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Crystal transition from Na–cellulose IV to cellulose II monitored using synchrotron X-ray diffraction

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ABSTRACT

Oriented samples of Na–cellulose IV, a hydrate form of cellulose II, were prepared from ramie fibers by mercerization. Crystal transition from Na–cellulose IV to cellulose II was monitored using synchrotron X-ray fiber diffraction under a controlled relative humidity. During drying of the Na–cellulose IV, the *d*-spacing of the $(1\,\bar{1}\,0)$ plane gradually decreased while the *d*-spacings of the (1 1 0), (0 2 0), and (0 0 2) planes remained almost constant. From these results, the transition mechanism from Na–cellulose IV to cellulose II can be understood as crystalline lattice contraction of Na–cellulose IV along the *a*-axis direction while maintaining its hydrophobic stacking sheet structure. In addition, the lattice contraction of Na–cellulose IV on dehydration occurred continuously throughout the drying process, and no clear transition point was observed. This dehydration behavior and instability of Na–cellulose IV implies a random location of water molecules in the crystalline lattice. Following the drying process, dried cellulose II was immersed in water, but it did not return to the Na–cellulose IV form. Therefore, the transformation from Na–cellulose IV to cellulose II was irreversible.

1. Introduction

Mercerization is a simple treatment of native cellulose fibers using an alkali solution that was discovered in the nineteenth century by John Mercer (Heines, 1944). This treatment is still used in the textile industry because it gives luster and improves the mechanical properties and dyeing affinity of cellulose fibers. Carrying out mercerization using a particular concentration of alkali solutions means that the two naturally occurring crystal forms of cellulose, cellulose I_α, and cellulose I_β (collectively known as cellulose I) (Atalla & VanderHart, 1984; VanderHart & Atalla, 1984), are converted into another polymorph, cellulose II, through several intermediate alkali-celluloses (Warwiker, 1971).

These intermediate structures formed during mercerization have been studied using X-ray diffraction (Hess and Trogus, 1931; Nishimura, Okano, & Sarko, 1991; Nishimura and Sarko, 1991; Okano & Sarko, 1984, 1985; Sobue, Kiessig, & Hess, 1939; Whitaker, Nieduszynski, & Atkins, 1974) and solid-state ^{13}C NMR spectroscopy (Kamide, Kowsaka, & Okajima, 1985; Kunze, Ebert, Schröter, Frigge, & Philipp, 1981; Philipp, Kunze, & Fink, 1987; Porro, Bédué, Chanzy, & Heux, 2007; Takahashi & Ohkubo, 1993; Takahashi, Ookubo, & Takenaka, 1991; Yamada, Kowsaka, Matsui, Okajima, & Kamide, 1992; Yokota, Sei, Horii, & Kitamaru, 1990). The following transition scheme on mercerization is generally accepted as being correct. Immersion of natural cellulose fibers, such as ramie and cotton, into a 3–5N NaOH solution leads to a penetration of the alkali solution between the cellulose molecular chains, which form a complex with the alkali ions and water molecules, called Na–cellulose I. On washing Na–cellulose I with excess water, the alkali ions are excluded from the crystalline lattice, and this is converted into another intermediate form, Na–cellulose IV. Na–cellulose IV has no alkali ions in its crystalline lattice, and is the hydrate form of cellulose II. This is also supported by the fact that a simple drying of Na–cellulose IV converts it into cellulose II.

Nishimura and Sarko (1991) reported on the crystal structure of Na–cellulose IV using X-ray diffraction analysis and stereochemical modeling. The model they proposed is based on a two-chain monoclinic $P2_1$ unit cell ($a = 9.57$ Å, $b = 8.72$ Å, $c = 10.35$ Å, and $\gamma = 122.0^\circ$) that contains two water molecules with antiparallel chain packing. This unit cell is larger by about 9% from the two-chain monoclinic unit cell of mercerized cellulose II having dimensions of $a = 8.10$ Å, $b = 9.03$ Å, $c = 10.31$ Å, and $\gamma = 117.10^\circ$ (Langan, Nishiyama, & Chanzy, 2001) due to intercalated water molecules.

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All of the water molecules located between the corner chains form hydrogen bonds with the surrounding cellulose chains.

Recently, we reported that the conversion of cellulose I to Na–cellulose IV by mercerization significantly improves the rate of enzymatic hydrolysis (Wada, Ike, & Tokuyasu, 2010). However, the stability of Na–cellulose IV, which is important for its practical applications, and the mechanism of the transition from Na–cellulose IV to cellulose II on drying are not fully understood. Therefore, in this study, we investigated the crystal structure of Na–cellulose IV using synchrotron X-ray fiber diffraction and solid-state ^{13}C NMR spectroscopy and, furthermore, the drying process from Na–cellulose IV to cellulose II was monitored using synchrotron X-ray diffraction under a controlled relative humidity (RH).

2. Experimental section

2.1. Preparation of samples

The source material used in this study was purified ramie (*Boehmeria nivea* Gaud.) fibers supplied by the Teikoku Boseki Co. (Japan). A bundle of ramie fibers (cellulose I) was aligned and fixed to a stainless steel stretching device, which was then immersed in a 3.5N NaOH solution to prepare the Na–cellulose I. The Na–cellulose IV and cellulose II samples were prepared using a repetitive alkali mercerization process with stretching of the fibers, as reported in previous publications (Hori & Wada, 2006; Langan et al., 2001). After thoroughly washing the alkali solutions with deionized water, the samples were either kept in water at room temperature or dried in air to form Na–cellulose IV or cellulose II, respectively.

2.2. Synchrotron X-ray fiber diffraction analysis

Synchrotron X-ray fiber diffraction was carried out at the BL38B1 beam line located at the SPring-8 facility (Hyogo, Japan). The oriented fibers were mounted on a goniometer head and synchrotron-radiated X-rays (λ = 1.0 Å) were irradiated for a period of 120 s orthogonal to the fiber axis. In the measurements on Na–cellulose IV, air with RH = 90% generated using a humidity generator (Shinyei SRG-1R, Japan) flowed over the sample to maintain it in the wet condition. The fiber patterns were recorded using a camera system equipped with a flat imaging plate (IP) (R-Axis V, Rigaku) at room temperature. The sample-to-IP distance was calibrated using Si powder (d = 3.1355 Å).

The peak positions of the fiber diffraction patterns were measured using the R-Axis display software package (Rigaku). After indexing the d-spacings, the unit-cell parameters were determined using a least-squares method.

2.3. Solid-state CP/MAS ^{13}C NMR spectroscopy

Solid-state ^{13}C NMR spectra were obtained using a CMX 300 spectrometer (Chemagnetics, USA) operating at 75.6 MHz. The sample was placed in a 4.0 mm zirconia rotor, and was spun at a frequency of 5 kHz in a solid-state probe at the magic angle. All spectra were obtained using a ^{1}H NMR 90° pulse length of 2.5 μs, with a cross-polarization time of 1.0 ms and a 60 kHz CW proton decoupling. The recycle time was 3 s. The spectra were calibrated using adamantane as a standard. The rotor was sealed using a Teflon cap to avoid any drying out of the Na–cellulose IV sample. Deconvolution of the spectra was carried out using a nonlinear least-square fitting procedure, where a Lorentzian function was applied to each peak.

2.4. Monitoring of the crystal transition using synchrotron X-ray diffraction

Monitoring of the drying of Na–cellulose IV was also carried out in the BL38B1 beam line at the SPring-8 facility (Hyogo, Japan), as described above. Oriented samples of Na–cellulose IV were mounted on a goniometer head in flowing humidity-controlled air from a humidity generator (Shinyei SRG-1R) at a flow rate of 1 L/min. The fiber patterns were recorded from RH = 100% to 0% in decreasing steps of 10%. The sample that had dried at RH = 0% was subsequently rewetted using a few drops of water, and the measurement was performed again at RH = 100%. Each X-ray diffraction measurement was carried out after a stabilization time of 10 min.

The equatorial and meridional X-ray diffraction profiles at each RH step were obtained by analyzing the fiber diffraction diagrams using the R-Axis display software package (Rigaku). The peak positions were determined by peak fitting the X-ray diffraction profiles, as reported previously (Wada, Okano, & Sugiyama, 1997).

3. Results and discussion

3.1. Synchrotron X-ray fiber diffraction

The synchrotron X-ray fiber diffraction diagram of the ramie fibers showed a typical pattern of cellulose I (Fig. 1a). When swollen in a 3.5N NaOH solution, the ramie fibers were converted to Na–cellulose I (Fig. 1b). Compared with cellulose I, the pattern was obscure because of the low crystallinity of Na–cellulose I and the scattering resulting from excess NaOH solution. The peak intensities were weak except for the two strong equatorial peaks occurring at 4.45 and 4.23 Å. The innermost equatorial peak occurred at 12.50 Å, which was the result of swelling of the crystalline lattice by the alkali solution.

On washing with water, all of the alkali in the crystalline lattice of Na–cellulose I was removed, causing a transition to Na–cellulose IV to occur. The X-ray diffraction pattern of a Na–cellulose IV fiber recorded at RH = 90% is shown in Fig. 1c. The d-spacings of the reflections were measured and indexed to a two-chain monoclinic unit cell (Nishimura & Sarko, 1991). The unit-cell parameters were refined as a = 9.21 Å, b = 9.87 Å, c = 10.35 Å, and monoclinic angle γ = 124.7°. The absence of any 0 0 l reflections for odd values of l indicated that the space group was $P2_1$. However, the strong reflections near the meridian on the third layer line could not be indexed to a monoclinic unit cell. Similar reflections were reported in the fiber patterns of cellulose III$_{II}$, showing that they are not true Bragg reflections but the result of diffuse scattering (Wada, Heux, Nishiyama, & Langan, 2009).

The X-ray diffraction pattern of cellulose II fibers obtained after drying Na–cellulose IV is shown in Fig. 1d. The pattern of cellulose II has sharper and more numerous peaks than the pattern of Na–cellulose IV, which means a larger crystallite size and a higher crystallinity of the cellulose II sample, but the two patterns are similar to each other (Fig. 1c and d). A major difference is the position of the innermost equatorial reflections, indexed as 1 $\bar{1}$ 0. That of cellulose II appeared at 7.29 Å versus that of Na–cellulose IV occurring at 8.42 Å. All the reflections in the pattern (Fig. 1d) were indexed using a two-chain monoclinic unit cell with a = 8.10 Å, b = 9.08 Å, c = 10.36 Å, and γ = 117.3°. From the absence of odd value 0 0 l reflections, the space group is $P2_1$. The scattering near the meridian on the third layer line, which was observed in the diagram of Na–cellulose IV, as discussed above, was also observed, but was weaker. The similarity between the patterns of Na–cellulose IV and cellulose II suggests no significant difference in the molecular conformation and packing of the cellulose