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## Change in mechanical interaction between cellulose microfibril and matrix substance in wood cell wall induced by hygrothermal treatment

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**Abstract** To investigate in detail the mechanical interactions and associations between cellulose microfibrils (CMFs) and the matrix substance, we measured the dimensional changes in cellulose crystals in wood cell walls after different treatments. The transverse expansion of CMFs observed after hygrothermal treatment and subsequent drying suggests that the matrix substance compresses the CMFs transversely under green conditions. However, as heat treatment breaks or weakens the association of the CMFs and the matrix substance, under hygrothermal treatment and drying at high temperature the matrix substance cannot compress the CMFs in the direction of the chain.

**Key words** Cellulose microfibril · Matrix substance · Wood cell wall · X-ray diffraction · Mechanical interaction

### Introduction

Our previous report<sup>1</sup> discussed the mechanical interactions between cellulose microfibrils (CMFs) and the matrix substance in the wood cell wall during water desorption. In general, it is considered that drying wood below the fiber saturation point changes the mechanical properties of the amorphous matrix substance in the cell wall, but has little effect on the crystalline CMFs. However, X-ray measurements of the 200 and 004 *d*-spacings of cellulose crystals in the cell wall during water desorption revealed that CMFs shrink longitudinally and expand transversely with decreasing moisture content. Similar observations of longitudinal shrinkage of CMFs have been reported by Sobue et al.,<sup>2</sup> who suggested that the shrinking matrix substance, which is tightly bonded with the crystalline cellulose, compressed

the cellulose crystals longitudinally during water desorption. Regarding the association between the CMFs and the matrix substance, Shigematsu et al.<sup>3</sup> reported that the affinity of cellulose for hemicellulose is greater than that for lignin. Moreover, on the basis of softening measurements of wood pulp samples, Salmén and Olsson<sup>4</sup> suggested that in wood, xylan is associated with lignin, whereas glucomannan is more associated with cellulose. These results suggest that the mechanical interactions between the CMFs and the matrix substance induce longitudinal compression and transverse tension in CMFs during drying.

However, the idea that transverse tension is generated in CMFs is problematic if one considers transverse Young's moduli of the CMFs and the matrix substance. According to previous data, the transverse Young's moduli of cellulose crystals and the matrix substance are 27.2 GPa<sup>5</sup> and 2–4 GPa,<sup>6–8</sup> respectively, meaning that the CMFs are significantly stiffer than the matrix substance. Therefore, it would be difficult for the shrinking matrix substance to pull the CMFs transversely. Another possible explanation for the transverse expansion of CMFs is that CMFs are already compressed transversely by the swollen matrix substance when under green conditions. If this explanation is correct, the compressive stress induced in the CMFs should be released as the matrix substance shrinks during drying, and the CMFs should expand transversely. One method to verify this idea is to release the internal stress of the matrix substance without drying the wood. It is known that the matrix substance in the cell wall softens when green wood is heated, and it has also been reported that the residual stress inside a green log can be reduced by heat treatment.<sup>9</sup>

To verify the above possibility, we measured the changes in the 200 and 004 *d*-spacings of cellulose crystals in wood cell wall caused by hygrothermal treatment. Moreover, to investigate the influence of heat treatment on the association between the CMFs and the matrix substance, the changes in their *d*-spacings induced by drying at high temperature (105°C) were measured and compared with those caused by drying at room temperature. On the basis of the results, we discuss in detail the mechanical interactions and associations between the CMFs and the matrix substance.

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## Experimental

Flat-sawn sections (2 mm thick) of earlywood and 5-mm-thick crosscut sections were used to measure the 200 and 004  $d$ -spacings, respectively. The wood samples were prepared from sapwood of 25-year-old sugi (*Cryptomeria japonica* D. Don) trees grown in the Nagoya University Forest. The samples were conditioned in a small cabinet with H<sub>2</sub>O for 1 month to allow them to reach the fiber saturation point, and then the  $d$ -spacings of each sample were measured. Each sample type was then divided into three groups to perform X-ray measurements after either hygrothermal treatment, drying at high temperature, or drying at room temperature.

### Hygrothermal treatment

The samples were wrapped in wet paper, sealed in a stainless-steel cylinder with a small amount of water, and heated in an electric oven at 105°C for 48 h. The samples were then held in a small cabinet with H<sub>2</sub>O until reaching room temperature, and the  $d$ -spacings were measured. The samples were then dried in a desiccator with silica gel and X-ray measurements were performed again.

### Drying at high temperature

The samples were dried in an electric oven at 100°C for 24 h, held in a desiccator with silica gel until reaching room temperature, and then the  $d$ -spacings were measured.

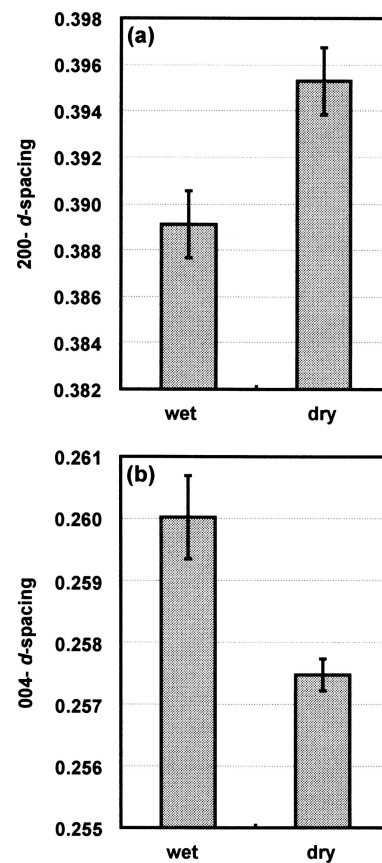
### Drying at room temperature (control)

The samples were dried in a desiccator with silica gel at room temperature. After the weights of the samples had equilibrated, the  $d$ -spacings were measured.

### X-ray measurements

The weight of each sample was measured at the time of the X-ray measurement. After all of the experiments had been completed, each sample was dried at 105°C in an oven for 24 h and the oven-dried weight was measured. The moisture content of the sample at each step was calculated from those weights.

All X-ray measurements were made with the reflection technique using an X-ray diffractometer (Shimadzu XD-D1w) under the following conditions. The incident X-ray radiation was from the Cu K $\alpha$  band ( $\lambda = 0.154$  nm) with a power of 35 kV and 35 mA passed through a Ni filter, and collimated by the slit of 0.1 degree. The scattering angles ( $2\theta$ ) for the 200 and 004 reflections were 20–24 degrees and 32–37 degrees, respectively. The wood samples for the 200 reflection were fixed in a sample holder so that the fiber axis was vertical. To prevent changes in the moisture content during the X-ray measurements, moisture-conditioned air



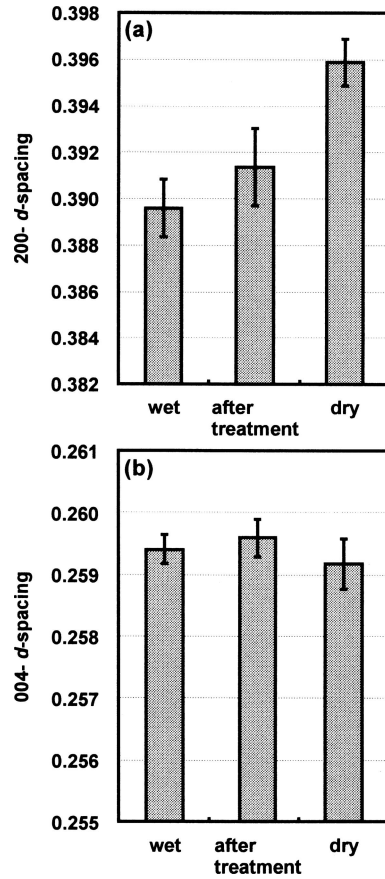
**Fig. 1a,b.** Changes in the  $d$ -spacings induced by drying at room temperature. **a** 200  $d$ -spacing and **b** 004  $d$ -spacing. Bars, standard deviation

was circulated through the sample cell. The  $d$ -spacings were calculated using the Bragg equation on the basis of the peak position of the 200 or 004 plane in the obtained equatorial diffraction curve. As shown in our previous report,<sup>1</sup> the error induced by the attachment or detachment of a sample is extremely small.

## Results and discussion

Figure 1 shows the changes in the  $d$ -spacings of cellulose crystals in the wood cell wall triggered by drying at room temperature (control). The changes in the 200 and 004  $d$ -spacings represent the dimensional changes of cellulose crystals in the transverse and longitudinal directions, respectively. The CMFs in the cell wall were observed to expand transversely (Fig. 1a) and contract longitudinally (Fig. 1b), consistent with our previous results.

Figure 2 shows the changes in the  $d$ -spacings of cellulose crystals induced by hygrothermal treatment and subsequent drying at room temperature. The hygrothermal treatment resulted in a small transverse expansion in the CMFs in spite of the fiber-saturated condition (Fig. 2a), and the significance of the difference in the 200  $d$ -spacing before and after treatment was at the 1% level. However, the longitu-

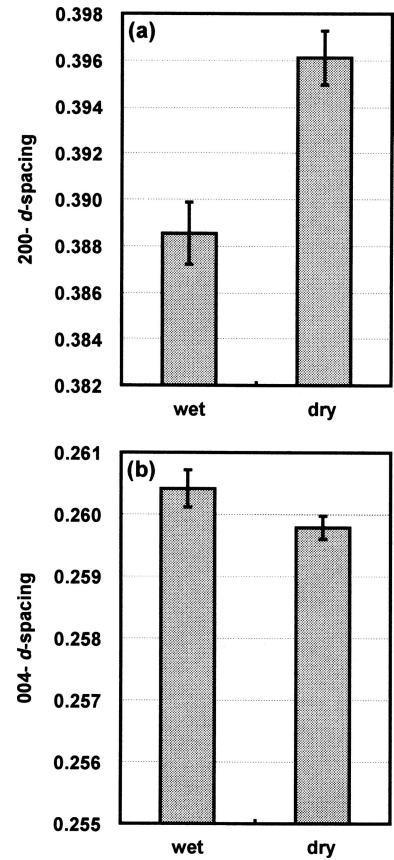


**Fig. 2a,b.** Changes in the *d*-spacings induced by hygrothermal treatment and subsequent drying at room temperature. **a** 200 *d*-spacing and **b** 004 *d*-spacing. Bars, standard deviation

dinal dimension of the cellulose crystals in the cell wall was almost unaffected, not only by the hygrothermal treatment but also by the subsequent drying at room temperature (Fig. 2b).

Figure 3 shows the changes in the *d*-spacings of cellulose crystals caused by drying at high temperature. The CMFs expanded transversely during drying at either high temperature or room temperature, and the average strains were similar, as shown in Table 1, which lists the average strains of the *d*-spacings caused by the different treatments. In contrast, slight longitudinal shrinkage of the CMFs was observed. However, in this case the strain was much smaller than that induced by drying at room temperature.

It is thought that cellulose crystals are not influenced by moisture and do not contract actively during drying. Therefore, the longitudinal contraction of the CMFs while drying at room temperature is probably the result of compressive stress induced by the shrinking matrix substance. However, the observation that the longitudinal dimension of the cellulose crystals is less influenced by hygrothermal treatment and drying at high temperature than by drying at room temperature suggests that the heat treatment breaks or weakens the association between the CMFs and the matrix substance. Thus, the CMFs do not shrink longitudinally by drying at room temperature after hygrothermal treatment.



**Fig. 3a,b.** Changes in the *d*-spacings induced by drying at high temperature. **a** 200 *d*-spacing and **b** 004 *d*-spacing. Bars, standard deviation

**Table 1.** The average strains (%) of cellulose crystals caused by different treatments

Treatment	Treatment	Average strain (%)	
		(200)	(004)
Drying at room temperature	Wet → dry	1.59	-0.98
Hydrothermal treatment	Wet → after treatment	0.46	-0.07
	Wet → dry	1.62	-0.09
Drying at high temperature	Wet → dry	1.94	-0.24

There are two possible explanations for the transverse expansion of the CMFs during room-temperature drying. First, the CMFs could be pulled transversely by the shrinking matrix substance during drying. Second, the CMFs may already be compressed transversely by the swollen matrix substance under green conditions. However, the results of the hygrothermal treatment eliminate the former possibility, because the CMFs expanded during treatments that did not include drying. This suggests that the matrix substance is softened by the hygrothermal treatment and the compressive stress on the CMFs is relaxed. Thereby, the CMFs

expand transversely, without the drying shrinkage of the matrix substance. Moreover, because some compressive stress probably remains after treatment, the CMFs further expand transversely during subsequent drying at room temperature. This idea is supported by the fact that the CMFs expanded transversely during drying at high temperature even though heat treatment breaks or weakens the association between the CMFs and the matrix substance. This study used normal wood samples of sugi in which microfibril angle is low. In further study, similar measurements in compression and tension wood will clarify the effect of the microfibril angle and give informative results about the effects of growth stress on CMFs in the wood cell wall.

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## References

1. Abe K, Yamamoto H (2005) Mechanical interaction between cellulose microfibril and matrix substance in wood cell wall determined by X-ray diffraction. *J Wood Sci* 51:334–338
2. Sobue N, Shibata Y, Mizusawa T (1992) X-ray measurement of lattice strain of cellulose crystals during the shrinkage of wood in the longitudinal direction (in Japanese). *Mokuzai Gakkaishi* 38:336–341
3. Shigematsu M, Morita M, Higuti M, Sakata I (1994) Interfacial bond strength between woody polymers. *Mokuzai Gakkaishi* 40:718–724
4. Salmén L, Olsson AM (1998) Interaction between hemicelluloses, lignin and cellulose: structure–property relationships. *J Pulp Pap Sci* 24:99–103
5. Mark RE (1967) Cell wall mechanics of tracheids. Yale University Press, New York, p. 119
6. Cousins WJ (1976) Elastic modulus of lignin as related to moisture content. *Wood Sci Technol* 10:9–17
7. Cousins WJ (1978) Young's modulus of hemicellulose as related to moisture content. *Wood Sci Technol* 12:161–167
8. Srinivasan PS (1941) The elastic and thermal properties of timber. *Quart J Indian Inst Sci* 4:222–314
9. Nogi M, Yamamoto H, Okuyama T (2003) Relaxation mechanism of residual stress inside logs by heat treatment: choosing the heating time and temperature. *J Wood Sci* 49:22–28