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Variation of microfibril angles and chemical composition: Implication for functional properties

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Wood cell walls are a composite material consisting of cellulose, hemicellulose, lignin and other minor components, such as pectin and extractives. Two main factors, cellulose microfibril angle (MFA) in S_2 layer (thickest layer) and chemical composition, govern functional properties of the cell wall such as Young's modulus and growth-stress. Recently it was suggested that a change of MFAs resulted in the change of required mechanical properties such as stiffness or flexibility [1–3]. The relationship between growth-stress and MFA and chemical composition has also been discussed [4, 5]. Reaction wood is one of the adaptations required for mechanical balance in wood, which forms in leaning stems or branches. The reaction wood in softwood, compression wood, is found on the lower side of leaning stems or branches. It has a higher MFA and more abundant lignin than normal wood. On the other hand in hardwood, tension wood forms on the upper side. Typical tension wood has cellulose-rich G-layer, which consists of highly longitudinally orientated microfibrils. A branch is often displaced downward by its own weight or snow and ice. The function of the reaction wood in the branch is to maintain it in its proper orientation. In this study, change of MFA and chemical composition were investigated by small angle X-ray scattering (SAXS) and FT-IR.

Samples used for SAXS and FT-IR were taken from a branch of *Cryptomeria japonica* (softwood) and *Liriodendron tulipifera* (hardwood) growing at the Wood Research Institute, Kyoto University. The softwood branch was cut into four disks, 30–60 cm distance from each other. The largest softwood sample had 10 annual rings, the second 8, the third 4 and the smallest 3. A hardwood branch was cut into 8 disks 40–60 cm from each other. 14 annual rings were found in largest disk. From the second to the eighth one, the number of annual ring was 12, 10, 9, 7, 4, 3, 2, 2, respectively. In both cases areas less affected by knots were chosen. 1 mm thick plates in the radial direction were prepared from the different parts of the branches. SAXS measurements were done at Synchrotron Radiation Facility (Spring-8, beamline: BL40B2, Harima, Hyogo, Japan). The longitudinal and radial plane of the sample was set at 45° to the incident beam and SAXS patterns were recorded on an imaging plate (active area 300 × 300 mm^2, pixel size 100 × 100 mm^2) for a 10-min exposure. The camera length was set at 1000 mm in general and the minimum effective Q range was approximately 0.01 $Å^{-1}$ with a wavelength 1.2 Å. Fig. 1 shows a typical SAXS pattern and an azimuthal intensity distribution obtained

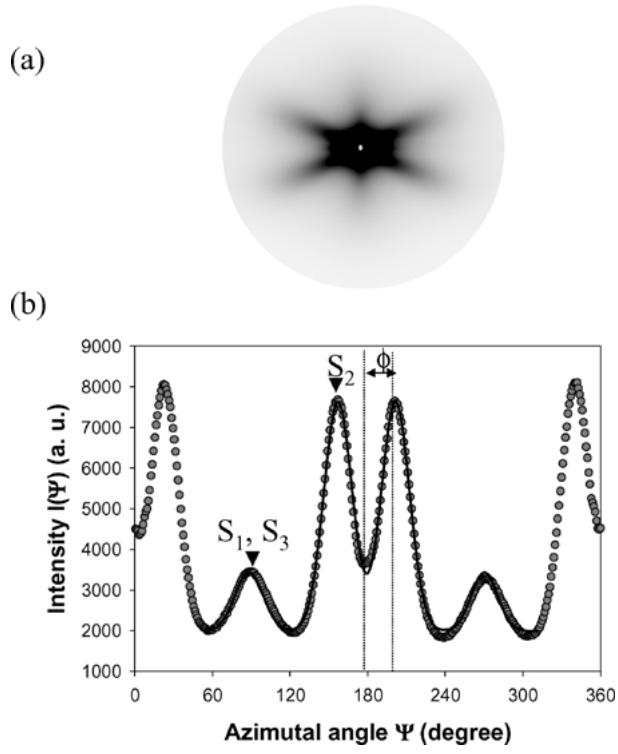

Figure 1 (a) Typical SAXS image and (b) azimuthal distribution (circle marker) from (a). Solid line is least-squares fitting.

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by the FIT2D program [6]. (I (Ψ), where the azimuthal angle $\Psi = 180^\circ$ corresponds to the cell axis direction in Fig. 1b) integrated from 0.151 $Å^{-1}$ to 0.177 $Å^{-1}$ at Q range ($Q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle). In the analysis, two Gaussian functions centered at $180^\circ \pm \Phi_1$ and $180^\circ \pm \Phi_2$ were fitted to the experimental curve by a least squares routine. The two distributions (Φ_1, Φ_2) on the azimuthal intensity distribution arise from S_2 layer, and S_1 plus S_3 layer as indicated in Fig. 1a. Accordingly, Φ_1 (dashed lines in Fig. 1b) corresponds to the distribution from MFA in S_2 layer. The conversion of Φ_1 to MFA (μ) and Φ_1 is simply expressed by the following function [2, 7].

$$\tan \Phi_1 = \cos\alpha \tan\mu$$
$$\tan \Phi_1 = 1/\sqrt{2} \tan\mu (\alpha = 45^\circ)$$

FT-IR spectra were measured from 4000 to 700 cm^{-1} at a resolution of 4 cm^{-1} using a PerkinElmer Spectrum One spectrometer equipped with a universal ATR accessory; normalization from 1800 to 800 cm^{-1} was performed. From these spectra consisting of 62 objects (spectra) and 200 variables (wavenumber), PCA was performed with the software Unscrambler (CAMO ASA, Norway). All the samples were observed by an optical microscope in order to check their anatomical features.

The experimental results of SAXS analysis are summarized in Fig. 2. In a softwood branch, MFAs were in general larger in the lower and basal parts of a branch indicating the formation of the compression woods (Fig. 2A). Moreover MFAs decreased continuously from the trunk towards the tip except (a) in upper side. These trends agreed with a previous report [3]. The distal on upper parts showed relatively large MFA, suggesting the formation of the compression wood in the upper part. The microscopic results supported this result and indicated a gradual decrease of reaction wood from a trunk to a tip. Because of the complex geotropic axis, the formation of compression wood is more complex phenomenon. Onaka [8] described how the growth in a branch was not eccentric, indicating absence of a reaction wood, when the axis of a branch was inclined about 50–60° and 150–160° from upright direction. In

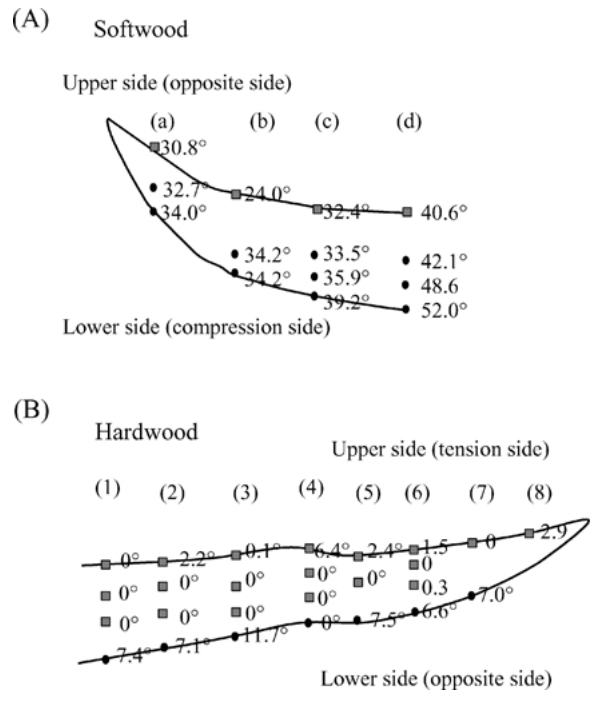

Figure 2 Map of MFAs in both softwood and hardwood. Solid circles indicate the samplings from lower part, and open squares indicate those from upper part with respect to the pith.

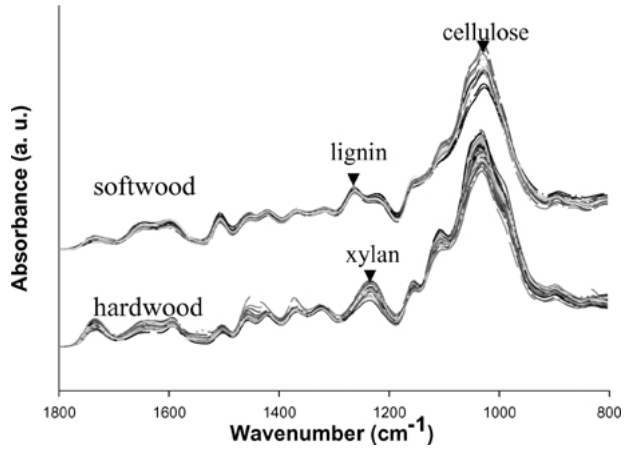

Figure 3 ATR FT-IR spectra region at 1800 to 800 cm^{-1}.

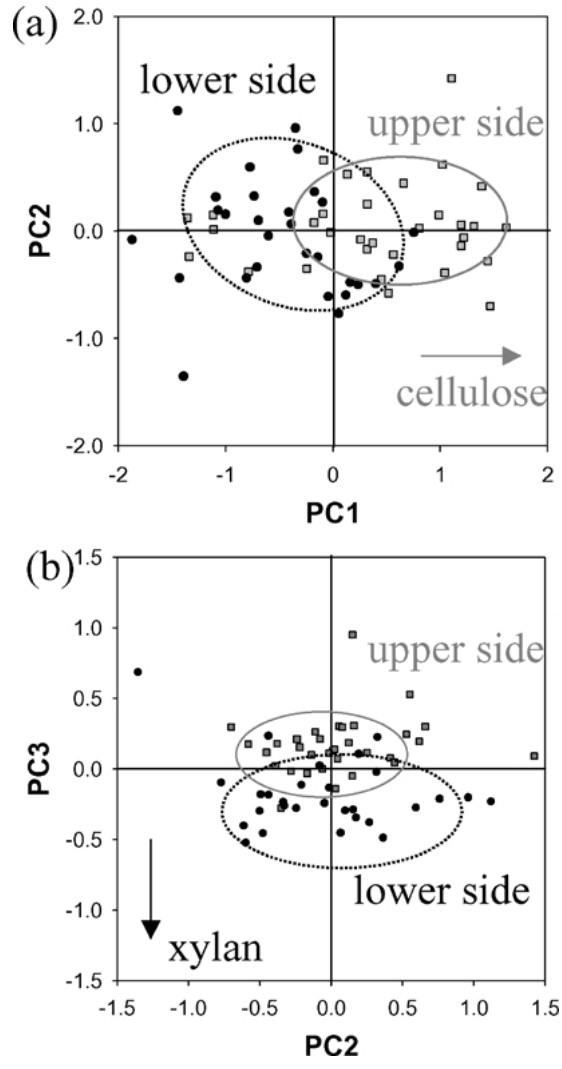

Figure 4 (a) PCA score plots (PC1 vs. PC2) and (b) PCA score plots (PC2 vs. PC3). For markers, see Fig. 2.

fact, our result at (a) on the upper side was indicated of the phenomenon described by Onaka [8]. Generation of compressive growth stress might be controlled by interaction between large MFA and large deposition of lignin [4]. Therefore in the position (a) on upper side the compression stress might increase. The results obtained from hardwood are shown in Fig. 2B. MFAs were almost 0°. Despite the lack of G-layer, the MFAs were clearly smaller in the upper and except position (4). In the case of species, which had no G-layer, large growth stress was measured in the upper region of a leaning stem where the MFAs were small [5]. Small MFAs on upper side in this study implies generation of large growth-stress which might sustain the branch.

The FT-IR spectra in the region of 1800–800 cm^{-1} of softwood and hardwood are shown in Fig. 3. This region is the fingerprint region for polysaccharides and lignin and is dominated by stretching vibrations of C–O, C–C, ring structures and deformation vibrations of CH_2 groups. The differences between spectra were small, but trends were noticeable. In softwood, the difference appeared near 1735–1715, 1219, 1060 and 1030 cm^{-1}. Peaks near 1735–1715 cm^{-1} and 1220 cm^{-1} were assigned to lignin [9, 10]. A peak around 1060 cm^{-1} was assigned to cellulose I_β corresponding to C3–O3–H alcohol [11], while a peak at 1030 cm^{-1} was found in softwood acetylglucomannan [12]. Therefore a part in which compression wood is formed might show a decrease of cellulose and glucomannan and an increase of lignin peak at 1219 cm^{-1}. These results agreed with previous report [8]. On the other hand, the height of the region at 1735–1715 cm^{-1} decreased

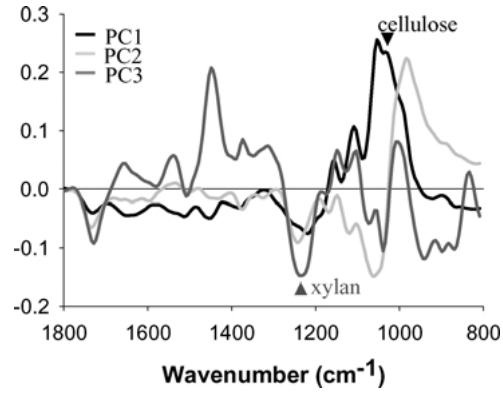

Figure 5 PCA loading from hardwood spectra.

on the lower side. Sarkanen *et al*. [9] assigned the 1715 cm^{-1} peak to $\nu_{C=O}$ of conjugated ester groups, and that at 1735 cm^{-1} was assigned to nonconjugated ester moieties. It was reported that compression wood lignin contained fewer ester groups than normal wood lignin and prominent peak at 1735 cm^{-1} existed in juvenile wood, which is quite flexible [9]. From results of the ester groups in juvenile and compression wood lignin they suggested that the ester groups may exert a plasticizing effect on the lignin by reducing the opportunity for internal hydrogen bonding [9]. Consequently, it was speculated that small changes of lignin induced a change of rheological property properties in wood cell walls. Principal component analysis (PCA) was performed on the spectra from the hardwood. It allowed detection of the small chemical difference between the upper side and lower side of a branch

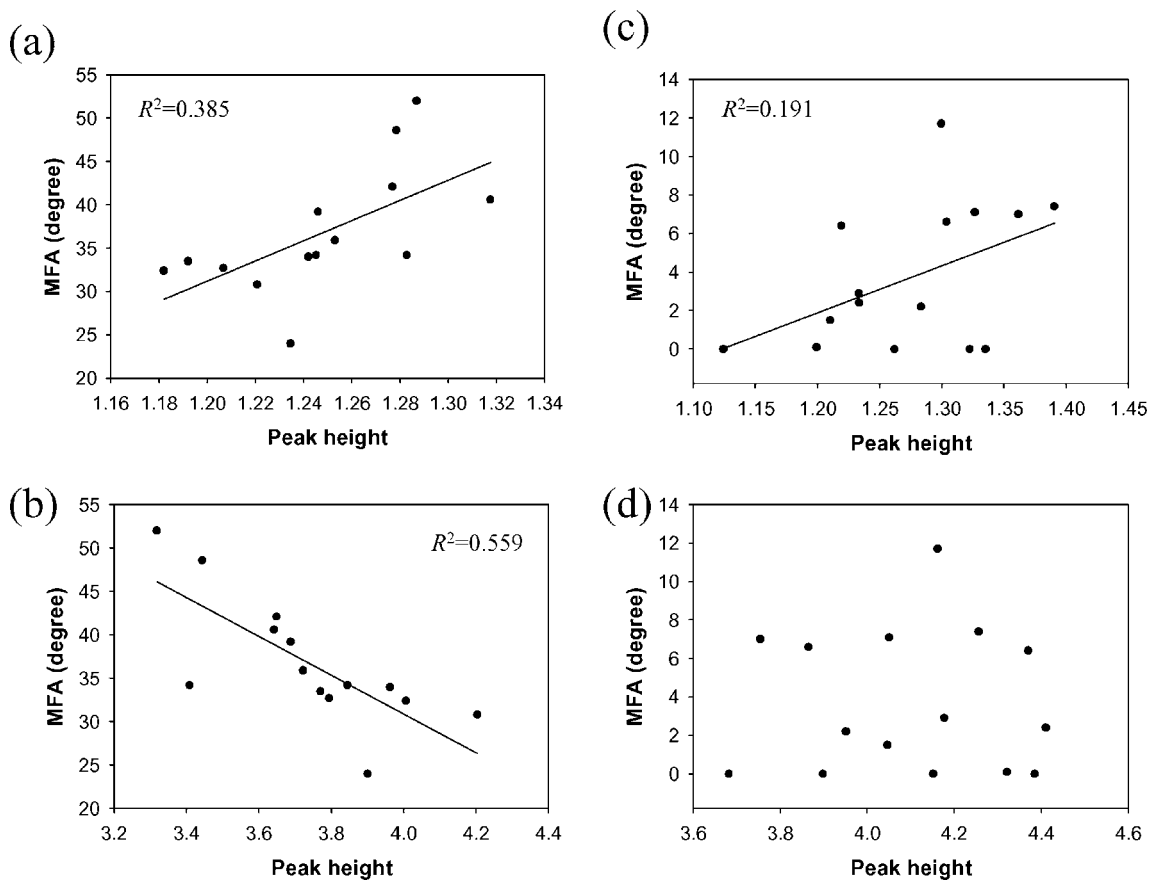

Figure 6 Correlation between MFA and chemical composition: (a) MFA vs. lignin (1264 cm^{-1}) in softwood, (b) MFA vs. cellulose (1034 cm^{-1}) in softwood, (c) MFA vs. xylan (1239 cm^{-1}) in hardwood, and (d) MFA vs. cellulose (1034 cm^{-1}) in hardwood.

(Fig. 4). PC1 (variability; 64%) and PC3 (variability; 7%) separate clearly two groups. The strong positive peak at 1034 cm^{-1} in PC1 loadings is shown in Fig. 5. Strong peak at 1035 cm^{-1} can be assigned to cellulose [11]. Therefore PC1 loadings had positive relationship with cellulose. The strong negative peak at 1239 cm^{-1} in PC3 loadings is shown in Fig. 5. The peak at 1240 cm^{-1} was assigned to xylan [13]. Therefore, PC3 might have negative relationship with xylan. From microscopic results, non-lignified fibers were observed on upper parts at (1)–(3) in Fig. 2. From (4) to (8), lignified fiber gradually increased. In summary, cellulose content decreases continuously from the trunk to the tip and upper parts had generally more cellulose than lower parts. Variation of MFA and small changes of chemical composition in cell wall were observed. In both softwood and hardwood, these changes seemed to be well regulated to manifest the mechanical function in order to keeping the branch in its ideal orientation.

We examined the correlations between MFAs, chemical components and measured peak height at three wavenumbers. The peak at 1034 cm^{-1} (cellulose) was used for both softwood and hardwood. Moreover, the peak at 1219 cm^{-1} (lignin) was used for softwood. The peak at 1239 cm^{-1} (xylan), which appeared characteristically in hardwood, was used for hardwood. Fig. 6 shows the correlations between MFA on most outer parts and chemical composition, of those areas which corresponded to SAXS measurements for MFA. In softwood, the correlation of MFAs with lignin content (Fig. 6a) was positive relationship. On the other hand, there was a negative correlation between MFAs and cellulose content (Fig. 6b). In the case of lignin, the same trend was also reported the [14]. In hardwood, although apparent correlation between MFAs and cellulose was not shown (Fig. 6d), the positive correlation between MFAs and xylan content could be seen (Fig. 6c).

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