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Novel method for producing amorphous cellulose only by milling

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ABSTRACT

The present study investigated a novel method for producing amorphous cellulose by milling without adding water. A new type of milling machine was developed (called a shear and cooling milling machine (SCMM)), which was capable of applying mechanical shear and cooling during the milling process. The SCMM consisted of a pair of mortars attached to a servomotor and a ring cooler. Wide-angle X-ray diffraction (WAXD) analysis was used to determine the cellulose crystallinity in samples produced using the SCMM at different milling temperatures. The results of WAXD for cellulose powder milled at lower temperatures exhibited no diffraction peaks. This experimental result demonstrates that the SCMM produces amorphous cellulose easily by cooled milling without the addition of water. The milling conditions, such as the applied shear and cooling, can be used to control the crystallinity of cellulose.

1. Introduction

Cellulose is a ubiquitous material obtained from plants. Used in clothing, paper, cosmetics, foods, chemicals, and biomass fuels, it is exceedingly important for human life. In particular, cellulose is used to make bio-ethanol and filler of polymer composite materials for industrial use. For the industrial usages of cellulose, the control of its crystallinity is an interesting and important research subject. Numerous methods of producing amorphous cellulose have been reported over the past two decades. Many physical and chemical techniques for modifying cellulose have been proposed, including ball-mill (Honda, Ichikawa, & Aranishi, 2003; Ito, Hioki, & Kuwabara, 2007; Sidiras, Koullas, Vgenopoulos, & Koukios, 1990), jet-mill (Otani & Ibuki, 2004), twin-extruder (Nojiri, 2008; Tsuboi, Yoshino, & Mori, 2012), and chemical treatments (Hosokawa & Nanba, 2005). These proposed methods had the disadvantages of requiring a long processing time (e.g., 20 h) to produce amorphous cellulose, a low productivity, high cost with expensive equipment for mechanical modification, or complicated chemical modification treatments with liquid waste disposal problems. Therefore, there is an urgent demand for the development of a simple and effective technique for controlling the crystallinity of cellulose in a practical manner, without the addition of water or organic chemicals. The purposes of the present study were to develop a simple and effective physical modification method for producing amorphous cellulose without adding water, and of controlling the crystallinity of cellulose in a practical, expedient manner. We developed a novel, simple milling machine (called a shear and cooling milling machine (SCMM)). The physical modification of cellulose from a hinokia cypress was investigated using the developed SCMM machine. The dependence of cellulose crystallinity obtained from the machine on the milling conditions was investigated by WAXD analysis.

2. Materials and methods

2.1. Cellulose samples

In the present study, we used a pure crystalline cellulose powder B600 produced by Lettenmiyer Co., Ltd. We controlled the moisture content of the cellulose samples to investigate its influence on crystallinity. A wet sample was prepared by adding water in an oven at room temperature. The moisture contents of the cellulose samples before milling were measured using an infrared moisture determination balance (FD-720, Kett Electric Laboratory Co., Ltd., Japan). The moisture contents of the cellulose samples were 11 wt% for the raw material sample and 20 wt% for the wet sample.

2.2. Novel milling machine and milling conditions

The shear and cooling milling machine (SCMM) is simple, in that it applies mechanical shear and cooling simultaneously during milling. Essentially, the SCMM is an improved commercial millstone-type milling machine (KGW-G015, West Co., Ltd., Japan) with cooling equipment attached. KGW-G015 was designed by Nishioka et al. (Katsuno et al., 2010) based on technology of rice starch forming. Point of similarity between the crystalline cellulose and rice flour is to milling by a mortar between narrow gap. However, appropriate milling conditions such as the temperature

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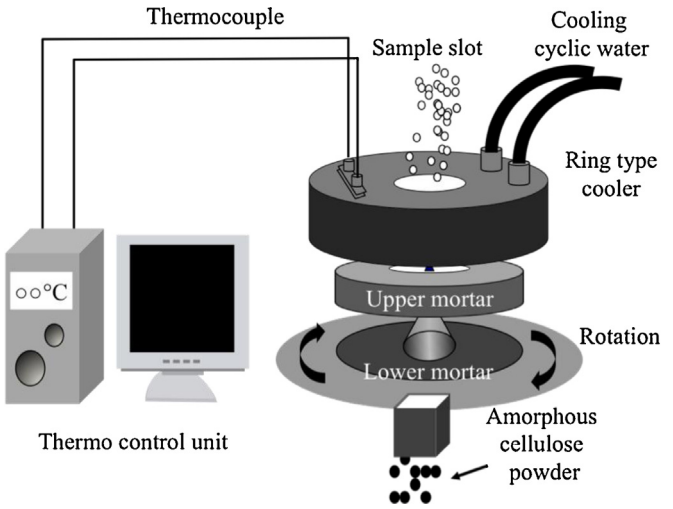

Fig. 1. Schematic illustration of the developed SCMM system.

make a great difference. Fig. 1 shows a schematic illustration of the SCMM, which is 250 mm wide, 200 mm deep, and 370 mm high. The SCMM consists of two metal mortars (diameter: 90 mm), a ring-type cooler, and a servomotor. As shown in Fig. 1, the ring-type cooler is installed on the upper mortar. The temperature of the upper mortar is monitored using an attached thermocouple and controlled using a thermal control unit. A difference may exist between measured temperature and real sample temperature. For the temperature control less than 0 °C, we use nonfreezing liquid as circulation fluid.

To precisely examine the effects of shear and cooling on the crystallinity of cellulose, the milling temperature of the SCMM was carefully controlled. The rotation speeds of the lower mortar during milling were 80, 180, 280, and 380 rpm. The upper mortar was not rotated, and there was a 10 μm gap between the upper and lower mortars. The milling temperatures, set by the thermal control unit, were −10, 0, 10, 15, 20, 30, 40, 60, and 140 °C.

2.3. Wide-angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) analysis of the cellulose powder was performed using a nickel-filtered Cu Kα radiation source (RINT RAPID-S, Rigaku-Denki Co., Ltd., Japan) generated at 40 kV and 30 mA. The cellulose powder samples were scanned at room temperature through a 2θ region of 5–35° at scanning rate of 1°/min. The intensity distribution curves were measured using a goniometer.

2.4. Scaning electron microscopy

The morphology of cellulose sample was performed by scanning electron microscopy (SEM) (VE-9800, KEYENCE Co., Ltd., Japan). Gold sputter coated samples were examined using a ion coater (IB-2, Eiko Engineering Co., Ltd., Japan).

3. Results and discussion

We studied the crystallinity of the cellulose samples by WAXD. Crystalline cellulose shows peaks at 2θ = 15 and 22.6°, and the observed broad peak at 2θ = 18.5° arise from amorphous cellulose region (Zugenmaier, 2001). The decrease and disappearance of the peaks at 2θ = 15 and 22.6° was due to the transition from a crystalline state to an amorphous state.

Fig. 2 shows WAXD results for the untreated cellulose powder B600 and milled raw cellulose powders of B600 (moisture content

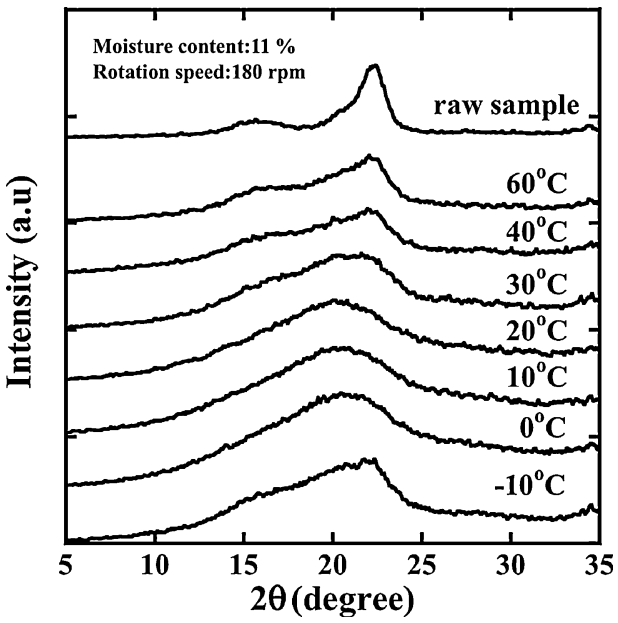

Fig. 2. WAXD results for the cellulose raw sample and cellulose powder samples milled at temperatures of 60 °C, 40 °C, 30 °C, 20 °C, 10 °C, 0 °C, and −10 °C (moisture content: 11%).

11 wt%) at different temperatures by SCMM. The crystalline peaks at 2θ = 15 and 22.6° were observed for the untreated sample. The milled samples at 60, 40, 30, and −10 °C also showed these peaks. It is clear that these milled samples still contained a crystalline cellulose structure. On the other hand, the milled samples at 0, 10, and 20 °C showed a surprising change in the WAXD pattern: the crystalline peaks at 2θ = 15 and 22.6° disappeared. These samples showed only the peak at 2θ = 18.5°, so these samples were amorphous. It is remarkable that an amorphous transition was caused by only SCMM milling at temperatures of 0–20 °C.

The degree of crystallinity D_C can be obtained using Eq. (1), which was proposed by Segal et al. (Isogai & Usuda, 1989; Segal, Creely, Martin, & Conrad, 1957)

$$D_C = \frac{(I_{(200)} - I_{(18.5)})}{I_{(200)}} \times 100. \quad (1)$$

In this equation, I_{200} is the maximum intensity of the 200 lattice diffraction which appears around the diffraction at 2θ = 22.6°, and $I_{18.5}$ is the intensity of the diffraction at 2θ = 18.5°.

Fig. 3 shows the relationship between the crystallinity and milling temperature for raw cellulose samples (moisture content 11 wt%). The crystallinity of the untreated cellulose powder B600 was 85%, while that of the milled cellulose powders at 0, 10, and 20 °C were 0%, indicating that these samples consisted of amorphous cellulose. We estimated the mechanism of the transition to amorphous cellulose to be as follows. Generally, the crystalline cellulose structure arises from hydrogen bonding between intermolecular hydroxyl groups and included water. In the temperature-controlled mill, this crystalline structure based on hydrogen bonding can effectively be destroyed. As the temperature decreases, hydrogen bonds in the crystalline cellulose become strong. As a whole, cellulose micro-fibrils become harder and brittler efficiency causing efficient cut of hydrogen bonds. When the temperature is higher than approximately 30 °C, the crystalline structure cannot be destroyed because decreasing elasticity due to temperature increase causes a lack of shear stress which destroys the hydrogen bonding of the crystalline structure.

Fig. 4 shows WAXD results for cellulose powder B600 under wet conditions (moisture content: 20 wt%) to examine the effects

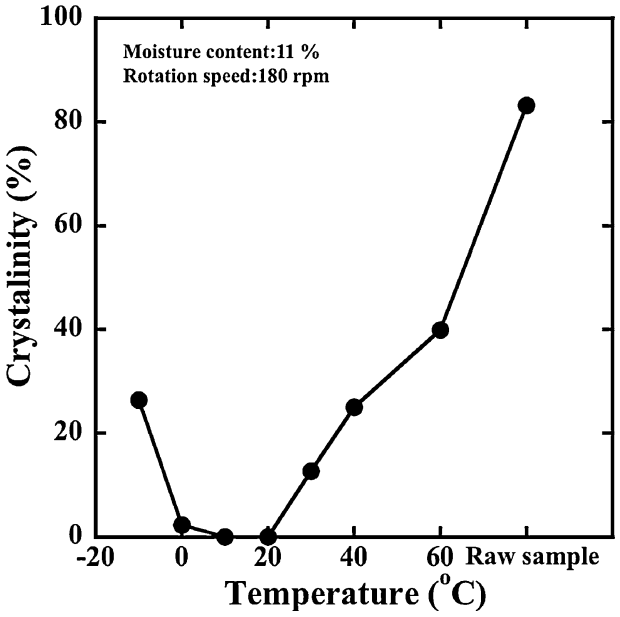

Fig. 3. Degree of crystallinity D_C of cellulose powder samples after milling at various temperatures.

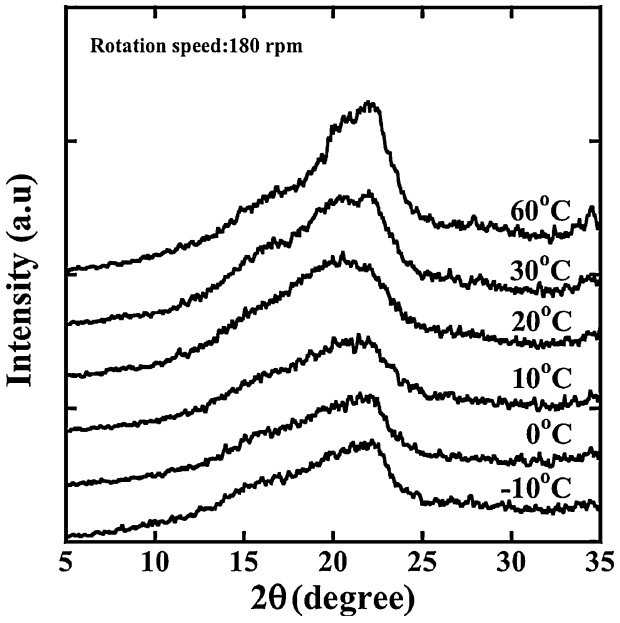

Fig. 4. WAXD results for cellulose powder samples treated at different milling temperatures (moisture content: 20%).

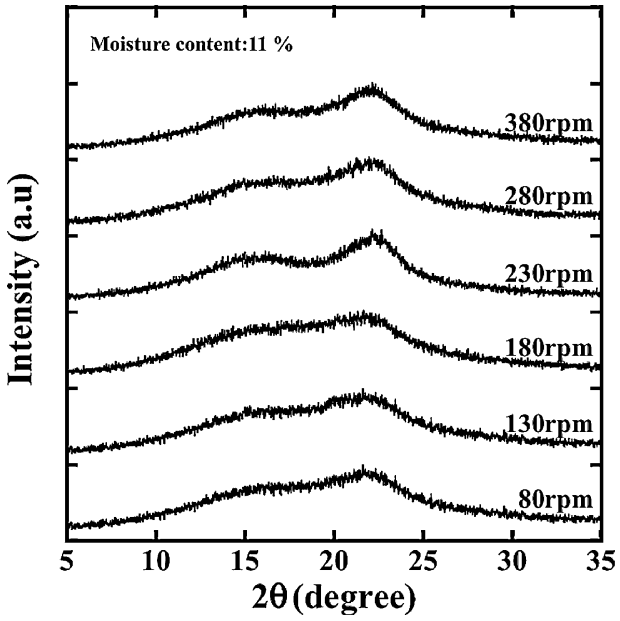

Fig. 5. WAXD results for cellulose powder samples milled at different rotation speeds (milling temperature: 15 °C).

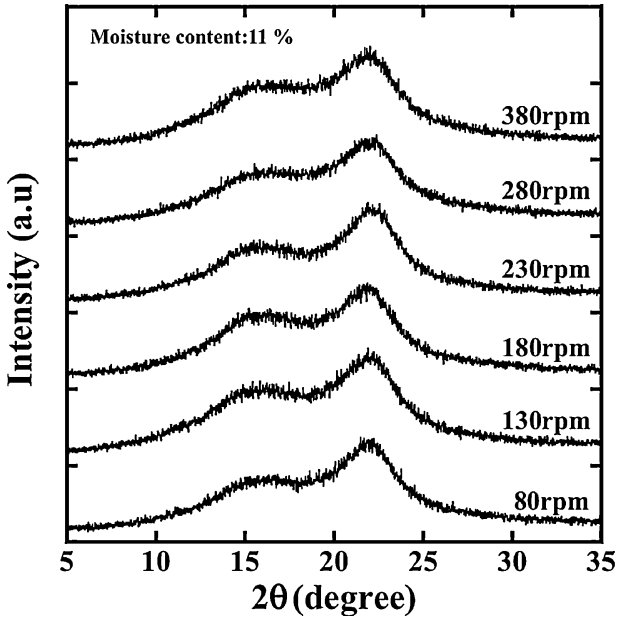

Fig. 6. WAXD results for cellulose powder samples milled at different rotation speeds (milling temperature: 140 °C).

of moisture content. From the results shown in Fig. 4, the crystalline peaks at $2\theta = 15$ and 22.6° were remarkably decreased by cooled milling treatments also for wet conditions. Fig. 4 demonstrates that the crystalline peaks at $2\theta = 15$ and 22.6° for the high moisture content (20 wt%) samples did not diminish after heated milling (30–140 °C). This means that excess water content does not decrease the cellulose crystallinity. We do not have to add excess water to obtain amorphous cellulose.

Figs. 5 and 6 show WAXD results for cellulose powder B600 milled at different rotational speeds at temperatures of 15 and 140 °C, respectively. The peak intensities of Fig. 6 after high rotational speed treatments (230, 280, and 380 rpm) were similar to those after 180 rpm treatment. High rotational speed treatment (230, 280, or 380 rpm) does not effectively force a transition to the amorphous state by SCMM. The peak intensities of Fig. 5 after low rotational speed treatment (80 or 130 rpm) do decrease slightly with decreasing rotational speed. The lower rotational speed effectively generated amorphous cellulose by milling at temperature of 15 °C.

To understand this result, detailed analysis of the work done by motors must be performed. The analysis using electric power meter is now going on. It will be reported in our future paper.

The mechanical treatment results in morphological changes on the cellulose fibers. SEM micrographs of the untreated and treated cellulose samples are shown in Fig. 7. It is clearly found from Fig. 7 that morphologies of untreated and treated cellulose are different.

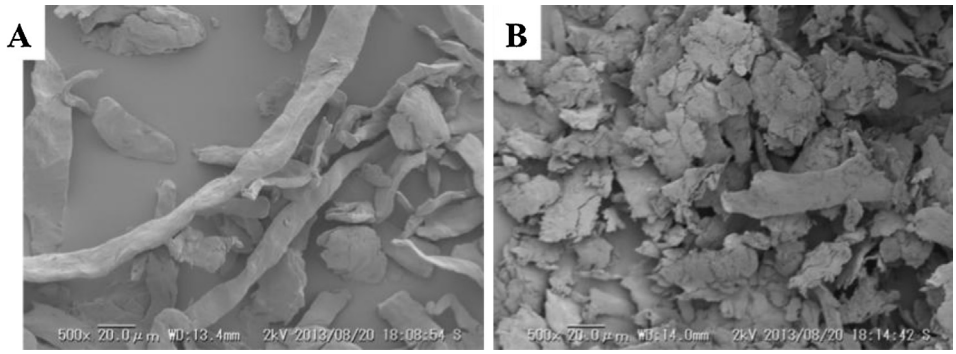

Fig. 7. SEM micrographs of the untreated and treated cellulose samples: (A) untreated sample and (B) treated samples.

The surface of untreated sample look smoother than that in the treated one. The cellulose samples broke to pieces into individual micro-sized particle after SCMM treatment.

4. Conclusions

The following new findings were obtained in the present study:

(1) A novel method for obtaining amorphous cellulose without adding water was proposed. A new milling machine (the SCMM) that can simultaneously apply mechanical shear and cooling during milling was developed.
(2) The crystallinity of cellulose samples produced by the SCMM at different milling temperatures was examined by WAXD analysis. The results confirm that amorphous cellulose can be obtained by milling while cooling to temperatures between 0 and 20 °C.

The residential time is less than 10 s. We can produce the amorphous cellulose about 30 g per 1 h by SCMM system. This is considerably shorter process time compared to conventional modification techniques for cellulose. By only cooled milling without adding water or any chemicals this methods provides amorphous cellulose.

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