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The thermal expansion of mannan I obtained from ivory nuts

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Abstract

We have investigated the thermal expansion of mannan I crystals obtained from the endosperm of ivory nuts using X-ray diffraction in the temperature range of from room temperature to 250 °C on heating. Seven major diffractions were observed, and all the *d*-spacings gradually increased with increasing temperature. However, discontinuities indicating a phase transition were observed at a temperature of 130 °C. The unit cell parameters showed an anisotropic thermal expansion between the intermolecular hydrogen bonded direction and the covalently bonded direction, where the *a* and *b* axes lengths increased, but the *c*-axis length decreased with increasing temperature. Although the reason for the contraction of the *c*-axis length on heating is not clear, the thermal behavior should be related to the crystal structure and hydrogen bonding system of mannan I.

Keywords: Thermal expansion; Ivory nut; Mannan; X-ray diffraction

1. Introduction

Mannan that consists of β-1,4-mannosyl residues is abundant in nature, and is obtained as a pure homopolymer from the endosperm of certain plants, such as ivory nuts (*Phytelephas* sp.), as well as from the cell walls of several green algae belonging to the Codiaceae and Dasycladaceae families (Frei & Preston, 1968; Meier, 1958; Timell, 1957). There are two polymorphs in mannan: the major form is mannan I, and the minor form is mannan II. Mannan I is found in a highly crystalline state in nature, and thus, the crystal structure has been extensively studied (Atkins, Farnell, Mackie, & Sheldrick, 1988; Chanzy, Dube, Marchessault, & Revol, 1979; Chanzy, Grosrenaud, Vuong, & Mackie, 1984; Chanzy, Pérez, Miller, Paradossi, & Winter, 1987; Frei & Preston, 1968; Nieduszynski & Marchessault, 1972; Yui, Miyawaki, Yada, & Ogawa, 1997), where two antiparallel chains crystallize without any intracrystalline water molecules in an orthorhombic unit cell. However, the crystal structure of mannan II is not as well known due to its semicrystalline state (Chanzy et al., 1984; Marchessault, Taylor, & Winter, 1990; Yui, Ogawa, & Sarko, 1992). It has also been reported that at least two hydrate states exist in mannan II (Heux, Hägglund, Putaux, & Chanzy, 2005).

Studies on the relationship between the structure and physical properties of a material are important for scientific and for industrial understanding. However, there has been little attention paid to resolving the relationship between structure at atomic level and physical properties of mannan. Therefore, we focused on the thermal expansion of mannan, because the thermal expansion behavior is one of the most basic and important physical properties of solid-state materials.

Mannan is often compared to another abundant natural polymer, cellulose, because of the similarities in their chemical structures. They both have a similar conformation of a two-fold ribbon-like helix, except that the configuration of the hydroxyl group at the ring C2 position is different in the two materials: axial in mannan and equatorial in cellulose.

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The thermal expansion behavior of cellulose crystals has been studied, and it has been reported that the anisotropic thermal expansion behavior is closely related to the crystal structure of cellulose (Hori & Wada, 2005, 2006; Wada, 2002). However, to the best of our knowledge, there have been no reports on the thermal expansion of mannan crystals. Therefore, we measured the thermal expansion of mannan I crystals using X-ray diffraction and compared the results to our previous results on the behavior of cellulose crystals.

2. Materials and methods

2.1. Materials

The endosperms of ivory nuts (*Phytelephas* sp.) were ground into a meal, and the powdered sample was purified using an alcohol–benzene and chlorite treatment, as previously reported (Chanzy et al., 1979; Timell, 1957; Wise, Murphy, & d'Addieco, 1946). The mannan was then extracted into a 1.25 M KOH solution over a period of 12 h at room temperature. After filtration, the filtrate was dialyzed against deionized water until neutrality was reached. The filtrate, where the mannan microcrystals were suspended in water, was concentrated by centrifugation, and this was then freeze-dried and stored in a desiccator until use.

2.2. FTIR spectroscopy

Approximately 1 mg of a freeze-dried sample was pressed into a pellet along with 200 mg of potassium bromide, and the pellet was then subjected to Fourier transform infrared (FTIR) measurements. The FTIR spectra were recorded using an accumulation of 64 scans at a resolution of 4 cm^{-1} employing a Jasco FT-IR 615 spectrometer.

2.3. X-ray powder diffraction

Wide-angle X-ray powder diffraction was carried out using a synchrotron radiation of wavelength 0.1 nm at the BL40B2 beam line at the SPring-8 facility at Hyogo in Japan. The powder diffraction patterns were recorded using a camera system equipped with a flat imaging plate (R-AXIS IV^{++}, Rigaku) at room temperature. The camera distance was calibrated using the characteristic *d*-spacings of Si powder.

2.4. X-ray diffraction under heat treatment

X-ray diffraction profiles as a function of temperature were obtained using nickel-filtered Cu Kα radiation with a wavelength 0.15418 nm, from a sealed beam X-ray generator (RINT 2200, Rigaku) operating at a voltage of 36 kV and an excitation current of 50 mA. A point-collimated beam was directed onto the sample and the X-ray profiles were taken using a position sensitive proportional counter (PSPC-10S, Rigaku) positioned at a distance of 30 cm from the sample. The sample was heated stepwise from room temperature to 250 °C using a heating rate between the temperature steps of 5 °C/min. A diffraction profile was recorded at each temperature using an accumulation time of 10 min in a helium atmosphere.

2.5. Data analysis

The peak fitting routine of the X-ray diffraction profiles was carried out using the Levenberg–Marquardt algorithm employing the nonlinear least squares fitting method. A pseudo-Voigt function and a fifth-order polynomial function were used to fit each crystalline peak and the background, respectively.

Accurate *d*-spacings were calculated from the different peak positions, and the unit cell parameters were determined from the *d*-spacings and the indices. For indexing, the orthorhombic unit cell defined by Nieduszynski and Marchessault (1972) was used (Fig. 6). The linear and volume thermal expansion coefficients (TECs), α and β, were determined using the following formulae:

$$\alpha = \frac{1}{l_{T=0}} \cdot \frac{\Delta l}{\Delta T} \tag{1}$$

$$\beta = \frac{1}{V_{T=0}} \cdot \frac{\Delta V}{\Delta T} \tag{2}$$

where l is either the *d*-spacing or the unit cell parameters, V is the volume of the unit cell, and T is the temperature (in °C).

3. Results and discussion

The FT-IR spectrum of the OH stretching region of the crystals of mannan I obtained from ivory nuts (Fig. 1)

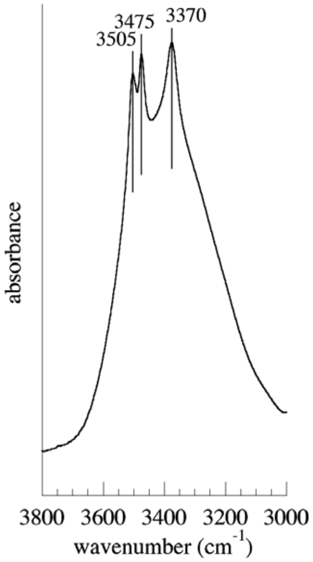

Fig. 1. FTIR spectrum of mannan I in the OH stretching region. Bands occurring at 3505, 3475, 3370 cm^{-1} are assigned to mannan I.

shows three absorption bands occurring at 3505, 3475, and 3370 cm^{-1}. This feature is similar to the previously reported spectrum of mannan I obtained from *Cymopolia* cell walls (Nieduszynski & Marchessault, 1972). However, the two bands occurring at 3505 and 3475 cm^{-1} were well resolved, as shown in Fig. 1. This is because the mannan I crystals prepared from ivory nuts had a higher crystallinity than mannan crystals from *Cymopolia*.

Fig. 2 shows the synchrotron X-ray powder diffraction diagram of the mannan crystals prepared from ivory nuts. The pattern obtained indicates that the sample used in our study was typical of mannan I crystals with a high degree of crystallinity. Seven diffraction rings numbered from the lowest angle (Fig. 2) were observed, whose *d*-spacings were calculated to be 0.671, 0.554, 0.487, 0.442, 0.375, 0.353, and 0.332 nm, respectively. These were indexed as the 101, 110, 111, 200, 210, 211, and 120 reflections according to the orthorhombic unit cell of Nieduszynski and Marchessault (1972). The unit cell parameters obtained from our data were $a = 0.884$ nm, $b = 0.712$ nm, and c (fiber repeat) = 1.030 nm. These seven diffraction rings and the orthorhombic unit cell were used to identify the thermal expansion characteristics of mannan I crystals.

The X-ray diffraction profiles of mannan I crystals at specific temperatures on heating from room temperature to 250 °C are shown in Fig. 3. The seven crystalline peaks observed in the profiles were all shifted toward lower 2θ angles with increasing temperature due to thermal expansion of the mannan I crystals. The peak intensities and widths of all seven peaks did not change during heating, and all the peaks returned to their initial positions on cooling to room temperature. This indicates that mannan I crystals do not undergo thermal decomposition in this temperature range.

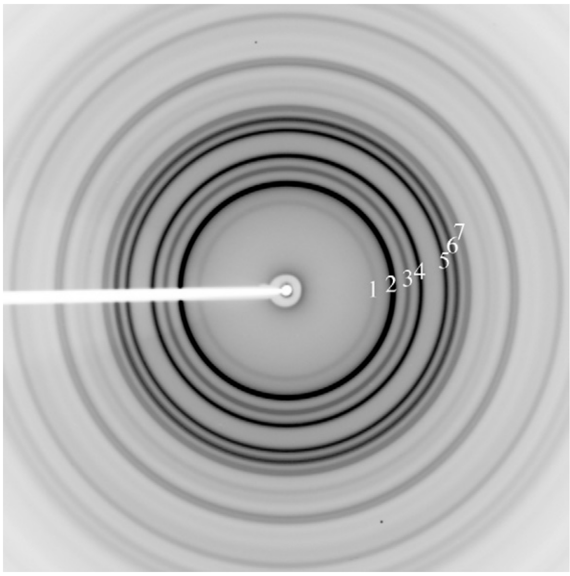

Fig. 2. X-ray powder diffraction pattern of mannan I recorded at room temperature. The seven rings numbered from 1 to 7 are typical of the mannan I diffractions used in this study.

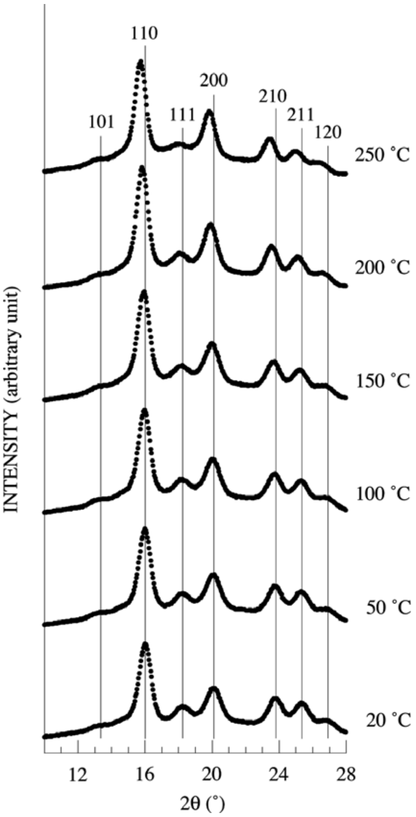

Fig. 3. X-ray diffraction profiles of mannan I at specific temperatures during heating from room temperature to 250 °C.

For a more precise analysis, we calculated the *d*-spacings of the seven peaks using a peak separation method for the X-ray diffraction profiles at each temperature, and changes in the *d*-spacings with temperature are shown in Fig. 4. All the *d*-spacings gradually broadened with increasing temperature, and the gradient showed a distinct increase at a temperature of 130 °C, indicating that a phase transition may occur at this temperature. A similar phase transition has been observed in cellulose II, in that case, the temperature was lower, around 100 °C (Hori & Wada, 2006; Takahashi & Takenaka, 1982).

To determine the thermal expansion coefficient (TEC) below and above this phase transition, we carried out a regression analysis using two connecting lines. The linear TEC values calculated using Eq. (1) are also shown in Fig. 4, and were in the range $0.5\text{–}11.8 \times 10^{-5}\,°\mathrm{C}^{-1}$. The value of the TEC below the phase transition was smaller than that above the phase transition at a temperature of about 130 °C.

The unit cell parameters of the a, b, and c axes at specific temperatures calculated from the *d*-spacings are shown in Fig. 5. The a and b axes gradually increased in length with increasing temperature, showing discontinuities at a temperature of 130 °C, showing the same behavior as the *d*-spacings in Fig. 4. This result indicates that the phase transition occurred at the temperature of 130 °C. In contrast, the c-axis length contracted with increasing temperature. Although the reason for the contraction of

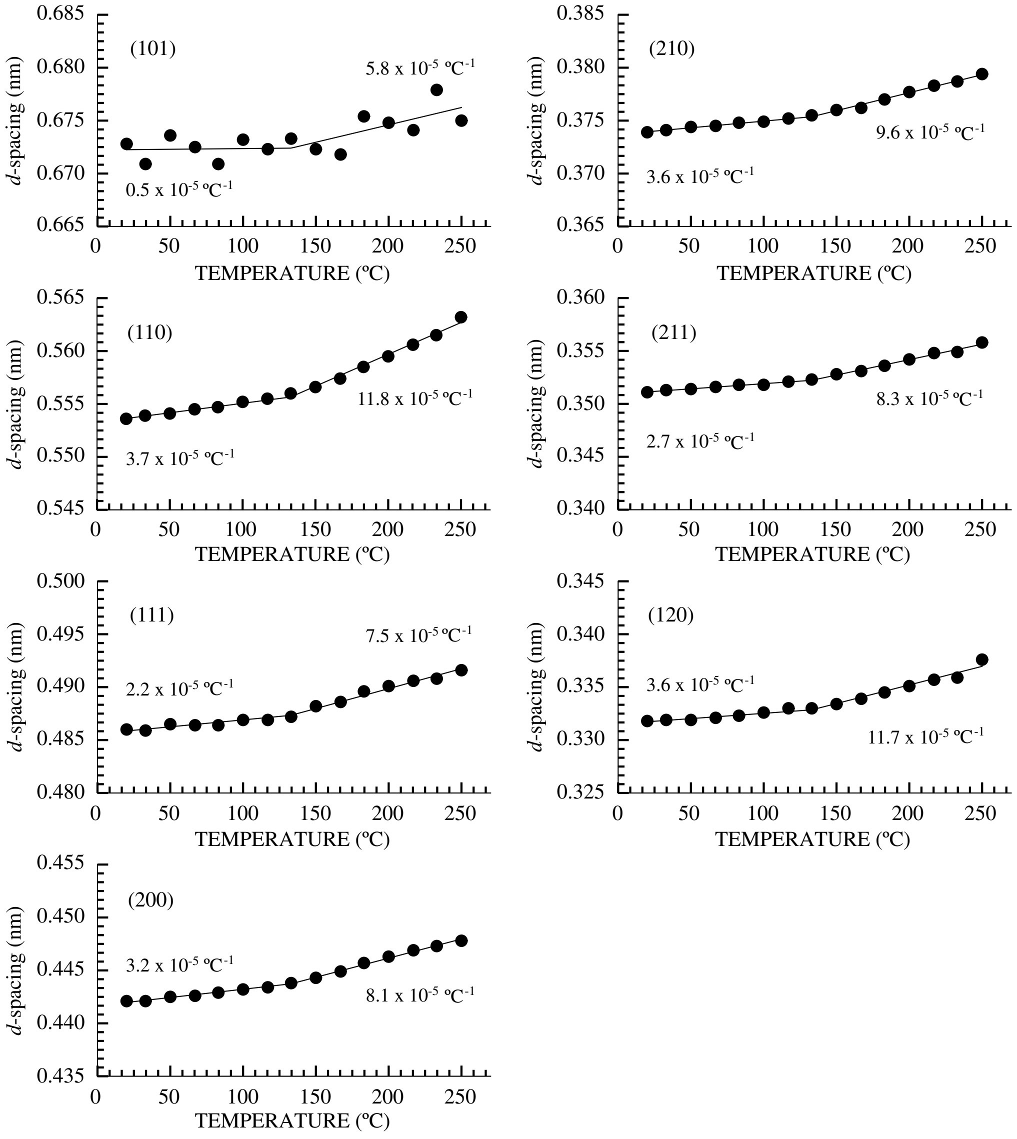

Fig. 4. Change in the *d*-spacing of mannan I during heating from room temperature to 250 °C.

the *c*-axis on heating is not clear, these changes in unit cell parameters with increasing temperature showed an anisotropic thermal expansion occurring between the *a* and *b* axes and the *c*-axis directions, which correspond to the intermolecular hydrogen bonded and covalently bonded directions, respectively. The scatter in the *c*-axis data was high, because only three diffractions with low intensities, the 101, 111, and 211 reflections, were used to calculate the *c*-axis values.

The linear TECs of the *a* and *b* axes below and above the phase transition temperature were also calculated using Eq. (1). The linear TECs below the phase transition temperature were $\alpha_a = 3.5 \times 10^{-5}\,°\mathrm{C}^{-1}$ and $\alpha_b = 3.8 \times 10^{-5}\,°\mathrm{C}^{-1}$. The TECs above the phase transition temperature were $\alpha_a = 8.6 \times 10^{-5}\,°\mathrm{C}^{-1}$ and $\alpha_b = 12.2 \times 10^{-5}\,°\mathrm{C}^{-1}$. The TEC values above the transition temperature were 2–3 times larger than the TEC values below the phase transition temperature. The values of the TEC between the *a* and *b* axes were similar, which showed an isotropic thermal expansion occurred in the lateral directions. This isotropic behavior is ascribed to the crystal structure of mannan I, where intermolecular hydrogen bonds between the O2 and O5 sites exist along both the [1 1 0] and [1 $\bar{1}$ 0] directions, as shown in Fig. 6. This behavior is in contrast to the reported anisotropic thermal expansion of cellulose I_β crystals in the lateral directions (Wada, 2002). In cellulose I_β, intermolecular hydrogen bonds only exist along the *b*-axis direction, but they do not exist along the *a*-axis direction. Thus, cellulose I_β crystals show a 20 times higher expansion along the *a*-axis direction than along the *b*-axis direction. From the TEC data of previous cellulose experiments and the mannan data in this study, we conclude that the thermal expansion behavior of mannan is closely related to its crystal structure, and especially to the intermolecular hydrogen bonding in this compound.

In addition to the unit cell parameters, the area of the *ab* plane, *S* and the volume of the unit cell, *V*, at specific temperatures were also calculated using Eq. (2), and the results

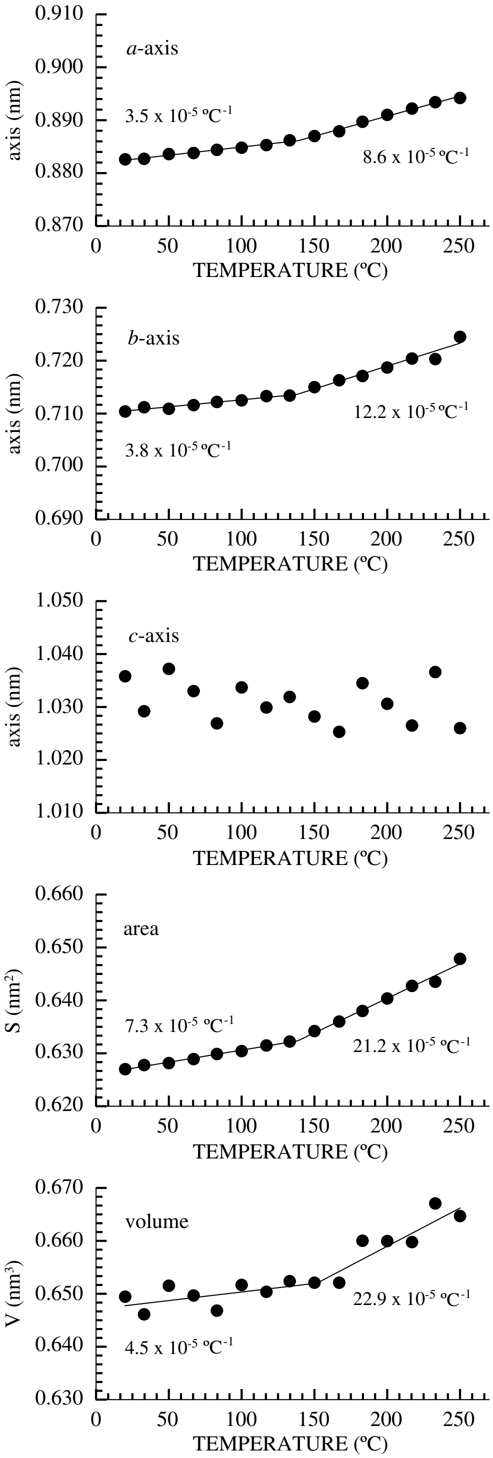

Fig. 5. Change in the unit cell parameters, the area of the *ab* plane, S, and the volume of the unit cell, *V*, of mannan I during heating from room temperature to 250 °C.

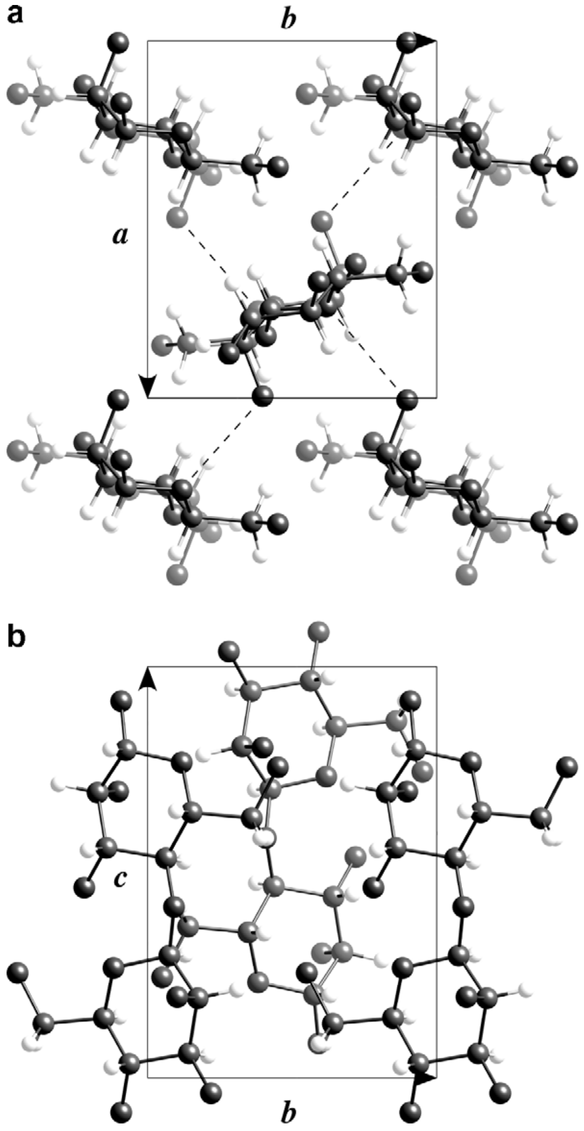

Fig. 6. The chain arrangement and unit cell of mannan I viewed parallel to the chain axis (a) and the *a*-axis (b) (Nieduszynski & Marchessault, 1972). The dotted lines are a schematic representation of the intermolecular hydrogen bonds.

are shown in Fig. 5. Changes in the lateral area, *S*, and volume, *V*, of the unit cell also show a discontinuity occurring at a temperature of about 130 °C, which indicates the existence of a phase transition at this temperature. The lateral area, *S*, also increased with increasing temperature. In total, *S* increased by 3.3% on increasing the temperature from room temperature to 250 °C. This is smaller than the reported value of 4.5% in highly crystalline cellulose I_β (Wada, 2002). The volume, *V*, increased with increasing temperature, showing an increase of 2.3% at a temperature of 250 °C, which is also smaller than the increase in volume of 3.7% reported for cellulose I_β (Hori & Wada, 2005). The small expansion of mannan I compared to cellulose I_β indicates that mannan I is a more thermally stable structure than cellulose I_β.

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