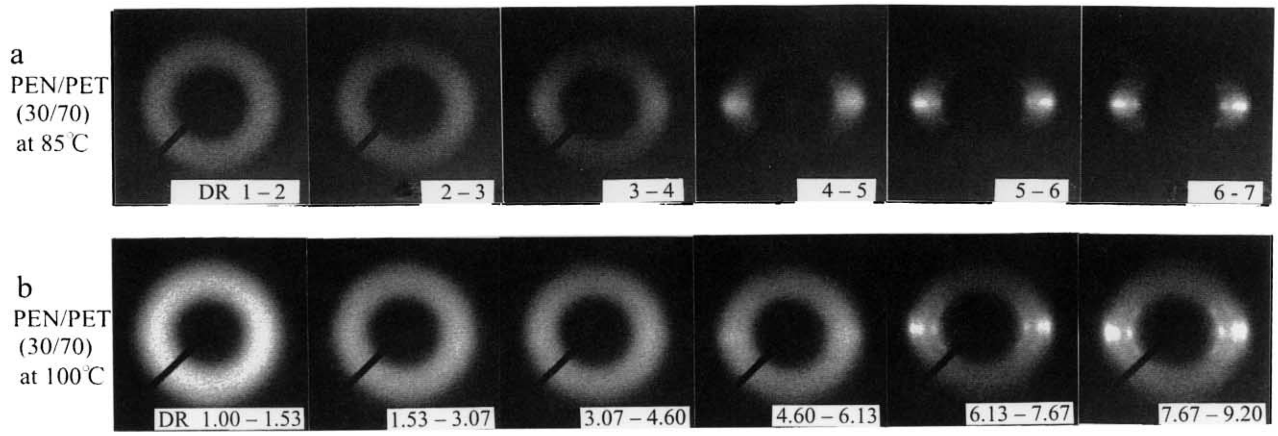

Fig. 7. Change of WAXD patterns of unoriented amorphous films of 30/70 PEN/PET blend during drawing at (a) 85°C and (b) 100°C at drawing rate of 4 mm/min.

3.2.3. Drawing of PEN/PET (30/70) blend

The WAXD patterns and the equatorial intensity profiles of PEN/PET (30/70) blend uniaxially drawn at 85°C are shown in Figs. 7a and 8a. At DR 2–3 and DR 3–4, a diffuse amorphous oriented halo could be observed on the WAXD pattern while their corresponding equatorial intensity profiles showed the symmetric scattering peaks indicating the amorphous oriented structure of the blend. These represent the typical characteristic of PET. Drawing at DR 4–5 showed the formation of the broad asymmetric peak, which was influenced by the amorphous intensity of PEN on the intensity profile on the equator and sharpened with the increase of DR. At DR 5–6 and DR 6–7, four faint spots on the first layer line, above and under the 010 reflection of the equator, were observed which could be attributed to the crystallization of PET to its triclinic. The corresponding equatorial intensity profiles, however, suggest only the paracrystalline reflection from the blend.

Drawing at 100°C showed the oriented amorphous structure at DR 1.53–6.13 as exhibited in Fig. 7b. At DR 6.13–7.67 and DR 7.67–9.20, four $0\bar{1}1$ spots on the first layer line were observed suggesting the direct crystallization from oriented amorphous structure to triclinic structure of PET. The equatorial intensity profile in Fig. 8b showed a steep peak on top of a broad reflection at (010) plane and sharp reflections at (100) and ($\bar{1}10$) planes confirming the presence of PEN on the crystalline reflections of PET.

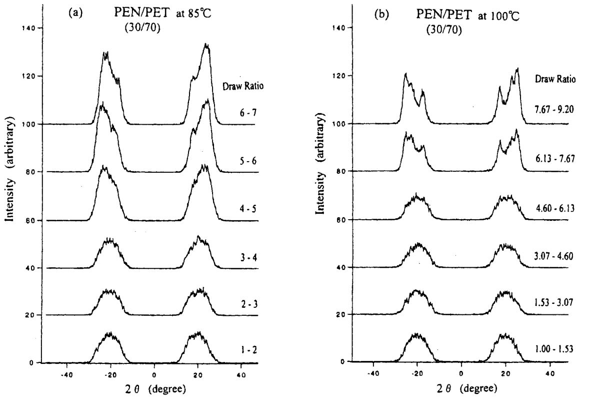

Fig. 8. Change of the intensity profiles on the equator of the WAXD patterns of Fig. 7 at (a) 85°C and (b) 100°C.

Further drawing at 130°C, however, the sample was cut off after 4 min which was earlier than the PEN/PET (50/50) because of the increased of PET content.

4. Conclusion

Transparent PEN/PET blend films were prepared by melt blending at 310°C for 2 min. The uniaxial drawing of the blend films exhibited the blending effects in terms of their mechanical properties and structural formation of oriented crystallization. For example, though the pure PET film becomes partially melted, thinner and then cut by drawing at 100°C, the film blended with only 10% PEN is possible to be drawn (see Fig. 1b). The stiffness of PEN film can be reduced by blending with PET which has a low Young's modulus value making it useful as packaging material. From the in situ X-ray measurements of the blend films, the drawing of pure PEN film at 100°C, which is under its T_g, indicates the formation of the paracrystalline structure (imperfect crystal); when blended with PET, well-defined crystal reflections of PEN were observed (see Figs. 4b, 6b and 8b). It should be noted that the sudden crystallization of PEN by necking is a problem in the polymer processing. It is expected that blending with PET can control the rate of crystallization. From these results, it is considered that the PEN/PET blend will be of much use for practical application such as packaging material.

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