Three-dimensional orientation of cellulose crystals under dynamic elliptic magnetic field

F Kimura and T Kimura
Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan
E-mail: fkimura@kais.kyoto-u.ac.jp

Abstract. Cellulose microparticles prepared by hydrochloric acid hydrolysis of cotton cellulose were mixed with UV-curable resin precursor and subjected to a frequency modulated magnetic field. The obtained alignment was fixed by photopolymerization of the matrix resin precursor. The observation of the obtained sample from three different orthogonal directions exhibited optical anisotropy, indicating that the three-dimensional alignment is achieved.

1. Introduction
Recently, we have developed a new technique that enables three-dimensional alignment of crystalline powders [1,2]. This technique is based on the use of dynamically modulated (elliptic) magnetic fields. With this technique, we can prepare from a powder sample a pseudo single crystal in which the individual crystallites are aligned three-dimensionally. This technique is applicable to the biaxial crystal systems including the orthorhombic, monoclinic, and triclinic systems. An excellent property of the pseudo single crystal is that it gives rise to the X-ray diffraction pattern identical with that obtained from a real single crystal [2], enabling a single crystal analysis. This technique is also useful for the processing of composites in which crystalline fillers are aligned three-dimensionally.

It is known that the single crystal analysis with X-ray diffraction is the most useful technique for determination of the three dimensional structure of new compounds. However, growing a single crystal to a size suitable for the X-ray measurement is becoming more difficult because the structure of the compound is getting more complicated. Recently, new analytical techniques such as the ab-initio or direct space method have been proposed [3-5] to solve the crystal structure from a powder diffraction pattern. Unfortunately, these techniques are limited to specialists because the determination of the correct cell constant and the structure is not easy from one-dimensional information. A pseudo single crystal can provide sufficient data for the determination of the crystal structure.

In this paper, we report a preparation of a pseudo single crystal of cellulose microcrystals. Natural cellulose fibers are of polycrystal of microcrystals, so the decomposition to the microcrystal is a key issue. In addition, microcrystals from naturally occurring cellulose have two crystal forms: Iα (triclinic) and Iβ forms (monoclinic). A microcrystal is a composite of the two forms, the ratio of which depends on sources. At present time, we do not have enough knowledge regarding to which size a polycrystal should be decomposed in order to obtain microcrystals. In this paper, we report a preliminary work on the preparation of a pseudo single crystal.
2. Experiments

Whatman CF11 cellulose (cotton cellulose) was mixed with 4 N hydrochloric acid and stirred at 80 °C for 4 h to obtain a cellulose suspension. The acid was removed by centrifugation and prolonged dialysis with pure water. An ethanol solution of saturated sodium dodecyl sulfonate (0.5ml) was added to the cellulose suspension (ca. 40ml). Supernatant of the suspension was removed by decantation, and the ethanol was added to the remaining suspension; this procedure was repeated several times to replace the water with ethanol. The ethanol was evaporated at room temperature until the sample became paste-like. Then a UV-curable resin precursor (No. 8815 of Kyoritsu Chemical and Co. Ltd., viscosity of 1200 mPa s) was added to the paste to obtain a suspension with resin precursor. A small amount of the resin suspension was poured into a plastic container with 5 mm diameter and 10 mm height. The container was mounted on a sample-rotating unit inside a superconducting magnet (12 T). Two hours after exposure to the frequency-modulated sample rotation, the resin was irradiated with UV light inside the magnet for 30 minutes to fix the alignment.

The sample rotating unit was placed in the center of the bore of a superconducting magnet generating a 12-T horizontal magnetic field (the $x$ axis). The rotation axis was vertical (the $z$ axis). The rotation was not uniform, but the frequency was periodically changed every 90 degree. In the present study, we set the values of the frequency as 15 and 60 rpm (figure 1). Two hours after exposure to the frequency-modulated sample rotation, the resin was irradiated with UV light inside the magnet for 30 minutes to fix the alignment.

3. Results and discussion

Under a static magnetic field, the easy magnetization axis aligns parallel to the applied field, while the hard magnetization axis has a freedom of rotation around the field direction, resulting in a planar alignment on the plane perpendicular to the applied field. Under a rotating magnetic field, the hard magnetization axis aligns perpendicular to the plane of rotation of the field, while the direction of the easy magnetization axis is not fixed. That is, the hard axis aligns uniaxially. By using a dynamic modulated elliptic magnetic field, both the easy and hard axes are fixed with respect to the sample coordinates. Although a cellulose microcrystal has a biaxial

![Diagram illustrating the frequency-modulated sample rotation](image-url)

**Figure 1.** Diagram illustrating the frequency-modulated sample rotation. The $x$, $y$, and $z$ axes are laboratory coordinates; the $x$ and $y$ axes are on the horizontal plane and the $z$ axis is in the vertical direction. The $x'$, $y'$, and $z'$ axes are imbedded in the sample that is rotated around the $z'$ axis (parallel to the $z$ axis). The rotation is performed nonuniformly. The $x$ axis coincides with the direction of the magnetic field.

![Cellulose fiber and microcrystal](image-url)

**Figure 2.** Magnetic anisotropy of cellulose fiber and microcrystal. $\chi_//$, and $\chi_\perp$ are magnetic susceptibilities parallel and perpendicular to fiber axis, respectively. $\chi_1$, $\chi_2$, and $\chi_3$ are three different susceptibilities of microcrystal. A polycrystal (a fiber) is decomposed to single crystals (microcrystals) by acid hydrolysis. A fiber is uniaxial while a microcrystal (triclinic (Iα form) or monoclinic (Iβ)) is biaxial.
nature, a large cellulose fiber only exhibits the uniaxial nature because it is polycrystal. Therefore, it is necessary to decompose a large fiber to microcrystals in order to achieve three-dimensional alignment (figure 2). If the decomposition of large fibers is made by an appropriate acid treatment, we will obtain microcrystals that undergo three-dimensional alignment. The decomposed sample mainly exhibited the \( \beta \) form (monoclinic) according to the X-ray diffraction analysis (results are not shown).

Figure 3 shows the optical polarized microscopic photographs with a color plate of the cellulose microparticles/resin composite obtained from the application of modulated magnetic field. The images in figure 3(a) (through view) were taken from the direction of the hard magnetization axis (the fiber axis). If the decomposed particles are yet polycrystal (that is, uniaxial with respect to the fiber axis), we do not observed color change when the sample was rotated 90 degree under the polarized microscope. However, we observed the color change. Upper images in figures 3 (b) and (c) (side-views 1 and 2) showed blue and orange colors even if the tilt angles of the sample are the same. If the particles were yet polycrystal, we would observe the same color at the same tilt angles. These observations indicate that the decomposes particles are not polycrystals but micro (single) crystals. From these results, we conclude that we succeeded to obtain a pseudo single crystal of cellulose \( \beta \) form. Unfortunately, the X-ray diffraction measurement was not successful because the concentration of the microcrystal was not enough high to obtain diffractions.

References

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