Fine Structures in As-Polymerized and Sintered Poly (tetrafluoroethylene)*1

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Abstract : The parallel packing of elementary fibrils was directly visualized in the interference image of an as-polymerized rod-like particle of poly(tetrafluoroethylene) (PTFE) by transmission electron microscopy (TEM). The diameter of the elementary fibril was determined at ca. 6 nm. Then, morphology of sintered PTFE was discussed on the basis of TEM observation of the surface replica.

1. Introduction

It is recognized that natural cellulose fibers consist of microfibrils of an approximately constant lateral size in some cellulose species: each of the microfibrils is comprised of molecular chains of cellulose [1]. Such microfibrils of a constant lateral size, however, have never been recognized in synthetic polymers.

As reported previously, we could observe elementary fibrils of the constant diameter in rod-like emulsion particles of PTFE by transmission electron microscopy (TEM) [2].

In this report, we still discuss the fine structure of as-polymerized and sintered PTFE on the basis of morphological observation by TEM.

2. Experimental

2.1 Sample Preparation

Rod-like emulsion particles of PTFE were prepared by synthesis under continuous conduction of tetrafluoroethylene gas using C2F5COONH4 of 0.23 mol/L as an emulsifier and ammonium persulfate as an initiator. Slow agitation during polymerization was adopted.

A sintered sheet of PTFE was prepared from the fine powder F-104 (molecular weight: ca. 4.5 × 10^6), a commercial product of Daikin Industries, Ltd.

2.2 Transmission Electron Microscopy (TEM)

The prepared suspension of PTFE rod-like particles was further diluted with distilled water for TEM observation. A drop of the diluted suspension was mounted onto the carbon/collodion support film deposited on a Cu grid for TEM, and then the specimen was dried. For lattice imaging, Au-coated microgrids were used, on each of which a thin carbon support film was deposited.

Conventional two-stage replication of the surface of sintered PTFE was carried out using a cellulose acetate film and Pt-Pd shadowing.

TEM was performed with a Hitachi H-500 operated at 75 kV for morphological observation and with a JEOL JEM-200CS operated at 200 kV for lattice imaging.

3. Results and Discussion

3.1 Fine Structure of a Rod-Like Particle

In our previous papers, it was reported that the cross-section of the rod-like particle of PTFE was approximately triangular [3] and that microfibrils ca. 6 nm in diameter came out of such rod-like particles of PTFE, when the particles were set on a polyethylene film and then deformed by stretching the film [4]. From these results, it is expected that the particle consists of closely packed elementary fibrils of ca. 6 nm diameter.

Fig. 1 is an electron micrograph of rod-like particles taken at a rather large amount of defocus. The parallel fringes running in the longitudinal direction of each particle are the interference image, namely one of the phase-contrast images. The average spacing of the fringes measured 4.9 nm. If each rod-like particle has a structure as illustrated in Fig. 2, consisting of closely packed elementary fibrils of ca. 6 nm diameter, then this measured spacing of 4.9 nm corresponds to the so-called (100) "macro-lattice" spacing of hexagonally-packed elementary fibrils.

Fig. 3 shows the crystal lattice image taken from a rod-
like particle. The lattice fringes running in the vertical direction of the figure are observed. The fringes have a spacing of 0.49 nm, and thus correspond to the (100) planes of hexagonal crystal lattice of PTFE. The width of the area in which the fringes are coherently recognized is greater than 10 nm, and definitely exceeds the diameter of each elementary fibril. This suggests that the elementary fibrils in a rod-like particle are closely pack-

![Fig. 1](image1.png)

**Fig. 1** Electron micrograph of as-polymerized rod-like particles of PTFE.

The parallel fringes running in the longitudinal direction of each particle are the interference image, namely one of the phase-contrast images, directly demonstrating that each of the particles is made up of elementary fibrils.

![Fig. 2](image2.png)

**Fig. 2** Schematic drawing of the fine structure of the rod-like particle of PTFE.

The particle consists of closely packed elementary fibrils of ca. 6 nm diameter.

![Fig. 3](image3.png)

**Fig. 3** Lattice image of a rod-like particle of PTFE.

The long axis of the rod-like particle is in the vertical direction.

![Fig. 4](image4.png)

**Fig. 4** Electron micrograph of the surface replica of the PTFE sheet, which was sintered at 370 ℃ for 2 h and then cooled down to room temperature at a rate of ca. 50 ℃/h.

Many flat-on lamellae are observed. Arrowheads show typical examples of "cobbles" on the basal surfaces of the lamellae.
ed, and keep partly in coherent contact with each other.

3.2 Microfibrillar Structure in Sintered PTFE

Fig. 4 is an electron micrograph of the surface replica of the PTFE sheet, which was sintered at 370°C for 2 h and then cooled down to room temperature at a rate of ca. 50°C/h. Many flat-on lamellae are observed. In each of the lamellae, a great number of cobbles are recognized, for example, as indicated with arrowheads, which were reported by Bunn et al. [5]. Such a cobble seems to correspond to the end of a microfibril or the folded part of a microfibril [2]. That is to say, a PTFE lamella shown in Fig. 4 seems to consist of microfibrils ca. 20 nm in diameter which fold back and forth on themselves at both of the top and bottom surfaces of the lamella. The microfibrils ca. 20 nm in diameter may be made up of seven [2] elementary fibrils of ca. 6 nm diameter.

3.3 Meander Structure

In 1973, Pechhold et al. [6] proposed the Meander model which illustrates that molecular chains may curve and fold in bundles in polymer melts. As reported previously [2], when the elementary fibrils were heated above the melting point of PTFE, the PTFE chains were not separated but still existed in bundles though the interchain distance was expanded. From such a phenomenon and the results shown in Sections 3.1 and 3.2, the Meander model seems to be applicable to the fine structure of as-polymerized [7,8] and sintered PTFE.

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References