



Morphological study by TEM on uniaxially oriented thin films of PET, PEN and their blends

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Abstract

Uniaxially oriented thin films of poly(ethylene terephthalate) (PET), poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) and their blends were prepared by applying shear strain to their respective melts, and the resulting morphologies were studied by transmission electron microscopy. Selected-area electron diffraction of each film revealed well-defined uniaxial orientation of polymer chains in the shearing direction. In the uniaxially oriented thin film of PEN, stacked-lamellar structure with the average long period of 27 nm consisting of a crystalline region about 15 nm thick and an amorphous one about 12 nm thick was found here and there in the dark-field image: PEN-type. On the other hand, stacked-lamellar structure was rarely observed in the case of PET: PET-type. In PET/PEN blends, the morphologies changed from the PET-type to the PEN-type with increasing content of PEN.

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1. Introduction

In most polymer processings such as extrusion, injection molding, fiber spinning, etc. molten polymers are exposed to the flow fields, and accordingly the flow-induced structural changes have been noted from scientific and industrial points of view. In actual polymer processings, however, very complex deformation histories are involved. Therefore, many studies have been carried out so far under nearly ideal conditions such as a unidirectional flow field and for polymers with simple primary structure such as polyethylene [1–7], isotactic polystyrene [8–10] and isotactic polypropylene [11–13] in order to clarify the effect of flow field on morphology or on molecular orientation in the final products manufactured from melts or solutions. As to the crystallization of these polymers subjected to unidirectional flow (or stress), it is well known that a characteristic morphology, viz. the so-called ‘shish-kebab’ or ‘row (-nucleated) structure’, is often formed

[1–15]. From an industrial standpoint, however, it is strongly desired to elucidate the effect of the flow field on promising polymers for practical use such as poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalene dicarboxylate) (PEN).

PET is the most commonly utilized polyester, and a wide variety of products such as fibers, films and bottles are manufactured. On the other hand, PEN is known to have better characteristics in mechanical properties, greater thermal stability and lower gas permeability than those of PET, because PEN has rigid naphthalene rings in its main chain instead of benzene rings in PET. However, PEN is utilized only for some limited purposes because of the high cost of its monomer material. In order to compromise its superior properties with economic policy, recently, the research on blends of PET and PEN (PET/PEN blends) has extensively been performed [16–21]. The major object of this paper is to know the effect of unidirectional flow field on the crystalline morphology of PET, PEN and their blends, and the study in this paper is performed on their uniaxially oriented thin films which can be directly examined by transmission electron microscopy (TEM).

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2. Experimental

2.1. Specimen preparation

PET and PEN chips used in this study were kindly supplied by Teijin Ltd. The respective 0.5 wt% solutions in 1,1,1,3,3,3-hexafluoro-2-propanol of PET, PEN and their blends (wt%/wt%: PET/PEN = 80/20, 50/50 and 20/80) were prepared. Each solution was dropped and spread on a glass slide and then covered with another glass slide (both glass slides were pre-heated at 280, 310 and 300 °C for PET, PEN and their blends, respectively, and these temperatures are examples of the spinning temperature for high-speed spinning of the respective polymers). That is to say, the solution was sandwiched between two glass slides on the hot plate thermostated at a desired temperature. Just after evaporation of the solvent, a thin molten polymer film was sheared/crystallized by displacing one of the two glass slides quickly by hand and then quenched to room temperature. The average relative displacing speed of the glass slides was measured to be 12 m/min by using a digital video camera. The shear rate will be, accordingly, estimated at about $4 \times 10^6 \text{ s}^{-1}$ if the film thickness is assumed to be 50 nm which value was judged empirically from the transmittance for 200 kV electrons [22].

Crystallized polymer thin films thus prepared on the glass slides were coated with vapor-deposited carbon under vacuum for reinforcement. In order to calibrate the diffraction camera length, gold (Au) was vapor-deposited onto some of the films before carbon coating. A drop (a hemisphere 3–4 mm in diameter) of aqueous solution (ca. 25%) of polyacrylic acid (PAA) [23] was placed on the appropriate portion of the specimen film on the glass slide and hardened by drying for one day at room temperature. Hardened PAA with the specimen film was detached from the glass slide, and then the PAA was dissolved in water. Finally, the floating specimen film was mounted on a copper grid for TEM and dried under ambient condition.

2.2. Transmission electron microscopy (TEM)

Morphological observation and selected-area electron diffraction (SAED) by TEM of resulting specimens were performed at room temperature with a JEOL JEM-200CS operated at an accelerating voltage of 200 kV. All the images and SAED patterns were recorded on photographic films (Mitsubishi MEM) which were then developed with Mitsubishi Gekkol (full strength) at 20 °C for 5 min.

3. Results and discussion

Fig. 1(a) is a bright-field image of the oriented thin film of PEN, and Fig. 1(b) is the corresponding SAED pattern which was obtained from the encircled area (ca. 8 μm in diameter) in Fig. 1(a). Fig. 1(c) is a bright-field defocus-

contrast image of a different portion of the oriented thin film of PEN: this image was taken at a rather large amount of defocus (under-focus) and is a so-called phase-contrast image [24]. It is seen in Fig. 1(a) that rather elongated large entities having a width of some micrometers were produced in the film by applying the shear strain and were well oriented along the shearing direction: it is emphasized here that the shearing direction is vertical in all the figures in this paper. The surfaces of these elongated large entities appear to be relatively smooth.

In PEN, at least two crystal modifications, viz. α - and β -modification, have been reported. The crystal structure of the α -modification was determined by Mencik [25] to be triclinic (space group = P_1 ; $a = 0.651 \text{ nm}$, $b = 0.575 \text{ nm}$, c (chain axis) = 1.32 nm , $\alpha = 81.33^\circ$, $\beta = 144^\circ$, $\gamma = 100^\circ$; theoretical crystal density (ρ_c) = 1.407 g/cm^3). The unit cell of β -modification was proposed at first by Buchner et al. [26] to be triclinic ($a = 0.926 \text{ nm}$, $b = 1.559 \text{ nm}$, c (chain axis) = 1.273 nm , $\alpha = 121.6^\circ$, $\beta = 95.57^\circ$, $\gamma = 122.52^\circ$; $\rho_c = 1.439 \text{ g/cm}^3$), then modified by Liu et al. [27] to be monoclinic ($P2_1/n$ 1 1; $a = 1.304 \text{ nm}$, $b = 0.926 \text{ nm}$, c (chain axis) = 1.300 nm , $\alpha = 131.47^\circ$, $\beta = \gamma = 90^\circ$; $\rho_c = 1.368 \text{ g/cm}^3$) and recently determined by van den Heuvel et al. [28] to be monoclinic ($P12_1/a1$; $a = 0.949 \text{ nm}$, $b = 1.331 \text{ nm}$, c (chain axis) = 1.261 nm , $\alpha = 90^\circ$, $\beta = 135^\circ$, $\gamma = 90^\circ$; $\rho_c = 1.425 \text{ g/cm}^3$). In this study, however, the result reported by Buchner et al., which was cited in the report by Miyata et al. [29] on high-speed spun PEN fibers produced from 'same' pellets, was used for indexing the reflections assigned to β -modification in our SAED patterns, because in our next paper the uniaxially oriented thin film of PEN will be morphologically compared with the high-speed spun PEN fibers.

The SAED pattern (Fig. 1(b)) shows a well-developed fiber pattern, which consists of the reflections assigned to both α - and β -modifications. In general, the β -modification can only be obtained under a special thermal condition, i.e. at relatively high crystallization temperatures [26,30]. In the case of high-speed spun PEN fiber, however, Hamana et al. reported in their patent that the structure of high-speed spun PEN fibers obtained at a spinning speed of 3–7 km/min primarily consisted of β -modification crystal [30], and Nagai et al. reported that the change of crystal modification from β to α occurred in the high-speed spun PEN fibers during annealing under stress [31]. In the case of high-speed spun PEN fiber, the equatorial intensity profile of wide-angle X-ray diffraction (WAXD) clearly showed coexistence of both α - and β -modifications [32–35]. Presence of the reflections assigned to both α - and β -modifications in Fig. 1(b), therefore, indicates that the uniaxially oriented thin film of PEN prepared for TEM by applying the shear strain can be regarded as an appropriate model specimen for high-speed spun PEN fiber.

While the surface of the uniaxially oriented thin film of PEN is relatively smooth in Fig. 1(a) which was recorded nearly in focus (namely, at the Gaussian focus), the stacked-

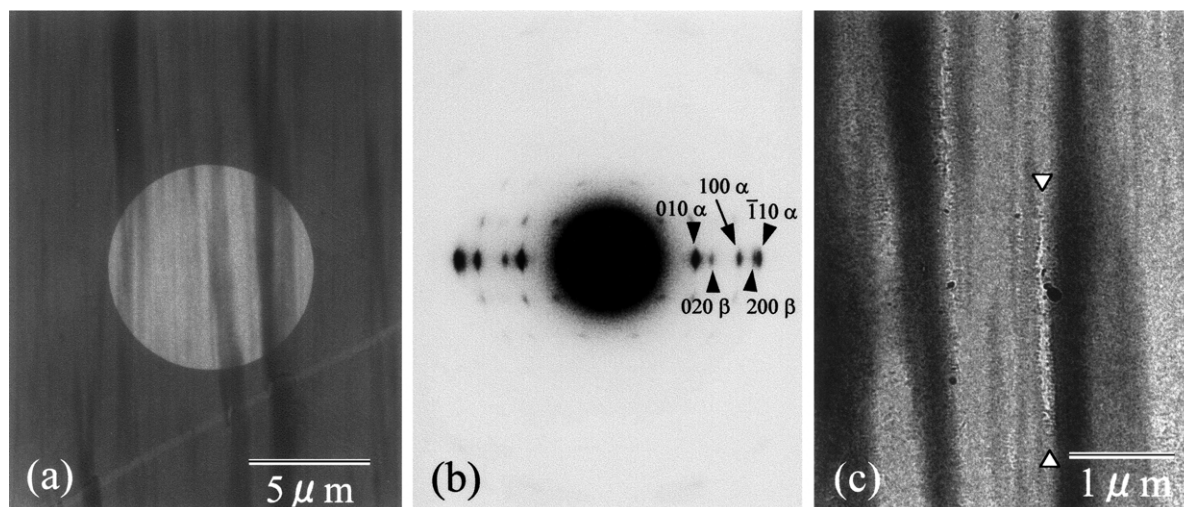


Fig. 1. Uniaxially oriented thin film of PEN. (a) Bright-field image recorded nearly in focus (namely, at the Gaussian focus). (b) SAED pattern obtained from the encircled area (ca. $8 \mu\text{m}$ in diameter) in (a). (c) Bright-field defocus-contrast image of a different portion from the specimen area shown in (a). In the photograph (c), the most remarkable region showing a stacked-lamellar-like texture is indicated with a set of arrow heads. The shearing direction is vertical in all photographs.

lamellar-like textures formed in the shearing direction are observed in Fig. 1(c) which is the bright-field defocus-contrast image of the same specimen film but of a portion different from the specimen area in Fig. 1(a). It should be noted here that reliability is not high for the dimension of each fine structural entity obtained in such a figure judging from the imaging mechanism for ‘defocus contrast’ [22]. In such stacked-lamellar-like textures recognized in Fig. 1(c), however, the magnitude of the long period is fairly reliable [22,36], and was estimated at about 30 nm.

Fig. 2 is a dark-field image of the uniaxially oriented thin film of PEN. Enlarged photographs A and B with reversed contrast, respectively, correspond to the rectangular areas marked with letters A and B in the original image. This image was taken by using simultaneously the $\bar{1}10_{\alpha}$ and 100_{α} (and probably using the 200_{β} together) because it was too difficult to select one of these two (or three) reflections even with a small objective aperture (in this study, its actual size is $20 \mu\text{m}$ in diameter): here, the subscripts, α and β , mean the α - and β -modifications of PEN, respectively. In the right half of Fig. 2 that is a typical dark-field image of this specimen film, fine bright spots (10–30 nm in size) are observed and are aligned along the shearing direction over about 500 nm (see Part B of Fig. 2). These bright spots are to be regions contributing to the $\bar{1}10_{\alpha}$, 100_{α} and 200_{β} reflections which were utilized for dark-field imaging. That is to say, each of the bright spots corresponds to a crystallite (or a cluster of some crystallites) having an orientation to give one of the $\bar{1}10_{\alpha}$, 100_{α} and 200_{β} reflections in the SAED pattern.

On the other hand, as demonstrated in the left half of Fig. 2 that was obtained less frequently and seems to correspond to a thicker portion in the specimen film than the portion of the right half in Fig. 2, fine bright striations oriented in the horizontal direction are observed in many places (see Part A

of Fig. 2). The average width and average length of the bright striations were, respectively, measured to be about 15 nm and 100 nm. The striations correspond each to a crystalline lamella (or a part of a longer crystalline lamella). Such striations appear to be stacked each other in a group in the shearing direction over about 500 nm or more, and to form a stacked-lamellar structure (or a shish-kebab-like structure) in the shearing direction. From the left half of Fig. 2, the structure is found to have the long period of about 27 nm which consists of a crystalline region about 15 nm thick and an amorphous one about 12 nm thick. The average value of long period was estimated at 27 nm from some similar micrographs. Because the length of a sequence of the bright spots aligned in the shearing direction in the right half of Fig. 2 and that of a sequence of bright striations stacked in the shearing direction in the left half of Fig. 2 are almost same, it is supposed that each of the bright spots (namely, of the small crystallites) was grown further in the direction perpendicular to the shearing direction into a bright striation (probably, an edge-on lamella) under certain conditions, for example under a condition given by the thickness of specimen film. Although a difference of 3 nm was found between the average long periods obtained from the defocus-contrast images (e.g. Fig. 1(c)) and the dark-field images (e.g. the left half of Fig. 2), the difference seems to be within the error limits, taking into account some scatter of the respective measured values of long period and also small numbers of measurements.

Fig. 3(a) is an SAED pattern obtained from the uniaxially oriented thin film of PET, and Fig. 3(b) is a dark-field image obtained by using simultaneously the $\bar{1}10$ and 100 reflections which appeared on the equator as in Fig. 3(a). In Fig. 3(a) (and also Fig. 4(a) and (b)), the concentric reflection rings are from vapor-deposited Au: the innermost intense ring is the 111 reflection of Au and the weak next

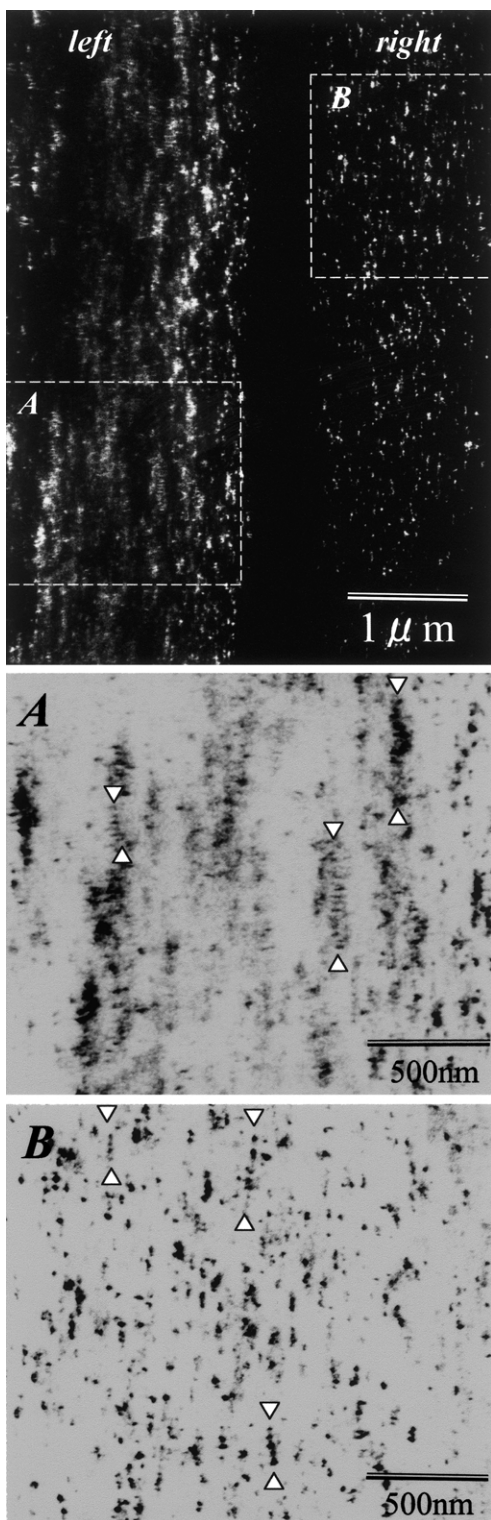


Fig. 2. Dark-field image of a uniaxially oriented thin film of PEN. This image was taken by using the $\bar{1}10_{\alpha}$, 100_{α} and 200_{β} reflections simultaneously. Photographs *A* and *B* were, respectively, enlarged with reversed contrast from the corresponding areas marked with letters *A* and *B* in the original image. In the Photographs *A* and *B*, some of the most remarkable regions showing a stacked-lamellar structure are indicated with a set of arrow heads. The shearing direction is vertical.

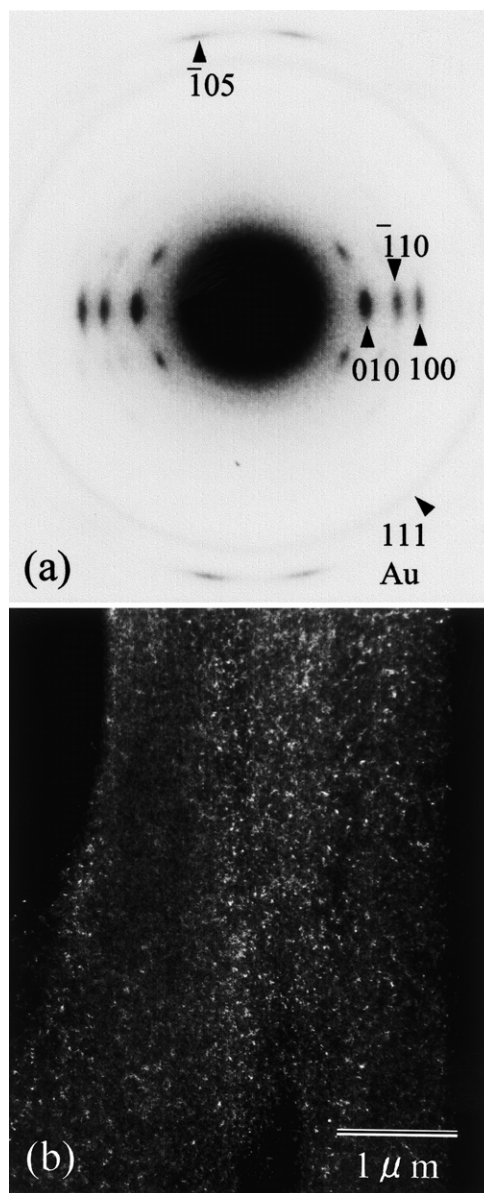


Fig. 3. Uniaxially oriented thin film of PET. (a) SAED pattern. (b) Dark-field image taken by using the $\bar{1}10$ and 100 reflections simultaneously. The shearing direction is vertical in both photographs. In (a), the reflection rings are from vapor-deposited Au: the innermost intense ring is the 111 reflection and the next weak ring which appears to superpose itself on the $\bar{1}05$ reflection of PET is 200 . In this figure and also in Fig. 4, indexing of the reflections of PET crystal was performed on the basis of the unit cell constants reported by Heuvel et al. [42]: $P\bar{1}$; $a = 0.449$ nm, $b = 0.588$ nm, c (chain axis) = 1.072 nm, $\alpha = 100^{\circ}$, $\beta = 118^{\circ}$, $\gamma = 111^{\circ}$; $\rho_c = 1.500$ g/cm³.

ring which appears to superpose itself on the $\bar{1}05$ reflection of PET is the 200 one of Au. The SAED pattern (Fig. 3(a)) shows a well-developed fiber pattern similar to the WAXD pattern of high-speed spun PET fiber reported by Ochi et al. [37]. This similarity indicates that the uniaxially oriented thin film of PET prepared by applying the shear strain is a relevant model specimen for high-speed spun PET fiber, as in the case of PEN. In the dark-field images, only the morphology similar to that in the right half of Fig. 2 was

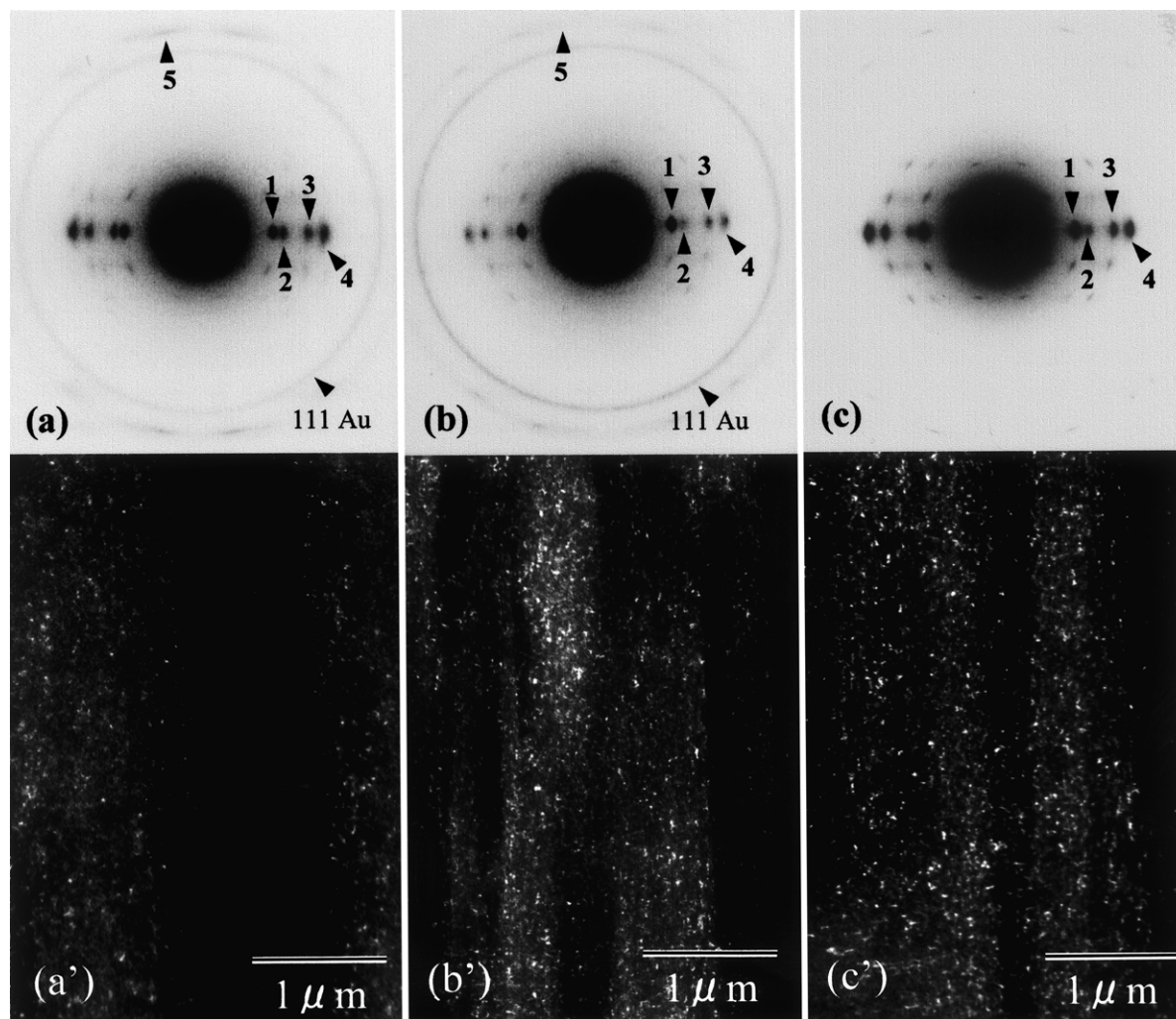


Fig. 4. SAED patterns ((a)–(c)) and dark-field images ((a')–(c')) of the uniaxially oriented thin film of; (a) and (a') PET/PEN = 80/20, (b) and (b') PET/PEN = 50/50, (c) and (c') PET/PEN = 20/80. These dark-field images were obtained by using both of the equatorial reflections marked with letters '3' and '4'. The shearing direction is vertical in all photographs. In (a) and (b), the reflection rings are from vapor-deposited Au. The specimen film utilized for obtaining the SAED pattern of (c) was not coated with Au in order to determine whether the reflection marked with '5' is observed or not.

observed, as shown in Fig. 3(b), in other words, only fine bright spots (10–20 nm in size) were observed. However, as demonstrated in Fig. 3(b), these spots appeared to be more scattered than ones in PEN shown in the right half of Fig. 2. In addition, in the case of PET, it should be emphasized that a striation corresponding to a crystalline lamella observed in the left half of Fig. 2 for PEN has never been recognized so far in our study. Thus it seems that PET is less likely to crystallize in a lamellar form than PEN.

Fig. 4(a')–(c') are dark-field images of the uniaxially oriented thin films of PET/PEN blend for the three different compositions (PET/PEN = 80/20, 50/50 and 20/80), and Fig. 4(a)–(c) are, respectively, the corresponding SAED patterns. It is well known that the transesterification reaction readily occurs when polyesters are blended near and above their melting points [16–21,38]. Stewart et al. [16] and Ihm et al. [18] 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

on the reaction. In our preliminary experiments, all the SAED patterns, which were obtained from the uniaxially oriented thin films of PET/PEN blends (PET/PEN = 80/20, 50/50 and 20/80) prepared by applying the shear strain after keeping them in their molten state for 5 min, showed no crystalline reflections, in other words, 5 min is long enough for the transesterification reaction to occur, and accordingly in the resulting uniaxially oriented thin films of PET/PEN blends any crystalline structure was not formed. In this study, therefore, to minimize the transesterification reaction between PET and PEN, the shearing strain was applied to a molten thin film as soon as its melting was recognized.

All of the dark-field images (Fig. 4(a')–(c')) for PET/PEN blend films were obtained by using both of the equatorial reflections marked with letters '3' and '4' in their corresponding SAED patterns (Fig. 4(a)–(c)), when the typical four reflections that appeared always on the equator were marked with '1' through '4' from inner to outer reflection. The reflection marked with '1' is assigned to the

(010)_α lattice plane of PEN (lattice spacing = 0.566 nm). However, the reflection assigned to the (010) plane of PET (0.500 nm) and the one assigned to the (020)_β plane of PEN (0.478 nm) are to appear both around the location marked with '2'. Similarly, the reflection assigned to (1̄10) of PET (0.388 nm) and the one assigned to (100)_α of PEN (0.381 nm) are to appear both around the '3', and the reflection assigned to (100) of PET (0.342 nm), (200)_β of PEN (0.332 nm) and the one assigned to (1̄10)_α of PEN (0.330 nm) are to appear around the '4'. Accordingly, two or more reflections may have been used to obtain these dark-field images (Fig. 4(a')–(c')). By comparing these three SAED patterns (Fig. 4(a)–(c)) with each other, it is found that the reflection marked with '5' in Fig. 4(a) and (b) is important because this reflection corresponds to the (1̄05) plane of PET and one of the most characteristic reflections of PET. This reflection in question is not recognized in Fig. 4(c) in spite of no reflection rings from Au. Intensity of the reflection, however, increases with increasing content of PET, and consequently it is found that both components can be crystallized individually into respective crystallites at least under our experimental condition. In addition, it seems that the crystallization of PET was suppressed by PEN, because the reflection '5' in Fig. 4(c) was not recognized in spite of a 20% content of PET as mentioned above. On the other hand, the reflection marked with '1', which is assigned only to PEN, is clearly recognized in Fig. 4(a) for a 20% content of PEN.

In the dark-field images, the pronounced striations corresponding each to a crystalline lamella are hardly observed as in the case of PET. That is to say, the entities that were observed in the dark-field images are almost only fine bright spots. When these resulting morphologies, however, were compared with each other more carefully, two important facts were found as follows. One is that the average spot size increases with increasing content of PEN. The other is that the number of the striations slightly increases with increasing content of PEN. In the SAED patterns, however, the reflection '1' assigned only to PEN appears clearly in Fig. 4(a) (PET/PEN = 80/20) as described above. Thus it is considered that PET hindered the development of crystalline lamella of PEN.

4. Concluding remarks

Uniaxially oriented thin films of PET, PEN and their blends were prepared by applying shear strain to their respective melts, and the resulting morphologies were studied by TEM. SAED of each film revealed well-defined uniaxial orientation of polymer chains in the shearing direction. As to PET and PEN, by comparing the SAED patterns obtained in this study with the WAXD patterns obtained from high-speed spun fiber, it was indicated that their thin films prepared by applying the shear strain can be each treated as a suitable model specimen for the actual

high-speed spun fiber, which specimen is able to be directly examined by TEM. In the uniaxially oriented thin film of PEN, stacked-lamellar structure with the average long period of 27 nm consisting of a crystalline region about 15 nm thick and an amorphous one about 12 nm thick was found from place to place in the dark-field image. On the other hand, stacked-lamellar structure was rarely observed in the case of PET. In PET/PEN blends, the morphologies changed from PET-type to PEN-type with increasing content of PEN.

In our previous reports [23,39,40], morphologies of PEN which had been isothermally crystallized after being melted at 300 °C were examined: the morphology of PEN thin films which had been crystallized at 190 °C under a static condition (namely, without shear strain) [39], that of PEN which had been epitaxially crystallized at 190 °C on the friction-transfer thin layer of polytetrafluoroethylene [23], and those of PEN thin films which had been crystallized at temperatures ranging from 190 to 240 °C [40]. In particular, the (010)_α lattice images, in which the lattice fringes of 0.57 nm spacing were clearly recognized, were successfully obtained by high-resolution TEM [22,41] of the PEN thin film melt-crystallized isothermally at 190 °C [40]. Therefore it is quite promising to clarify, at a molecular level resolution, fine structures in uniaxially oriented thin films of PET, PEN and their blends which were prepared in this study.

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