Cellulose Microcrystal Film of High Uniaxial Orientation

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Cellulose samples with high degrees of crystallite orientation have a great advantage for studying crystal structure and physical properties of cellulose, which cannot be crystallized into macroscopic sizes. Although cellulose microcrystals in a suspension are known to undergo spontaneous parallel arrangements on a small scale,[1] such oriented regions are too small for an X-ray diffraction study. A strong magnetic field is reported to give a fairly good orientation to cellulose microcrystals,[2] but the availability of such a magnetic field is limited. Shearing of a suspension easily produces a high degree of orientation,[3] but the orientation could not be achieved in a solid material. Birefringent gel, produced by pressing on the cover slit, had been observed in the first study of liquid crystalline cellulose suspension.[4] We extended these studies and established a way to make a highly oriented gel of crystalline cellulose under shear flow conditions using simple equipment. Rotation of a glass vial containing an aqueous suspension of cellulose microcrystals resulted in the formation of a gellike layer on the inner surface of a glass tube. A film composed of highly oriented microcrystals was obtained by drying this gel layer.

The cellulose sample was prepared from the cell wall of a green alga *Cladophora* sp. collected on the coast of Chikura, Chiba, Japan. The alga sample was boiled repeatedly in 5% (w/v) aqueous KOH and subsequently in 0.3% aqueous sodium chlorite for several times until it became colorless.[5] The purified cell wall was homogenized into millimeter-size fragments using a double-cylinder type homogenizer (Physcotron, Microtech Nichion, Tokyo). The cellulose microcrystal suspension was prepared according to the method described by Marchessault *et al*,[4] which is commonly used for preparing nonflocculating cellulose suspensions. The sample was hydrolyzed with 50% sulfuric acid at 40 °C for 8 h with vigorous stirring. The resulting suspension was diluted 10 times with distilled water, filtered through a sieve to remove large particles, and concentrated by centrifugation. At this point the suspension contained ca. 5% sulfuric acid and 1% cellulose in a water base.

A 20 mL portion of this suspension was put into a 50 mL glass vial with an inner diameter of 3.6 cm. The vial was kept horizontal and rotated around its center (Figure 1) at 500 rpm at room temperature. After 1−2 h, a smooth layer of silky appearance started to form on the glass wall and thickened gradually to form a gellike layer of cellulose microcrystals (referred to as the "gel layer" in the following). After rotation for 12 h a gel layer of about 1 mm thick was formed. The gel layer was stable enough to remain on the wall for a short time but slowly creeped down from vertical walls when rotation was stopped; also it readily disintegrated by shaking it with a liquid. This layer could be dried into a film by repeated cycles (about 10 times) of rinsing with ethanol and drying in a warm air flow. The resulting dry film could be removed from the vial by a pair of forceps. The film was highly anisotropic and brittle in the direction vertical to the orientation, but mechanically stable enough for subsequent examinations. The solid content of the starting gel layer was determined to be 4.0% from weighing.

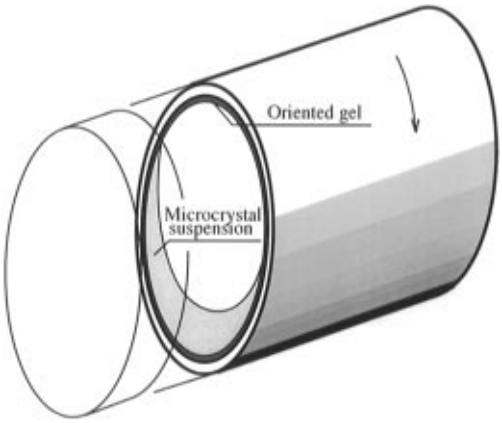

Figure 1. Schematic illustration of shearing method to prepare the oriented gel layer.

The high degree of orientation of this film is demonstrated by its X-ray diffraction diagram (Figure 2) and scanning electron micrograph of the surface (Figure 3). The azimuthal profiles of an equatorial reflection (200)[6] of the film sample and ramie fiber are shown in Figure 4. The axial orientation in the film sample is significantly higher than that of ramie fiber, which is one of the highest oriented samples of native cellulose. The Hermans order parameter

$$f = \frac{3\langle\cos^2\gamma\rangle - 1}{2}$$

was calculated from the azimuthal profile assuming a cylindrical symmetry. Here

$$\langle\cos^2\gamma\rangle = 1 - 2\langle\cos^2\phi\rangle$$

and

$$\langle\cos^2\phi\rangle = \frac{\int I(\phi)\cos^2\phi\sin\phi\,\mathrm{d}\phi}{\int I(\phi)\sin\phi\,\mathrm{d}\phi}$$

The order parameter f of the *Cladophora* film was 0.96, while that of ramie fiber was 0.90. The uniplaner orientation in the film was estimated from the equatorial profile of fiber diagrams taken by X-ray beam perpendicular and parallel to the film surface (Figure 4). A small difference in the intensity ratio of the 110 and $1\bar{1}0$ reflections is observed between the two modes. This indicates that $(1\bar{1}0)$ plane parallel to the film surface is slightly preferred. This tendency of uniplaner orientation is observed in the cell wall of *Cladophora* and also in the films obtained by drying the algal cellulose suspension. A cross section of the microfibrils in the cell wall of algal plants is known to be nearly square, 20 nm by 20 nm, exposing (110) and $(1\bar{1}0)$ planes, but the latter is slightly wider from a comparison of half-widths of reflections from these planes. This slightly flattened cross-sectional shape may be the cause of the planar orientation.

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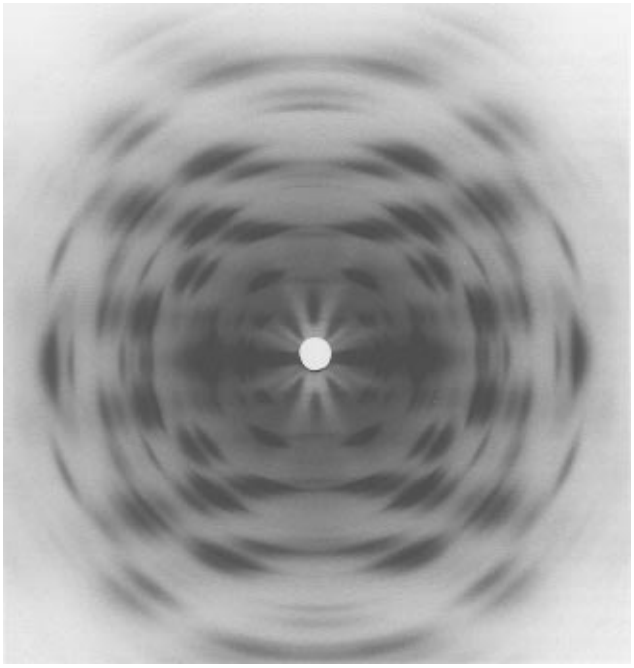

Figure 2. X-ray diffraction diagram of the oriented film of cellulose microcrystals. The X-ray beam was perpendicular to the film plane; the fiber axis is vertical.

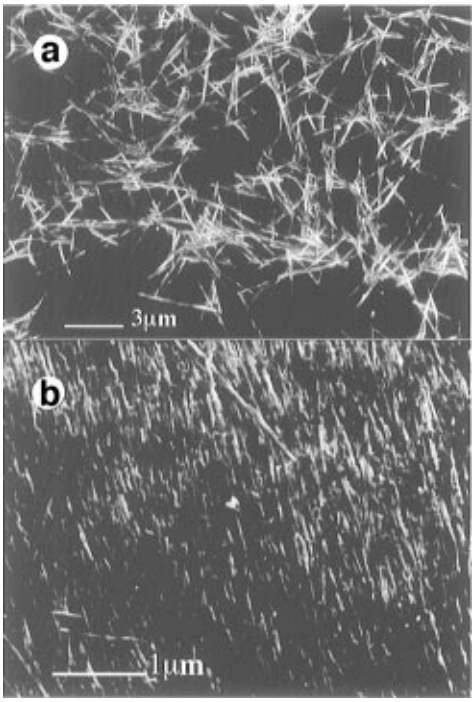

Figure 3. Scanning electron micrographs of (a) microcrystalline particles of *Cladophora* sp. produced by acid hydrolysis and (b) the surface of its oriented film.

Concentrated suspensions of rodlike particles are known to undergo phase separation leading to the liquid crystalline state. Reported examples are those of tobacco mosaic virus,[7] cellulose microcrystals,[1,4] and chitin microcrystals.[4,8] This phenomenon has been explained essentially by steric constraints to the rotational motion of rodlike particles.[7] This phenomenon is governed by the aspect ratio of the particle, with the lower critical concentration (volume fraction) for phase separation being determined by $c \approx 1/dL^2$, where d and L are the diameter and the length of the particles respectively.[7,9]

The particle size in our cellulose suspension was estimated by scanning electron microscopy to be $d =$ 40 nm and $L = 4\ \mu$m, corresponding to an aggregate of a few microcrystals 20 nm wide (Figure 3). This size leads to a critical concentration of roughly 12.5 μm^{-3} or 1.6% (w/w) using a density of 1.6 g/cm^3. This is above the concentration of 1% used in this experiment. Taking the electrostatic interaction into account, the concentration for the phase separation will be lower,[10,11] but the remaining sulfuric acid would suppress the double layer. In fact, no phase separation was observed when the suspension was left to stand. Therefore, the formation of gel layer observed here is a different phenomenon from the spontaneous phase separation mentioned above. In our case, orientation of rodlike particles by shear flow seems to play a key role in the formation of the concentrated phase.

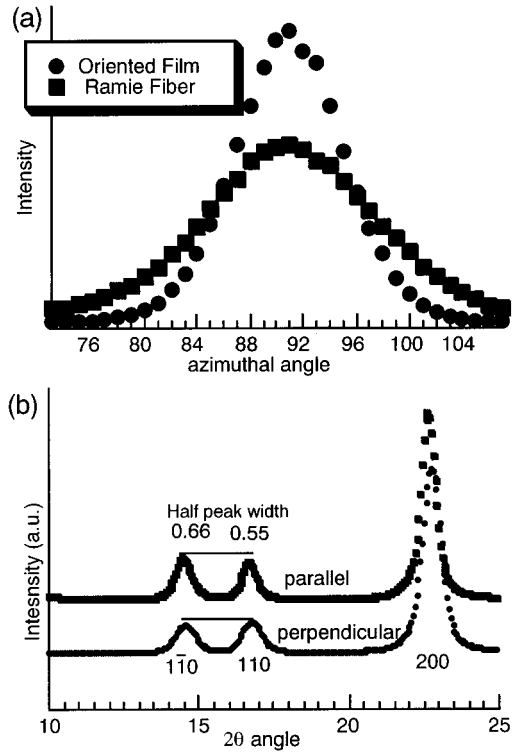

Figure 4. X-ray diffraction profiles of (a) azimuthal distribution of 200 reflection to compare the uniaxial orientation of *Cladophora* microcrystal film (X-ray beam perpendicular to the film surface) and ramie fiber; (b) equatorial intensity profile obtained by exposing the X-ray beam perpendicular to and parallel to the film surface.

The influence of electrolyte concentration was examined by washing the suspension repeatedly with centrifugation and dialysis to neutrality. The neutral suspension did not form the oriented gel layer in the rotating glass vial. Addition of a small amount of electrolyte (NaCl or acid) immediately raised the viscosity and enabled again the formation of gel layer. A quantitative analysis based on more detailed experiments is underway. If the mechanism and the conditions for gellike layer formation become clear, this shear-induced orientation and gel formation may give a new way to prepare oriented films of whiskerlike particles in general.

References and Notes

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