Porous Structure of Biaxially Drawn Polytetrafluoroethylene Film

It has been reported that drawing[1] and rolling[2] of unsintered polytetrafluoroethylene (PTFE) (coagulated dispersion PTFE), results in a porous fibrillar network structure. The microstructure, orientation, and mechanical properties of uniaxially drawn films of sintered PTFE have been investigated.[3,4] However, there is no report on the formation of a porous structure by drawing of sintered PTFE films.

In this study, sintered PTFE films were drawn biaxially, and the structure of surface and cross-section of the drawn films was observed by a scanning electron microscope (SEM).

EXPERIMENTAL

The polymer used in this study was granular PTFE (Polyflon M-12) with a particle size of about 25 μm. The PTFE films were prepared by preforming the PTFE powder (granular PTFE) into a cylindrical shape (520 mm in outside diameter, 200 mm in inside diameter, and 620 mm in length) by compressing in a die at room temperature at 20 MPa. The preformed PTFE was sintered in a circulating-air oven kept at 370°C for about 20 hours, and then cooled slowly to room temperature. The PTFE films were obtained by skiving the sintered PTFE to 200 μm thickness.

In order to remove the residual stress in the skived films and to obtain two kinds of samples with different thermal histories, the skived films were heat-treated in the melt at 350°C for 2 hours, and then cooled rapidly or slowly. The crystallinities of the rapidly cooled and slowly cooled PTFE films were 55 and 65%, respectively, and were estimated from density measurement.

These PTFE films were cut to square samples (210 × 210 mm) to fit into a biaxial drawing machine (Iwamoto Seisakusho Co., Ltd.) which was used for the simultaneous biaxial drawing of the PTFE films. The films were drawn biaxially by about twice the original width at a drawing rate of 5 mm/s at 250°C.

Observation of the free surface and the cross-section of the PTFE films was carried out using a SEM (Akashi Seisakusho Co., Ltd.).

RESULTS AND DISCUSSION

The scanning electron micrographs (a) and (b) in Fig. 1 show the morphologies of the free surface of the PTFE films which were heat-treated in the melt at 350°C for 2 hours and then cooled rapidly and slowly, respectively. It is noticed that granules with a diameter of about 3 μm grow over the surface which is smooth before the heat treatment. Both the number and the diameter of the granules increase with increasing time of the heat treatment. The origin of the granules has not been sufficiently investigated yet. For the higher crystallinity PTFE sample in Figure 1(b), randomly oriented bands with a diameter of about 0.3 μm are observed. This morphology is similar to the sheaf-like band structure of the coagulated dispersion PTFE (Polyflon F-103) reported by Yamaguchi.[5]

The micrographs (a) and (b) in Figure 2 show the morphologies of the free surface of the films which were obtained by the biaxial drawing of the heat-treated PTFE films of Figures 1(a) and 1(b), respectively. Both of them show a porous structure. These structures are similar to the fibril structure of high-molecular weight polyethylene reported by Sakami et al.[6] For the lower crystallinity sample obtained by rapidly cooling from the melt (as seen in Fig. 2(b)), net-like fibrils are formed by the simultaneous biaxial drawing. In the study of the uniaxially drawn PTFE by Davidson,[3] it was found that the noncrystalline regions showed substantially lower orientation than the crystals at all strains and no indication of reaching a limit in orientation at these strains. Considering his results, it is considered that the fibrillation in the biaxial draw ratio in this study is incomplete and the PTFE samples contain more noncrystalline regions. On the other hand, the micrograph seen in Figure 2(b) shows ivy-like fibrils

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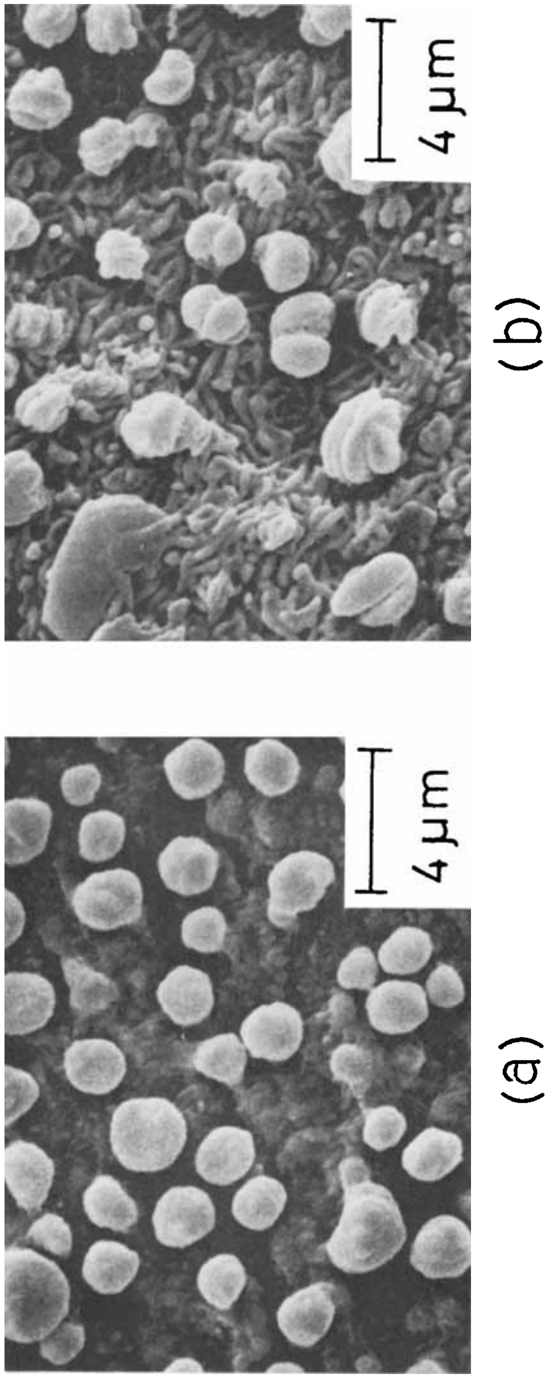

Fig. 1. Scanning electron micrographs of free surface of heat-treated PTFE films; (a) cooled rapidly and (b) cooled slowly, after heat treatment at 350°C for 2 hr.

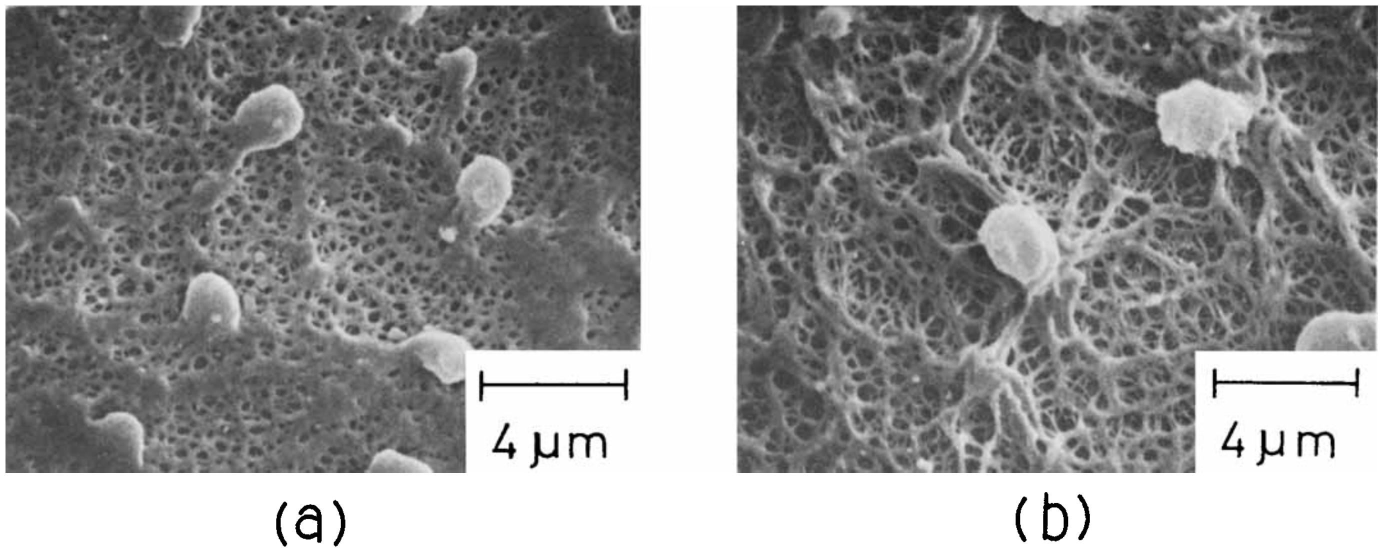

Fig. 2. Scanning electron micrographs of free surface of biaxially drawn PTFE films; (a) biaxial drawing of the film of Fig. 1(a), (b) biaxial drawing of the film of Fig. 1(b).

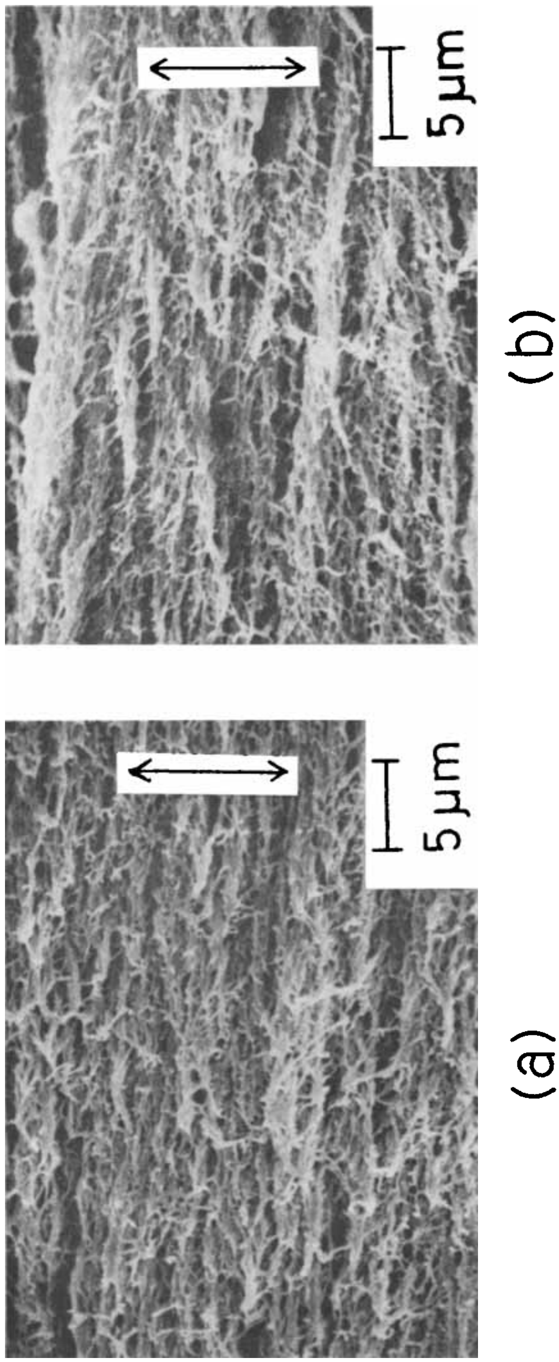

Fig. 3. Scanning electron micrographs of cross-section of biaxially drawn PTFE films; (a) cross-section of the film of Fig. 2(a), (b) cross-section of the film of Fig. 2(b). The arrow represents the vertical direction to the draw direction.

which are stretched sufficiently because of high crystallinity of this sample. However, the granules are only slightly broken by the biaxial drawing.

SEM observations of the cross-section of the biaxially drawn films indicate that the porous structure also exists inside the specimens. As seen in Figures 3(a) and (b), the porous structure exists inside both samples. However, the difference in the porous structure between the two samples is scarcely recognized. This indicates that the degree of crystallinity inside the specimens may be mostly independent of the cooling rate studies, that is, the cooling rate may be more effective at the surface. It was also found that porosity is composed of open-celled networks since pressurized water was able to penetrate this porosity at room temperature.

SUMMARY

Polytetrafluoroethylene films, which were obtained by rapid or slow cooling after heat treatment at 350°C for 2 hours, were drawn biaxially by about twice the original width at a drawing rate of 5 mm/s at 250°C. The structure of the drawn PTFE films was observed using a scanning electron microscope. Growth of granules with a diameter of about 3 μm was observed on the surface of the heat-treated PTFE films. By the biaxial drawing of the heat-treated PTFE films, fibrillation occurs and a porous structure is formed. The granules are only slightly broken by the drawing. In the lower crystallinity PTFE films, the fibrillation is incomplete and occurs on its surface.

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