ORIGINAL ARTICLE

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Mechanical interaction between cellulose microfibril and matrix substance in wood cell wall determined by X-ray diffraction

Abstract We investigated mechanical interactions between the cellulose microfibril and the matrix substance in wood cell walls. X-ray diffraction measurements showed that the peak positions of (200) and (004) from cellulose crystals in wood cell walls tended to shift lower and higher toward 2θ, respectively, during water desorption in wood. From our simulations, it is shown that the peak shift of (200) during water desorption is not due to changes in the scattering pattern of the amorphous substance or to lateral expansion of the cellulose crystals due to the Poisson effect in the cellulose microfibril, which is compressed in the molecular chain direction as the amorphous substance shrinks. This suggests that the cellulose microfibril expands transversely during water desorption in the wood cell wall, and that there is a mechanical interaction between the cellulose microfibril and the matrix substance.

Key words Cellulose microfibril · Matrix substance · Wood cell wall · X-ray diffraction · Water desorption

Introduction

Many investigations have been performed about the influences of environmental and histological factors, including temperature, moisture content, tree species, and cambial age of wood, on the mechanical properties of wood as an engineering material. In addition, development in the technique of microscopic observation in the 20th century helped to reveal that each cell wall lamella could be approximated as a two-phase structure consisting of the framework of cellulose microfibrils embedded in matrix substances. Thereafter, many researchers, such as Barber and Meylan,[1] Barrett et al.,[2] Cave,[3] and Koponen et al.,[4] formulated

origins of various mechanical properties of wood on the basis of the above-mentioned two-phase structural model, assuming that there is a mechanical interaction between the framework of cellulose microfibrils and the matrix substance.

Mechanical properties of wood change considerably with moisture content; examples include anisotropic swelling and shrinkage,[1,5–7] the moisture dependency of Young's modulus,[8–10] and mechano-sorptive creep.[11,12] The reason for such changes is probably that the properties of cell wall components change with water adsorption or desorption as pointed out by earlier authors, such as Barber and Meylan.[1] However, water molecules hardly influence the cellulose microfibril because it consists of highly oriented cellulose crystals. On the other hand, the matrix substance, which mainly consists of noncrystalline cellulose, hemicellulose, and lignin, swells or shrinks isotropically. If there is a mechanical interaction between the cellulose microfibril and the matrix substance, it is possible that swelling or shrinking of the matrix substance affects the cellulose microfibril; however, almost no experimental verification for it has yet been given.[13]

X-ray diffraction measurement is useful for investigating the fine composite structure in wood cell walls because they contain much crystalline cellulose. Previous studies indicate that the change of moisture content affects the X-ray diffraction patterns of wood.[13–16] For equatorial X-ray diffraction patterns, Nishimura et al.[16] reported that increasing moisture content changes the scattering pattern of amorphous substances, and shifted the peak position of (200) higher toward 2θ. Because the diffraction peaks from (200) occur very near the scattering pattern from amorphous substances, it is reasonable to consider that a change in the scattering pattern due to increasing moisture content would shift the peak position of (200) to some extent. However, if all of the peak shift of (200) cannot be explained by the change in the scattering pattern from amorphous substances, we need to consider that a transverse dimension of the cellulose microfibril varies during water adsorption or desorption. Sobue et al.[13] pointed out that the shrinking matrix compresses the cellulose microfibril in the molecular

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chain direction, causing lattice distortion, and induces a peak shift of (004). It is reasonable to suggest that the peak shift of (200) is caused by such lattice distortion along the molecular chain in view of the Poisson effect of the cellulose microfibril, or by the transverse shrinkage of the matrix. In either case, these possibilities suggest that there is a certain mechanical interaction between the framework of cellulose microfibrils and the matrix substance in wood cell walls.

This study examined the mechanical interaction between the cellulose microfibril and the matrix substance using precise measurements of the peak shifts of (200) and (004) that occur during water desorption in wood. Moreover, we simulated the influence of the change in the scattering pattern from amorphous substances on the peak position of (200), and we also discuss the transverse strain of the cellulose microfibril due to the Poisson effect caused by longitudinal compression. Thus, we provide experimental verification of cell wall mechanics based on the two-phase structural model.

Experimental

Sample description

All the wood samples were prepared from the sapwood of 25-year-old sugi (*Cryptomeria japonica* D. Don) grown in the Nagoya University Forest. For X-ray diffraction measurements of (200), three types of wood samples were used: (1) sawdust powder, 50–250 μm in diameter, (2) a 200-μm-thick flat-sawn section of early wood, and (3) holocellulose powder delignified with acidified sodium chlorite.[17] Both of the powdered samples were made into pellets approximately 1.3 cm in diameter and 1.5 mm thick. As a control, commercial grade microcrystalline powder (Merck) was used to measure both (200) and (004).

In our measurements, the X-ray diffraction intensities from the wood powders were too low to detect the peak position of (004) precisely. Therefore, only a 200-μm-thick crosscut section of early wood was used to measure it.

Moisture conditioning

The pellet made of wood powders was too brittle to bear repeated measurement. Therefore, the samples were evenly divided into five groups. The moisture content in each group was equilibrated inside a desiccator at the respective relative humidity. Fresh water, saturated aqueous solutions of KNO_3 and NaCl, silica gel grain, and P_2O_5 powder were used to control the relative humidity. Ideally, an identical sample should be used to measure the peak shift due to water desorption. However, the pellets of wood powder used were too mechanically brittle to be subjected to repeated measurement from H_2O to P_2O_5. The weight of the sample (W) was measured at each equilibrium condition. In order to prevent any change in the moisture content during X-ray measurements, moisture-conditioned air was circulated through the sample cell.

X-ray measurements

X-ray measurements were made with the reflection technique using an X-ray diffractometer (Shimadzu XD-D1w). The incident X-ray was CuKα with a power of 35 kV, and 35 mA was passed through a Ni filter. The diffraction intensities for (200) and (004) were registered in the angular range from 20 to 24 degrees and from 32 to 37 degrees, respectively. The intensity curves, digitized and corrected for air scattering, polarization, and Compton scattering, and normalized into electron units, were used as input data for the computer program.

The wood sample used to measure (200) was fixed in a sample holder so that the fiber axis was vertical. Soon after measuring, the sample was dried for 24 h in an oven at 105°C, and then the oven-dried weight (W_0) was obtained. The moisture content (M) of the sample was calculated using the formula:

$$M = \frac{W - W_0}{W_0} \times 100(\%)$$

The peak position of (200) in an identical air-dry wood section was measured 11 times in order to examine the reproducibility of the X-ray measurements. Thereby, the average peak position of (200) was calculated as 22.452 degrees (SD = 0.056 degrees, $n = 11$). This result suggests that the error occurring by the attachment or detachment of the sample is extremely small.

Simulation of the virtual X-ray diffraction pattern of wood

Using a personal computer, we numerically drew the typical diffraction patterns from several crystal reflections and the scattering pattern from the amorphous substance in wood cell wall, and superimposed all of them to obtain a virtual X-ray diffraction pattern of wood. This enabled us to simulate how the apparent peak position of (200) would be affected by a change in the scattering pattern of the amorphous substance. We assumed that the apparent peak position of (004) would not be affected by the change of the scattering pattern of the amorphous substance, because the peak position of (004) was very distant from that of the amorphous substance.

The virtual X-ray diffraction pattern of wood consists of the diffraction pattern from (200), ($\bar{1}$10), and (110), and the scattering pattern of the amorphous substance. The profile of each diffraction pattern or scattering pattern was approximated by Gaussian

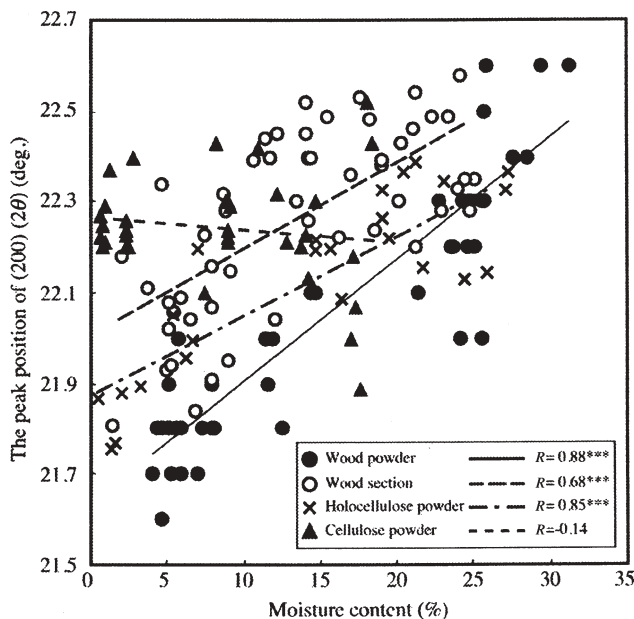$$I_G(2\theta) = I_{max} \cdot \exp\left[-4(\ln 2) \cdot \left(\frac{2\theta - 2\theta_0}{\omega}\right)^2\right]$$

Fig. 1. The peak shift of (200) during water desorption

Fig. 2. The peak shift of (004) during water desorption

where I_{max} is the maximum intensity, $2\theta_0$ is the peak position, and ω is the half width. The values of these three parameters were assumed using experimental data.

Results and discussion

Experimental results

Figure 1 shows the relationship between the peak position of (200) and the moisture content of various samples. The peak position of the cellulose microcrystalline powder did not vary with the moisture content. Because moisture-conditioned air was circulated through the sample cell to prevent any change in the relative humidity during the X-ray measurements, this result indicates that water molecules in the air do not influence the peak position of (200). For the wood powder, holocellulose powder, and wood section, the peak position shifted lower toward 2θ as the moisture content decreased. The magnitude of the peak shift of the wood samples was clearly larger than that of the holocellulose powder. These results imply that the peak shift of (200) is correlated with the proportion of matrix substances in the samples.

Figure 2 shows the relationship between the peak position of (004) and the moisture content. The peak position of (004) of the cellulose microcrystalline powder remained constant with varying moisture content, as with (200). Unlike the (200) reflection, the peak position of the wood section shifted higher toward 2θ as the moisture content decreased. Table 1 shows the magnitudes of the peak shifts of (200) and (004) as the moisture content decreased from 25% to 5%.
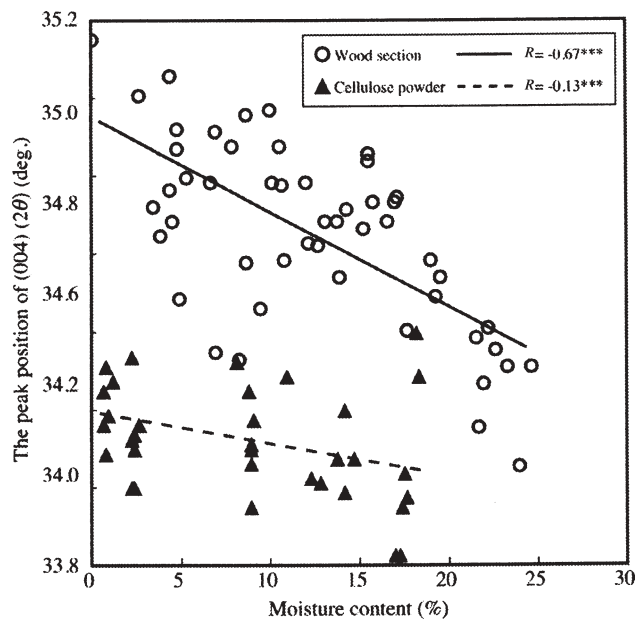
Table 1. The observed peak shifts of (200) and (004) of the diffraction angle (2θ) when the moisture content decreases from 25% to 5%

Sample (sugi)	$\Delta(2\theta)_{200}$ (degrees)	$\Delta(2\theta)_{004}$ (degrees)
Wood powder	−0.54	–
Wood section	−0.39	0.49
Holocellulose powder	−0.36	–

Simulated results

Using ball-milled wood powder, Nishimura et al.[16] revealed that the peak position of the scattering pattern of the amorphous substance shifts from 18.2 to 21.5 degrees with water adsorption, which is near the peak position of (200). Their results suggest that the peak position of (200) varies with the change in the scattering pattern of the amorphous substance, because both X-ray diffraction patterns often overlap. Therefore, we tried to simulate how the apparent peak position of (200) would be affected by the change of the scattering pattern of the amorphous substance.

First, we postulated that only the peak position of the scattering pattern shifts along the equator during water adsorption, as shown in Fig. 3a. Case (a) in Fig. 4 shows the simulated result on the effect of a change in the peak position of the scattering pattern on the apparent peak position of (200). The apparent peak position of (200) becomes higher as that of the scattering pattern increases. If we assume that the peak position of the scattering pattern shifts from 18.2 to 21.5 degrees during water adsorption with reference to Nishimura et al.,[16] the peak shift of (200) would amount to 0.041 degrees higher toward 2θ in case (a). Even if the peak position of the scattering pattern shifted beyond
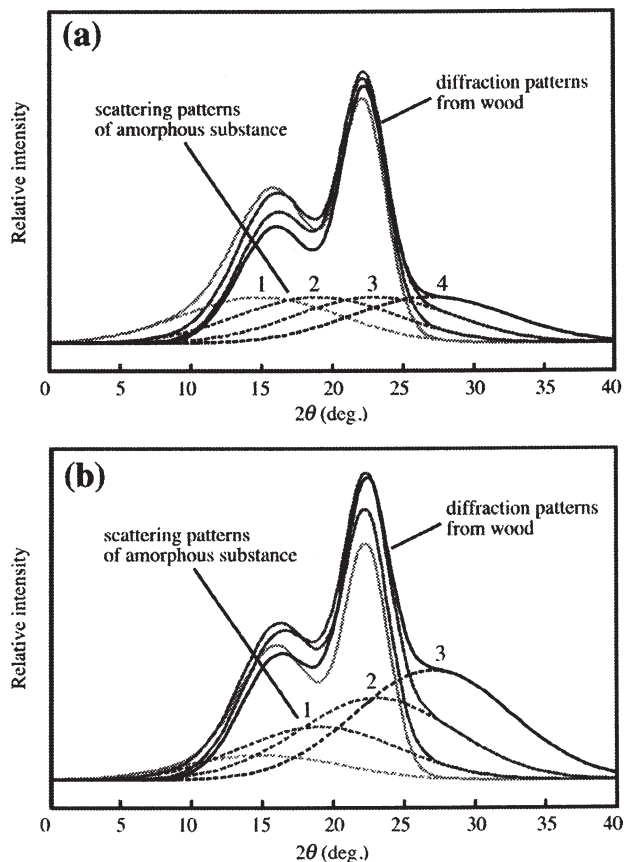
Fig. 3. Simulation of the effect of changes in the peak position (**a**), and changes in the peak position and maximum intensity of the scattering pattern (**b**) of the amorphous substance on the X-ray diffraction pattern of wood. We postulated that the scattering pattern tends to shift from *1* to *4* or *3* during water adsorption

Fig. 4. Simulated results on the effect of changes in the scattering patterns of the amorphous substance on the apparent peak position of (200). *Case a*, only the peak position of the amorphous substance varies during water adsorption (see Fig. 3a). *Case b*, both the peak position and the maximum intensity of the amorphous substance vary during water adsorption (see Fig. 3b). * The range marked by the *asterisk* is that of the peak shift of the scattering pattern of the amorphous substance[16]

this range, the peak shift of (200) would not exceed 0.12 degrees in this case. Therefore, this hypothesis is insufficient in explaining the experimental results shown in Table 1.

We then postulated that both the peak position and the maximum intensity of the scattering pattern changed in parallel during water adsorption, as shown in Fig. 3b. In this simulation, we assumed that the intensity of the scattering pattern of the amorphous substance increases with water adsorption. Case (b) in Fig. 4 shows the simulated result on the effects of changes in the peak position and the maximum of the scattering pattern upon the apparent peak position of (200). In this case, the peak shift of (200) is 0.048 degrees higher toward 2θ when we assume that the peak position of the scattering pattern shifts from 18.2 to 21.5 degrees with reference to Nishimura et al.[16] In addition, in this simulation, the maximum peak shift of (200) is less than 0.22 degrees. This case is also insufficient in explaining the experimental results shown in Table 1.

Discussion

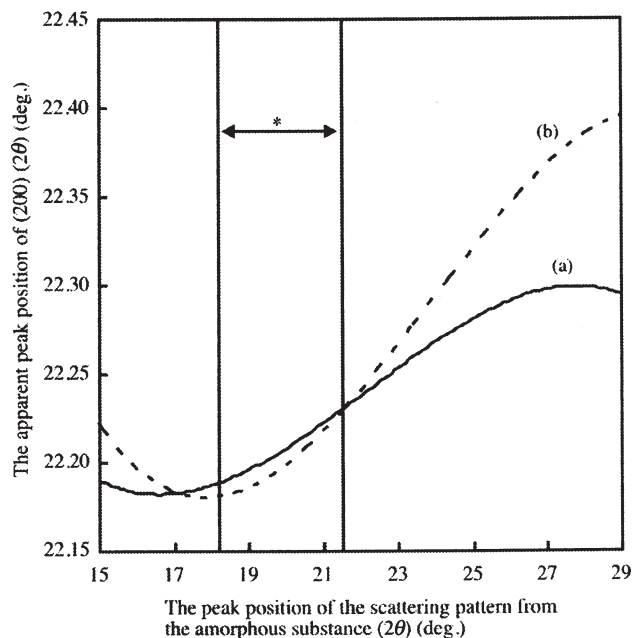In our simulations, the changes in the peak position and the maximum intensity of the scattering pattern exceeded the actual results, nevertheless, the simulations cannot fully explain the experimental results. This suggests that the apparent peak shift of (200) is caused not only by a change in the scattering patterns of the amorphous substance, but also by distortion of the lattice spacing of the (200) plane. Because the peak position of (004) is very distant from that of the amorphous substances, it is natural to consider that the main cause of the peak shift of (004) is distortion of the lattice spacing of the (004) plane.

The lattice spacing (D) is expressed by the Bragg equation as follows:

$$D = \frac{\lambda}{2 \cdot \sin\theta}$$

where λ is the X-ray wavelength of the incident beam (0.154 nm, CuKα), and θ is the Bragg angle. Therefore, a shift of the (200) peak lower toward 2θ means that in wood cell wall the lattice spacing of the (200) plane is increasing, while a shift of the (004) peak higher toward 2θ means that the lattice spacing of the (004) plane is decreasing.

With respect to the peak shift of (004), Sobue et al.[13] postulated that the shrinking matrix, which is tightly linked to the cellulose microfibril, compresses the cellulose microfibril in the molecular chain direction, causing the lattice spacing of the (004) plane to decrease during water desorption in wood. Then, the question of what causes the lattice spacing of the (200) plane to increase during water desorp-

tion becomes important. One possible reason is that the cellulose microfibril tends to expand laterally due to the Poisson effect of the axially compressed cellulose microfibril, increasing the lattice spacing of the (200) plane. In our study, the peak position of (004) increased 0.49 degrees when the moisture content decreased from 25% to 5%, which is equivalent to a contractive strain (ε_L) of 1.53%. If the strain in the (200) plane (ε_T) is caused only by the Poisson effect from the axially compressed cellulose microfibril, its strain can be calculated using the following equation:

$$\varepsilon_T = -\varepsilon_L \cdot \nu_{LT} \tag{1}$$

where ν_{LT} is Poisson's ratio of lateral expansion to the axial compression in the cellulose microfibril crystal. When $\nu_{LT} = 0.1$[18] or 0.38[19] are substituted into Eq. 1 on the basis of references, the calculated value of ε_T is 0.153% or 0.581%, respectively. According to Table 1, however, the peak shift of (200) is equivalent to transverse strains of 2.51% (wood powder) or 1.52% (wood section), which differ considerably from the ε_T calculated from the Poisson effect of axially compressed cellulose. This suggests that the cellulose microfibril expands transversely during water desorption in wood cell walls. Because the cellulose microfibril crystal seldom reacts with water molecules, this expansion should be attributed to the matrix substance filling in the gaps between the cellulose microfibrils. The mechanism of this process is currently unknown. One possibility is that the swelling matrix substance compresses the cellulose microfibril transversely and then the compression is released by the drying shrinkage of the matrix. A detailed experiment to test this theory is required. However, this study confirms the existence of a mechanical interaction between the cellulose microfibril and the matrix substance in wood cell walls.

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