

Internal fine structures in the high-speed-spun fibers of poly(ethylene 2,6-naphthalene dicarboxylate)

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Abstract

Morphological study on the poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) fibers, which were prepared at spinning speeds ranging from 2 to 10 km/min, was performed by combining the surface etching techniques with the surface observation methods. From the results by scanning electron microscopy (SEM) of the etched fiber surfaces, it was clarified that well-developed fibrillar structure which runs continuously along the fiber axis exists in the high-speed-spun (HSS) PEN fibers spun at a spinning speed beyond 4 km/min. Fine network structure was observed on the lateral surface of each fibril by SEM. From the results by atomic force microscopy (AFM), it is proposed that several crystalline lamellae are closely stacked in each of the constituents which form the fine network structure.

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1. Introduction

The chemical structure of poly(ethylene 2,6-naphthalene dicarboxylate) (PEN) can be expressed by replacing the benzene ring in poly(ethylene terephthalate) (PET) with the naphthalene ring which is stiffer than the benzene ring. Two crystal modifications, i.e. α - and β -forms, have been reported, and the unit cell parameters for α - and β -forms were, respectively, determined by Mencik [1] and Buchner et al. [2]. PEN has better characteristics such as high strength, high modulus, good heat-resistance and so on than PET. These excellent characteristics of PEN have received much attention in the various fields, especially in the field of high-performance fibers. Actually, many researches on PEN fibers have already been accomplished, but PEN fibers are commercialized only for some limited purposes because of the high cost of its monomer material. In particular, the researches on the PEN fibers produced by a high-speed

spinning technique which can control the fiber structure, crystallinity, molecular orientation, etc., have been extensively performed so far. Nagai et al. [3] and Miyata et al. [4] reported the effect of spinning speeds up to 5 and 9 km/min, respectively, on structural and mechanical properties of the PEN fibers. Wu et al. [5] reported the effect of spinning speeds up to 10 km/min on structural and mechanical properties of the PEN fibers which were produced from the higher molecular weight PEN than those used by Nagai et al. [3] and Miyata et al. [4]. Iizuka et al. [6] reported necklike deformation behavior during the high-speed spinning of PEN at spinning speeds lower than 5 km/min using on-line profile measurement. One has expected and tried to obtain PET/PEN blend fibers with a better cost-to-performance ratio. The relations between the spinning speed (or the PET/PEN blend ratio) and structural (or mechanical) properties were reported by Miyata et al. [7] for high-speed-spun (HSS) PET/PEN blend fibers spun at spinning speeds up to 9 km/min, and by Wu et al. [8] for such blend fibers up to 10 km/min. Wu et al. also examined the behavior of the transesterification reaction between PET and PEN.

Alkaline hydrolysis for polyester fabrics has been done

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so far in order to impart the hydrophilicity to them or to improve the comfort of them, and therefore many studies on the alkaline hydrolysis of polyester fiber, especially of PET fiber, have been reported from both industrial [9,10] and academic [11–15] standpoints. The alkaline hydrolysis is utilized also as a means of preparing specimens for investigation of the polyester fiber structure. Ochi et al. [14] investigated the radial anisotropy, i.e., whether or not a skin-core structure exists, in the HSS–PET fibers using alkaline etching. We already utilized the alkaline etching as a specimen-preparation technique for transmission electron microscopy (TEM) to investigate the surface morphology of the PET fibers [15]. On the other hand, to investigate the morphology of crystalline polymers such as polyethylene and polypropylene, the permanganic etching is often used as a specimen-preparation technique [16–20], and we have already confirmed that amorphous regions are more preferentially removed than crystalline entities in the case of the permanganic etching for PET fiber [21]. From the facts mentioned above, these two etching techniques can be expected as an analysis technique for investigating the morphology of PEN fiber at resolutions ranging from the crystallite level to macroscopic one. In the previous paper [22], we reported the scanning electron microscopy (SEM) image of the alkaline-etched surface of the HSS–PEN fiber spun at 6 km/min and the image showed number of grooves (which are to develop finally into slits) running along the fiber axis in the etched surface. This result, thus, indicated the existence of the fibrillar structure in the PEN fibers.

In this report, we investigate, by SEM and atomic force microscopy (AFM), finer structures of each fibril in the alkaline-etched PEN fibers. In addition to the alkaline etching, we also apply the permanganic etching technique to the PEN fibers for morphological investigation of them.

2. Experimental

2.1. Materials

PEN pellets were supplied by Teijin Co., Ltd. (Matsuyama, Japan). The intrinsic viscosity of the polymer is 0.62 dl/g. Prior to spinning, the polymer was held/dried at 130 °C for 8 h under vacuum, and then the temperature was raised to 210 °C and kept for 2 h for crystallization of the polymer. The crystallized polymer was reserved at 160 °C under vacuum before use.

Spinning temperature was controlled to be 310 °C. Molten polymer was extruded through a spinneret of 1.0 mm diameter at a mass flow rate of 4.0 g/min/hole, and was spun at various speeds from 2 to 10 km/min by using a take-up device located at 330 cm below the spinneret.

2.2. Alkaline etching

Alkaline etching was carried out in the aqueous solution of 2.0 M NaOH and 0.1 wt% cetyltrimethylammonium bromide (CTAB) at 50 °C with mild mechanical agitation. CTAB works as an accelerator for the hydrolysis reaction. In a preliminary test, it was confirmed that CTAB has no effect on the morphology of etched surface. The ratio of the volume (or mass) of etching solution (namely, of etchant) to the mass of filament was carefully chosen to be sufficiently large because the concentration of the etching solution should be practically constant during an etching treatment. After the treatment, samples were rinsed thoroughly in distilled water and then air-dried.

2.3. Permanganic etching

The technique utilized here for permanganic etching with potassium permanganate (KMnO_4) is the same as that developed by Bassett et al. [16–19] and Hudson et al. [23]. The etching solution was a freshly prepared 0.5 wt% KMnO_4 solution in a 2:2:1 mixture of distilled water, concentrated phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4). A filament of each kind of fiber was treated in the solution at 30 °C with mild mechanical agitation. This condition was determined by trial and error to be just appropriate for our purpose. The amount of etching solution was large enough to regard its concentration as constant during processing. After the etching treatment, samples were rinsed thoroughly in distilled water and then air-dried.

2.4. Optical microscopy

The fiber diameter was measured with an optical microscope BX60 (Olympus Optical Co., Ltd.). To obtain a reliable value of fiber diameter, the measured diameters from 10 or more filaments for each of PET and PEN fibers were averaged.

2.5. Observations of surface morphology

To obtain information on the surface morphology of fibers, SEM observation was performed on a S-3000N (Hitachi, Japan) for samples coated with vapor-deposited gold (Au), and AFM observation was performed on a SPM-9500J2 (Shimadzu, Japan) directly for un-coated samples. The AFM observation was carried out in the dynamic mode for the etched fibers which had been fixed on the sample holder by using double adhesive tape.

3. Results and discussion

Huijts et al. [24] reported that the intrinsic birefringence of PET and that of PEN, both of which were obtained from the linear relationship between birefringence and molecular

orientation measured by polarized Raman spectroscopy, were, respectively, 0.244 and 0.487. Iizuka et al. [6], however, proposed that the values of intrinsic birefringence for PET and PEN, both of which were estimated by the semi-empirical molecular orbital calculation (MOPAC), were, respectively, 0.311 and 0.604. Although there is some difference between the corresponding values which depend on the methods, it turns out that the intrinsic birefringence of PEN is about twice as high as that of PET. In addition, some different values of intrinsic birefringence were reported for PEN, and these values can be known from the table summarized by Miyata in his doctoral dissertation [25]. On the other hand, from the report by Miyata et al. [4] it turns out that the values of birefringence for HSS–PEN fibers spun at spinning speeds beyond 5 km/min are greater than 0.3 which is approximately 3 times as large as the highest measured value of birefringence for HSS–PET fibers. These facts indicate that the PEN fiber has fairly higher molecular orientation than PET fiber.

Fig. 1 is an optical micrograph of the ultra-HSS–PEN fiber (spun at 10 km/min) that was split by pulling. This micrograph demonstrates that the HSS–PEN fibers have a well-developed fibrillar structure. However, by SEM observation of the surface of the PEN fibers spun at various speeds (2–10 km/min) we were not able to obtain any information about the fibrillar structure. Fig. 2 is an SEM photograph of the PEN fiber spun at 6 km/min, showing a typical surface morphology of the PEN fibers spun at spinning speeds ranging from 2 to 10 km/min. Fig. 2 shows only the smooth surface of fiber spun at 6 km/min.

To obtain information relating to the fibrillar structure, we attempted surface etching of the PEN fibers by using the alkaline etching technique. Fig. 3 shows the relationships between the fiber diameter, measured with the optical microscope, and the treatment time of alkaline etching for the HSS–PET and HSS–PEN fibers, both of which were spun at 6 km/min. For the PET fiber, we observed the rectilinear relationship of the diameter with the treatment time. In the case of the PEN fiber, however, the reduction of

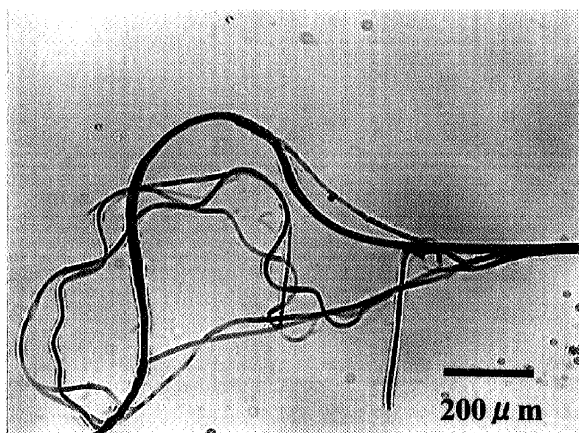


Fig. 1. Optical micrograph of the ultra-HSS–PEN fiber (spun at 10 km/min) which was split by pulling.

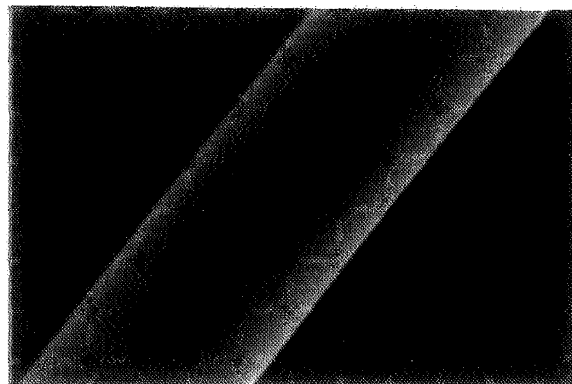


Fig. 2. SEM photograph of the high-HSS–PEN fiber spun at 6 km/min.

diameter with increasing treatment time was very small up to a treatment time of about 12 h, and then each filament of the fiber suddenly began to separate into fibrils (see Fig. 4). In Fig. 4, we can estimate the average diameter of these separated fibrils can be estimated at about 4 μm, although the average diameter of original (control) fibers is about 25 μm. In Fig. 4, however, non-separated fibers are also observed here and there.

Fig. 5 is an SEM photograph showing the surface morphology of the PEN fiber spun at 6 km/min, which fiber was alkaline-etched for 12 h but not separated yet into fibrils. This figure clearly demonstrates the well-developed fibrillar structure in the PEN fiber spun at 6 km/min. The average diameter of these fibrils is approximately consistent with the value estimated in Fig. 4 (viz., about 4 μm). Furthermore, each fibril was found to be continuously long in the direction of fiber axis, and therefore it is deduced that such fibrils were grown continuously along the fiber axis in the filament during spinning. The SEM photograph shown in Fig. 6 was taken at a much higher magnification for the PEN fiber spun at 6 km/min which had been treated for 12 h but not been separated yet into fibrils. Fine network structure is observed on each fibril in Fig. 6. The size of fine network is approximately 150 nm in the direction of

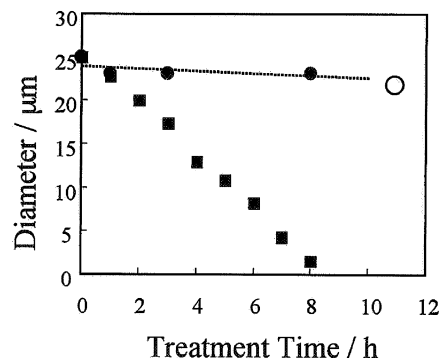


Fig. 3. Relationships between the fiber diameter and the treatment time in alkaline etching of PEN (●) and PET (■) fibers spun at 6 km/min. The symbol, ○, shows the position at which the filament of the PEN fiber began to separate into fibrils.

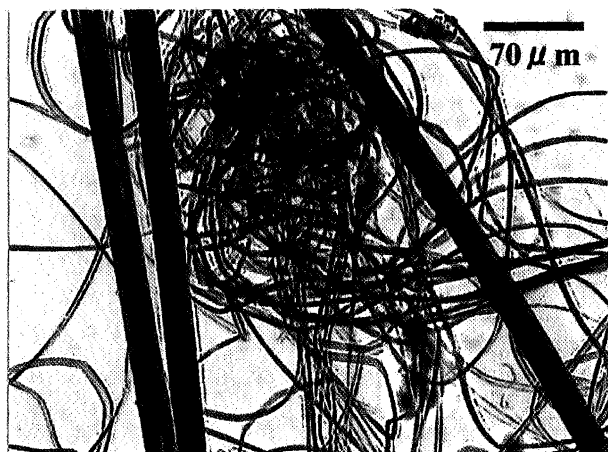


Fig. 4. Optical micrograph of an alkaline-etched PEN fiber (spun at 6 km/min). The treatment time of etching was 12 h.

fiber axis and 600 nm in the direction perpendicular to fiber axis.

To investigate more detailed surface morphology of the PEN fiber spun at 6 km/min, a dynamic mode (or tapping mode) of AFM was applied to each fibril observed in the alkaline-etched PEN fiber. The AFM image (Fig. 7(a)) clearly shows the fibrillar structure, as observed by SEM observation. Fig. 7(b) is the inclination-corrected image (namely, the image corrected to the inherent inclination of sample surface) obtained from a highly magnified image of the encircled area in Fig. 7(a). In Fig. 7(b), seemingly stacked-lamellar structure is observed and the structural size of a constituent (namely, a ‘lamella-like entity’) in the structure is 50–200 nm in the direction of fiber axis and approximately 600 nm in the direction perpendicular to fiber axis. These dimensions correspond well to ones obtained by SEM observation (see Fig. 6), notably in the direction perpendicular to the fiber axis. Since the value of 50–200 nm, however, is too large to be the so-called lamellar thickness, it is reasonably speculated that several crystalline lamellae are closely stacked in each of the constituents

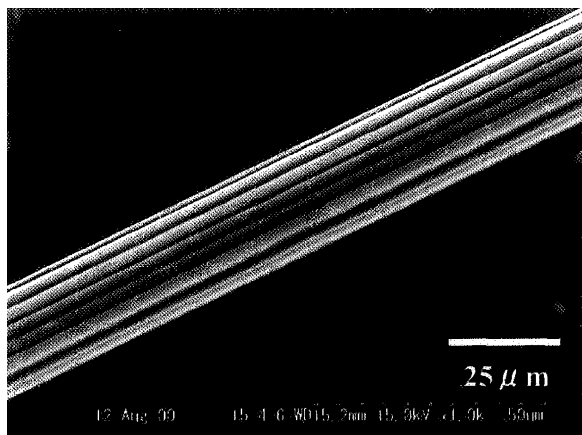


Fig. 5. SEM photograph of an alkaline-etched PEN fiber (spun at 6 km/min). The treatment time of etching was 12 h.

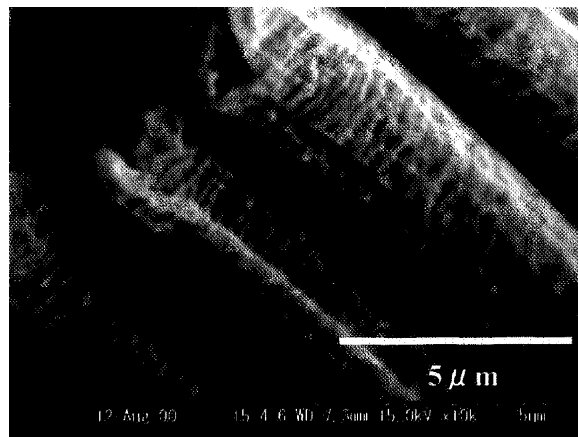


Fig. 6. SEM photograph of an alkaline-etched PEN fiber (spun at 6 km/min). The treatment time of etching was 12 h. This photograph was taken at a much higher magnification than that of Fig. 5.

which were visualized in Figs. 6 and 7(b). In order to confirm this speculation, therefore, we have tried to perform a small-angle X-ray scattering (SAXS) experiment. Actually, the value of the long period was estimated at 17.1 nm by SAXS for the HSS–PEN fiber spun at 6 km/min which was preheat-treated at 200 °C for 1 h with their ends fixed. It is thus concluded that each of the constituents visualized in Figs. 6 and 7(b) consists of a group of crystalline lamellae, the number of which are from 3 to 10 or more. On the other hand, we have reported before the morphological study by TEM of the uniaxially oriented thin film of PEN, and have successfully demonstrated that stacked-lamellar structure with 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 was formed in the film [26].

Fig. 8(a) is the wide-angle X-ray diffraction (WAXD) pattern (reversed contrast) obtained from actual HSS–PEN fibers spun at 10 km/min, showing a so-called fiber pattern, and shows the typical WAXD pattern for HSS–PEN fibers. Fig. 8(b) shows an electron diffraction (ED) pattern (reversed contrast) obtained by TEM from a selected area (ca. 8 μm in diameter) of the uniaxially oriented thin film [26]. The fiber axis is vertical in both Fig. 8(a) and (b). It is known that, in the HSS–PEN fibers, the α - and β -form crystals coexist, as indicated in Fig. 8(a), and the content ratio of α -form to β -form decreased with an increase in spinning speed [4]. Fig. 8(b) (the ED pattern) also shows a well-developed fiber pattern consisting of the reflections assigned to both α - and β -form crystals as in the case of the WAXD pattern obtained from HSS–PEN fibers. However, the relative intensity of the reflections from the α -form, as compared with those from the β -form, was much greater in the ED pattern (Fig. 8(b)) than that in the WAXD pattern (Fig. 8(a)) which was obtained from the ‘ultra’-HSS–PEN fiber spun at 10 km/min. The reason for thus difference of intensity relation between Fig. 8(a) and (b) may be ascribed to all of the following items or some of them: (1) the inevitable difference in the structure-formation mechanism

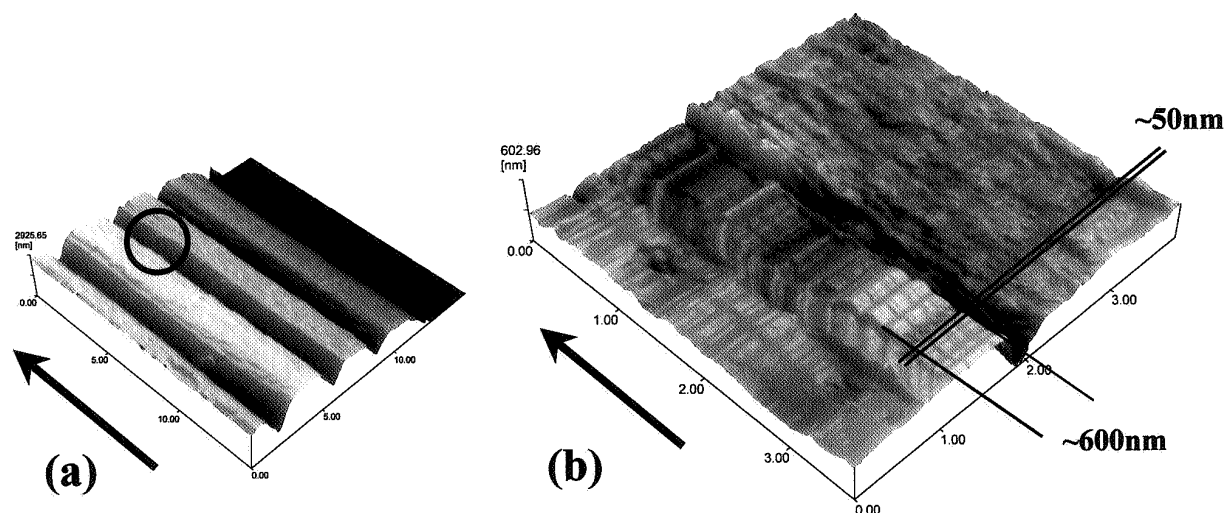


Fig. 7. AFM images of an alkaline-etched PEN fiber (spun at 6 km/min) in different scanning ranges: (a) $15\ \mu\text{m} \times 15\ \mu\text{m}$, (b) $4\ \mu\text{m} \times 4\ \mu\text{m}$. The treatment time of etching was 12 h. (b) is the inclination-corrected image obtained from a highly magnified image of the encircled area in (a). Arrows indicate the fiber axis in (a) and (b).

between the structure of HSS-fibers which was formed mainly by the elongational strain and that of uniaxially oriented thin film which was formed mainly by the shear strain, (2) the difference between the crystallization temperatures owing to the difference of experimental condition, (3) another complex difference. However, we consider the uniaxially oriented thin film to be an appropriate model specimen for HSS–PEN fiber at the present time because of the essential similarity that the α - and β -form crystals coexist in the film and also in the fiber.

In a similar manner as above, the alkaline surface-etching was also applied to other samples spun at 2–10 km/min. All the samples spun at spinning speeds beyond 4 km/min showed the sharp grooves (or slits), as observed in the fiber spun at 6 km/min. In the case of the fiber spun at 3 km/min, however, well-defined fibrillar structure was not recognized, and in the case of the fiber spun at 2 km/min, approximately smooth surface was observed. At the present time we cannot fully clarify the spinning speed dependence of the size of fibers in the direction perpendicular to the fiber axis (*viz.*, of the fibril diameter). It seems, however, that the thinner the initial diameter of fiber with increasing spinning speed, the finer the fibrils observed in the etched fiber. Accordingly the number of fibrils in each fiber seems to be approximately constant independently of the spinning speed.

In the alkaline surface-etching of PEN fiber, it seems to be reasonable to interpret that the portion having lower density is removed more preferentially. Here, the report by Miyata et al. [4] should be referred to, because they studied fiber-structure formation in the HSS–PEN fibers which had been prepared from same pellets as ones used in this study and also under the same spinning condition as that utilized here. Therefore, their results can be used to interpret our

results. Miyata et al. found the two breaking points in the plot which showed the relationship between birefringence and density of the fibers. One of the breaking points is at a birefringence of about 0.08: This value corresponded to the fiber spun at a spinning speed of 2.5 km/min at which the density of the fibers started to increase. The other (namely, the second breaking point) is at a birefringence of about 0.25 corresponding to 4.5 km/min at which the density started to increase more steeply. In the differential scanning calorimetry (DSC) analysis, Miyata et al. observed the glass transition at about $120\ ^\circ\text{C}$ for the PEN fibers spun at 1–3 km/min, but the glass transition became obscured for the PEN fibers spun at spinning speeds greater than 4 km/min. For the fibers spun at spinning speeds smaller than 3 km/min, an exothermic peak of cold crystallization, which shifted to lower temperatures and became smaller with increasing spinning speed, was observed at about 150 – $200\ ^\circ\text{C}$, but the exothermic peak disappeared for the fibers spun at speeds greater than 4 km/min. On the other hand, an endothermic peak of melting gradually shifted to higher temperatures for the fibers spun at speeds greater than 4 km/min (up to $293\ ^\circ\text{C}$ for the fibers spun at 9 km/min), although the endothermic peak appeared at a constant temperature of about $272\ ^\circ\text{C}$ for the fibers spun at speeds lower than 3 km/min. Miyata et al. clarified by WAXD and DSC, that the orientation-induced crystallization started to occur in the high-speed spinning process of PEN at a spinning speed of 4–5 km/min which corresponded to the second breaking point in the plot showing the relationship between birefringence and density of the resulting fibers.

The spinning speed of 4 km/min, beyond which the sharp grooves (or slits) appeared by the alkaline etching, corresponds to the lower limit of spinning speed for orientation-induced crystallization that was shown by

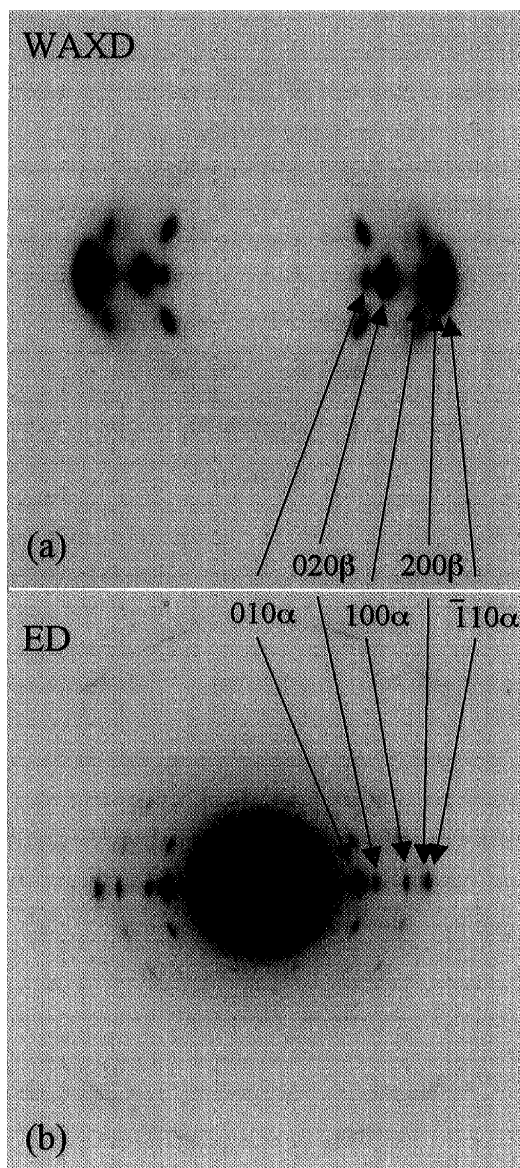


Fig. 8. (a) WAXD pattern (reversed contrast) obtained from the HSS-PEN fiber spun at 10 km/min. (b) Selected-area ED pattern (reversed contrast) obtained from the uniaxially oriented thin film of PEN [26]. In both patterns, the fiber axis is in the vertical direction.

Miyata et al. in the high-speed spinning process [4]. Actually, in our previous paper [22], we have confirmed that in the WAXD intensity profiles for PEN fibers spun at various speeds (2–10 km/min), two reflection peaks assigned to the β -form start to drastically increase in intensity at 4 km/min. Fig. 9 is an SEM photograph showing the surface morphology of the HSS-PEN fiber spun at 6 km/min, which fiber was treated by permanganic etching for 200 min. In Fig. 9, the morphology is almost same as that of the alkaline-etched surface (Fig. 5) which has grooves. These facts suggest that the preferential removal of amorphous regions took place, in both alkaline and permanganic etching for PEN fibers, as in the permanganic etching for PET fibers [21].

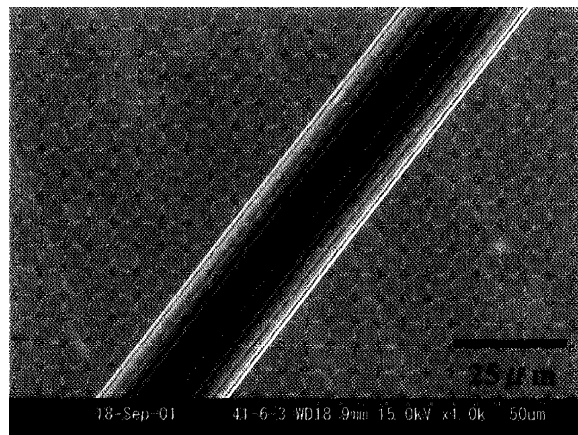


Fig. 9. SEM photograph of a PEN fiber (spun at 6 km/min) which was treated by permanganic etching for 200 min.

4. Conclusion

The morphological study on the PEN fibers, which were prepared at the spinning speeds ranging from 2 to 10 km/min, was performed by combining the surface etching techniques with the surface observation methods. It was clarified that well-developed fibrillar structure exists in the HSS-PEN fibers spun at spinning speeds beyond 4 km/min. Fine network structure was undoubtedly observed on the lateral surface of each fibril which appeared by etching of the PEN fiber spun at 6 km/min. From the results by AFM it is postulated that several crystalline lamellae are closely stacked in each of the constituents which form the fine network structure.

Acknowledgements

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