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ORIGINAL ARTICLE

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Microfibril angle of Norway spruce [*Picea abies* (L.) Karst.] compression wood: comparison of measuring techniques

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Abstract The structure of cellulose, especially the microfibril angles (MFAs), in compression wood of Norway spruce [*Picea abies* (L.) Karst.] was studied by wide- and small-angle X-ray scattering and polarizing microscopy. On the basis of the X-ray scattering experiments the average MFAs of the cell wall layers S_2 and S_1 of the studied sample are 39° and 89°, respectively; and the average diameter and length of the cellulose crystallites are 2.9 and 20.0 nm, respectively. The average of the whole MFA distribution is shown to agree with the one obtained by polarizing microscopy of macerated fibers.

Key words Microfibril angle · Wide angle X-ray scattering · Small-angle X-ray scattering · Wood cellulose · *Picea abies* (L.) Karst

Introduction

The microfibril angle (MFA) is an important property of wood cells (tracheids). MFA is a quantity that represents the orientation of cellulose in the cell wall along the stem axis. High MFAs of the S_2 layer result in low stiffness and increased longitudinal shrinkage of wood. The latter is reported to increase drastically when the microfibril angle exceeds about 40°.[1] On the other hand, stiffness of the cell wall increases fivefold as the MFA decreases from about 40° to 10°.[2] Thus, a high MFA of wood is a highly undesirable property. To produce high-quality timber it is important to know the relations between wood properties and dimensional changes (i.e., the variation of MFA and its effect on the shrinkage of wood).

Conventional techniques such as viewing pit angle apertures and polarizing microscopy have been used for measuring microfibril angles.[3,4] However, only a limited number of points (pits) can be measured with those methods. To obtain statistically better results X-ray scattering methods have been used. A piece of wood makes an ideal sample, and thus the result is an average of the order of 10000 tracheids. X-ray scattering methods are also advantageous for determining MFAs because they are quite fast even with a conventional X-ray tube and without an area detector. Furthermore, little sample preparation is needed compared to that required for microscopic methods.

The average MFAs of all wood cell wall layers can be determined simultaneously by means of wide-angle X-ray scattering (WAXS).[5–9] However, interpretation of the results requires expertise. Data analysis methods have recently been advanced, especially by Cave.[10]

A small-angle X-ray scattering (SAXS) method has also been used for determination of MFAs (e.g., by Wardrop[11] and Kantola et al.[12–14] and recently by the research group of Fratzl[15–17]). The results indicate that the SAXS intensity pattern includes one range where scattering from voids dominates and another range where the scattering arises from the electron density contrast between crystalline cellulose and surrounding material. The size of the cellulose crystallites has also been estimated from SAXS data.[15,18,19]

In this work compression wood of Norway spruce [*Picea abies* (L.) Karst.] was studied by means of WAXS, SAXS, and polarizing microscopy. The main aim was to determine the average MFAs of the individual cell wall layers. A sample of compression wood was chosen because the MFAs of the cell wall layers were expected to be large (Fig. 1) and thus easy to determine optically owing to the visible cavities in the cell wall. The cross sections of the cells of compression wood are circular, and the cell wall contains both S_2 and S_1 layers but not an S_3 layer.[20]

The WAXS experiments for determining the distribution of MFAs were done using both the reflections 004 and 200[21] to obtain information on both the MFAs and the

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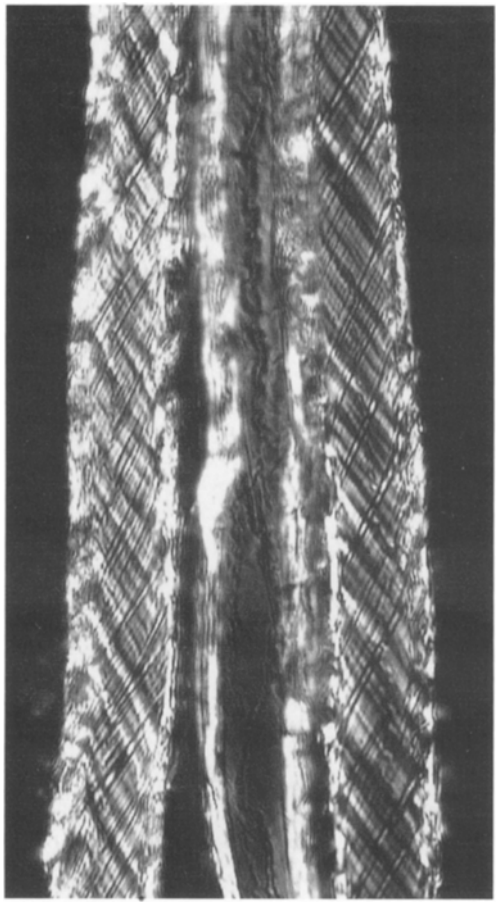

Fig. 1. Compression wood tracheids of Norway spruce photographed with a polarizing microscope. The visible cavities in the cell wall show the orientation of cellulose (ca. 44°) in the S_2 layer of the cell wall ×700

shape of the cell cross section.[10] It was shown that the average MFAs of layers S_2 and S_1 can be determined by curve fitting from both WAXS and SAXS data. The average size of the cellulose crystallites was also determined by WAXS and SAXS. The average of the whole MFA distribution was shown to agree with the one obtained by polarizing microscopy of macerated fibers.

Experimental

Wide-angle X-ray scattering

The geometry of the WAXS measurement is shown in Fig. 2. A diffractometer was used in a symmetrical transmission mode. Measurements are performed with CuK_{α_1} radiation (λ = 1.541 Å) selected by a ground and bent quartz monochromator (reflection $10\bar{1}1$). The sealed Cu anode X-ray tube (line focus) was powered by a Siemens Kristalloflex 710 generator (40 kV, 28 mA). The scattered photons were detected by a NaI (Tl) scintillation counter. The diffractometer is controlled by a microcomputer, in which X-ray diffraction software SPEC was used. The sample 1.0 mm

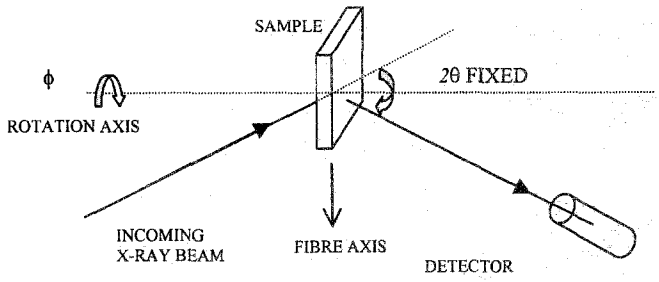

Fig. 2. Geometry of wide-angle X-ray scattering (WAXS) measurement

Table 1. Angles between the planes and plane 004 for reflections that have almost the same scattering angle (2θ) as the reflection 004

hkl	2θ (degrees)	Angle (degrees)
300	33.83	90
$\bar{2}22$	34.22	59.63
$\bar{3}10$	34.24	90
203	34.39	41.00
004	34.62	0
$\bar{1}31$	34.77	75.59
301	34.95	75.66
$\bar{1}23$	35.05	42.18

in thickness was prepared from compression wood of Norway spruce. The sample containing only earlywood was cut in the tangential direction.

For MFA measurements the divergence slit was circular (diameter 2.0 mm) and the receiving slits rectangular (width 0.6 mm, height 6.0 mm). The vertical divergence was 2.2° and the radius of the goniometer 180 mm. The detector was fixed to the reflection position. The sample was then rotated around its normal axis, and intensity was measured as a function of the angle ϕ (Fig. 2). A measuring time of 120 s was used for each angular step of 1.6°, the total measuring time being 7.5 h.

Reflections 200 and 004[21] were used for the MFA measurement, and information on both MFAs and the cell cross section were obtained by this means.[10] Theoretically, the MFA distribution can be measured directly using the reflection 004, but in practice the experimental distribution is contaminated by scattered intensity from nearby lattice planes (Table 1). The reflection 200 is well separated, but the intensity curve gives information on both the MFA distribution and the shape of the cell cross section. Only for cells with rectangular cross sections do both reflections 200 and 004 give identical results at an angle ϕ smaller than 40°, where the contribution of the other reflections is negligible.[6,10]

For determination of average sizes of crystallites, the divergence and receiving slits are both rectangular (width 0.6 mm and height 6.0 mm, width 0.05 mm and height 6.0 mm, respectively). The diffraction pattern was measured at an angular range from 2θ = 10°–40° with steps of 0.06° and a measuring time of 60 s for each step.

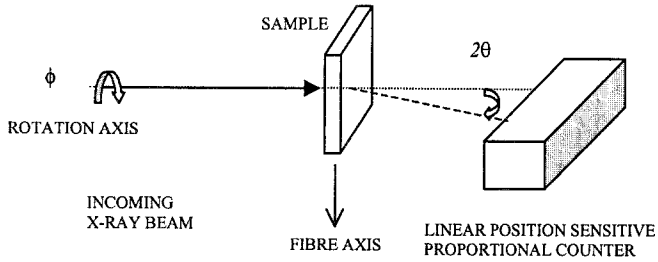

Fig. 3. Geometry of small-angle X-ray scattering (SAXS) measurement

Small-angle X-ray scattering

The geometry of the SAXS measurement is shown in Fig. 3. CuK_α radiation was monochromatized by means of the combined action of a Ni filter and a totally reflecting mirror (Huber small-angle chamber 701). The sealed Cu anode fine focus X-ray tube was powered by a Siemens Kristalloflex 710H (36kV, 25mA). The scattered radiation was detected by a linear one-dimensional position-sensitive proportional counter (MBraun OED-50M) combined with a multichannel analyzer. The data collection was controlled by a microcomputer, in which X-ray diffraction software SPEC was used.

The data were measured in two parts using camera lengths of 151 and 1165mm. The anode was placed in point focusing geometry, and the beam was collimated with slits into narrow but, for the present purpose, point-like profile measuring 0.1 × 2.0mm for the short camera and 0.8 × 4.0mm for the long camera length.

The only moving part in this setup is the sample, which rotates around its normal position. The sample was the one used for the WAXS measurement. The intensity of scattered X-rays is measured as a function of the rotation angle ϕ (Fig. 3) and the magnitude of the scattering vector

$$k = (4\pi/\lambda)\sin\theta \quad (1)$$

where θ is half of the scattering angle, and λ is the wavelength of CuK_α. A measuring time of 150s was used for each step of angle ϕ of 1.6°, the total measuring time being 9.3h. Additionally, intensity curves at ϕ = 0°, 45°, and 90° were measured with a good statistical precision using a measuring time of 1.0h.

Polarizing microscopy

Macerated fibers were prepared from the parallel samples using glacial acetic acid/hydrogen peroxide (1:1, v/v) at 60°C overnight.[22] Individual fibers were spread over a microscope slide, and the MFAs were determined by polarizing microscopy. A single cell wall layer was observed through the pit pores as described by Leney[3] and Donaldson.[4] The angular range was from 2° to 90°, and angles larger than 44° were determined using a half-wave plate.

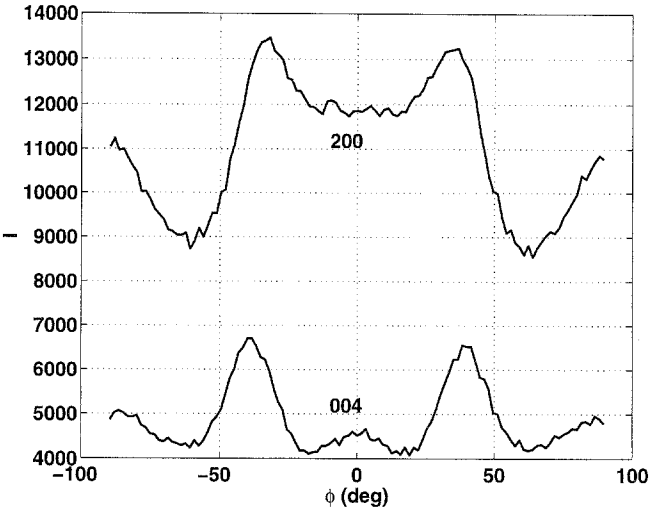

Fig. 4. WAXS results. The 004 distribution consists of two clearly separated peaks, and the 200 distribution is broad but has a clear contribution at zero degrees (the compression wood of Norway spruce)

Results

The WAXS results of the MFA measurements are shown in Fig. 4. The intensity curves of reflections 200 and 004 measured as a function of the angle ϕ are not identical, indicating that the cross sections of the cells are not rectangular. The two curves had maxima at about ±40° and ±90°, respectively, which may have arisen from the MFA distributions of the cell wall layers S_2 and S_1.

The differences of the intensity curves can be explained by the circular cross sections of the tracheids of compression wood (which affect the intensity of reflection 200) and the contributions of the reflection *hk*3 and *hk*0 (which affect the intensity of reflection 004). Because the largest maximum of the measured intensity curve (Fig. 4) is at about ϕ = ±40° and the angle between planes 004 and *hk*3 is about 40°–45° (Table 1), scattering from plane *hk*1 is largest at ϕ values of about ±80°. The angle between planes 004 and *hk*0 is about 90°, therefore scattering from these planes is largest at about ϕ = ±50°.

The MFA distributions of both cell wall layers S_2 and S_1 are assumed to be Gaussian functions, and a sum of two pairs of Gaussians were fit to the 004 data. In the case of reflection 200 the circular shape of the cross section of the cells was taken into account according to Cave.[10] The agreement between the calculated and the measured intensity curves was good for both reflections 200 and 004. The obtained average MFAs are also nearly equal: The mean MFA of the S_2 layer from the 004 data is 39°, and that from the 200 data is 37°. The mean MFA of the S_1 layer is 89° when using reflection 004 and 88° when using reflection 200. The accuracy of the determination of MFAs was estimated to be ±2°.

The number of determinations by optical microscopy was too small to obtain the shape of the MFA distribution reliably, and only the average of the MFA distribution was

calculated. To compare the X-ray results with those obtained with the optical method the angular average $<\phi>$ was calculated from X-ray scattering data:

$$\langle\phi\rangle = \frac{\int_{2^\circ}^{90^\circ} f(\phi)\phi \mathrm{d}\phi}{\int_{2^\circ}^{90^\circ} f(\phi)\mathrm{d}\phi} \quad (2)$$

where $f(\phi)$ is the MFA distribution obtained as a sum of two Gaussian functions. The angular averages $<\phi>$ are 47° and 49° for reflections 004 and 200, respectively. Optical measurements gave an average MFA of 44°.

Average sizes of crystallites by WAXS

The average size of the crystallites t was estimated by means of the well-known Scherrer formula

$$t = \frac{0.9\lambda}{B\cos\theta} \quad (3)$$

where λ is the wavelength of the radiation, θ is half of the scattering angle, and B is the full width at half maximum (FWHM) of the reflection. The effect of the instrumental broadening on the width of the reflections was included by assuming that the shapes of both the reflection and the instrumental function are Gaussian, and the FWHM B was calculated using the formula

$$B = \left(b_n^2 - b_1^2\right)^{1/2} \quad (4)$$

where b_n is the FWHM of reflection 200 or 004, and b_1 is the instrumental broadening, which is estimated as an FWHM of a reflection of a sample with large crystallites. Here LiF was used. The widths of the reflections were obtained by fitting a calculated intensity curve to the experimental one. The reflections were presented as Gaussians, and an experimental intensity curve of ball-milled microcrystalline cellulose (Avicel) was used as the amorphous background. The determined average sizes of the crystallites are 29 ± 2 Å from reflection 200 and 200 ± 10 Å from reflection 004.

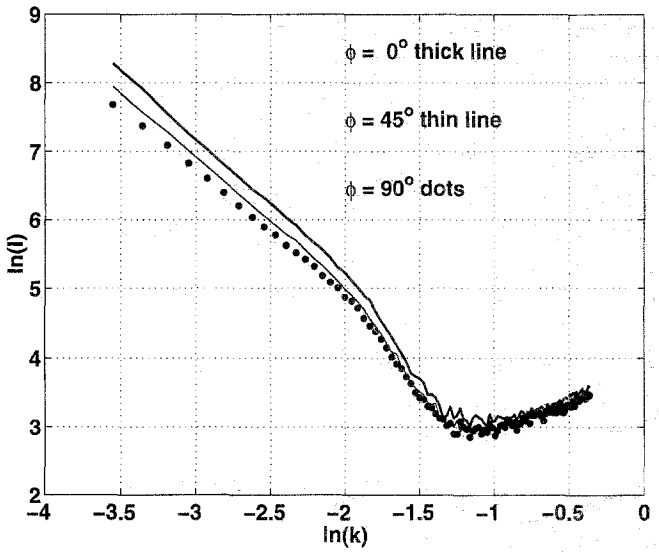

Fig. 5. Experimental SAXS intensities for three orientations of the wood sample (k values are between 0.03 Å^{-1} and 0.70 Å^{-1})

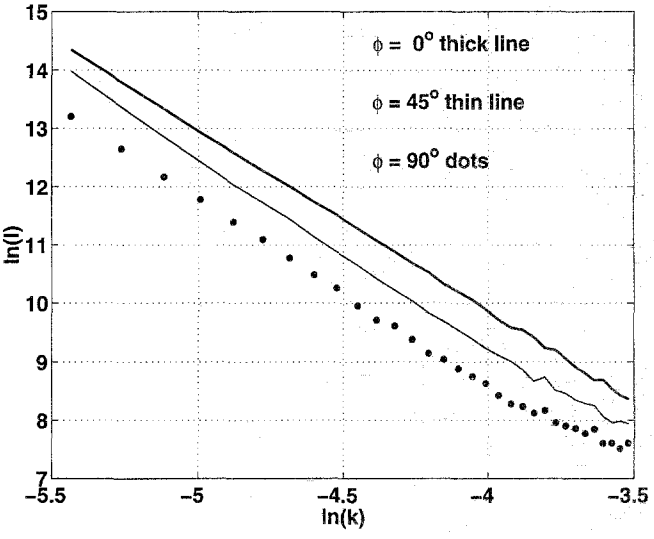

Fig. 6. Experimental SAXS intensities for three orientations of the wood sample (k values are between 0.0044 Å^{-1} and 0.030 Å^{-1})

MFAs by SAXS

Figures 5 and 6 present the SAXS intensities for three orientations of the wood sample corresponding the values of angle ϕ 0°, 45°, and 90°. The intensities are presented in logarithmic scale as a function of the magnitude of the scattering vector k. In Fig. 6 the k values are between 0.0044 Å^{-1} and 0.030 Å^{-1}, and in Fig. 5 they are between 0.03 Å^{-1} and 0.70 Å^{-1}. The SAXS intensity curve obeyed a power law $I(k) \propto k^{-\alpha}$ when k was smaller than 0.04 Å^{-1}. Recently, Jakob et al.[23] have shown by wetting experiments on normal wood of *Picea abies* that scattering at $k < 0.1$ Å^{-1} arises mainly from pores. The same value of the power law exponent α (3.3) was obtained using a fitting range 0.004–0.02 Å^{-1} at ϕ values of 45° and 90°. At ϕ = 0° a slightly smaller value (3.1) was determined using a fitting range 0.004–0.1 Å^{-1}. The exponent is typical for surface fractals and indicates that the pores have rough surfaces.[24]

At k from 0.1 to 0.6 Å^{-1} the intensity curve is similar to that obtained by Jakob et al.,[15,18,23] which they concluded arose from cylindrical cellulose crystallites. However, the intensity curve of the compression wood sample does not contain any maximum at about 0.5 Å^{-1}, which could be interpreted as the first side maximum of the intensity curve of a cylindrical particle. This difference may be explained by assuming that the size of the cellulose crystallites varies more than that in the normal wood sample of Norway spruce.[18] The SAXS intensity curve at ϕ = 0° resembles closely those at ϕ = 45° and 90°, which indicates that there are considerable amounts of cellulose crystallites parallel to

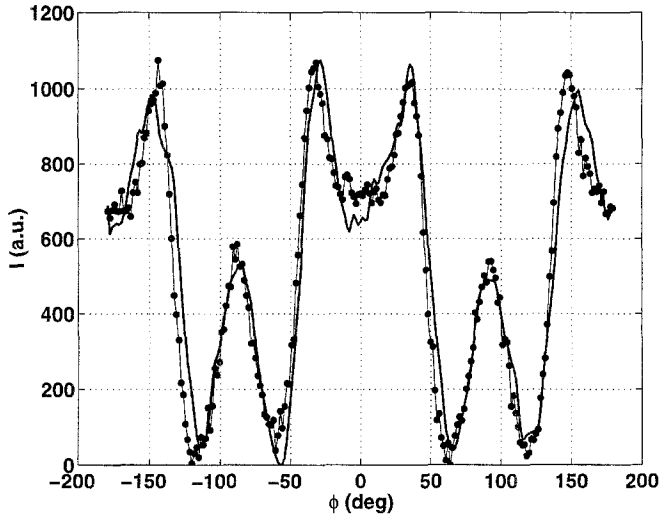

Fig. 7. Comparison of SAXS (*thin line*) and WAXS (*thick line*) results. For SAXS measurement k is between 0.08 Å^{-1} and 0.23 Å^{-1}

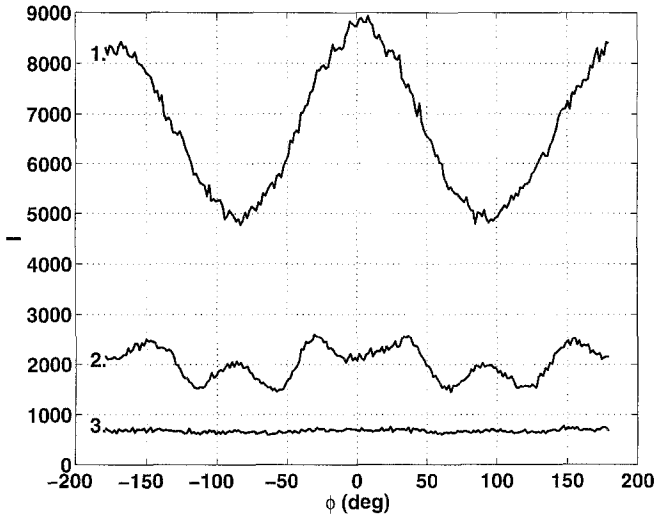

Fig. 8. SAXS intensities integrated over k as a function of the angle ϕ. The integration limits were 0.02 . . . 0.05 Å^{-1} for curve *1*, 0.08 . . . 0.23 Å^{-1} for curve *2*, and 0.23 . . . 0.40 Å^{-1} for curve *3*

the fiber axis. This may explain also the minor maximum of the 004 data at $\phi = 0°$ (Fig. 4).

The WAXS and SAXS results of MFA measurements are compared in Fig. 7. When k is between 0.08 Å^{-1} and 0.23 Å^{-1} the WAXS and SAXS results are nearly identical. At k values smaller than 0.08 Å^{-1} the SAXS data differ considerably from the WAXS data, demonstrating that at this range SAXS arises mainly from pores aligned parallel to the cell axis. At k values greater than 0.23 Å^{-1} the SAXS intensity is independent of the angle ϕ. It is considered that the scattering arises mainly from the amorphous materials of wood such as lignin. In Fig. 8 integrated SAXS intensities are presented as a function of the angle ϕ. The integration was carried out over three ranges of k: from 0.02 Å^{-1} to 0.05 Å^{-1} ("pore region"), from 0.08 Å^{-1} to 0.23 Å^{-1} ("crystallite region"), and from 0.23 Å^{-1} to 0.40 Å^{-1} ("amorphous region").

The average radius of the cylindrical cellulose crystallites and its standard deviation were determined by fitting a model SAXS intensity curve to the experimental one measured at angles ϕ of 45° and 90°. The model included the power law term $k^{-3.3}$, the structure factor of cylindrical particles with varying size and a polynomial of second degree. The polynomial of the second degree described the contributions of the intensity of the amorphous material in the sample and the first reflection $\bar{1}10$ of crystalline cellulose.

For simplicity, the cellulose crystallites were described as infinitely long cylinders. The structure factor by such a particle is proportional to

$$\frac{\left[J_1(kR)\right]^2}{(kR)^2}$$

where J_1 is the Bessel function of the first kind and of the first order, and R is the radius of the cylinder.[15,19]

We made fits using both normal[25] and uniform distributions for determining the average radius of the crystallites and its standard deviation. Fits were made separately to the SAXS intensity curves measured at rotation angles of 45° and 90°. The intensity at 45° arises mainly from crystallites of the S_2 layer and the intensity at 90° from crystallites of the S_1 layer.

Good fitting results were obtained using these distributions at both 45° and 90°. Both fits also gave about the same average radius of the crystallites (15 Å) and the standard deviation (4 Å). The fact that the same results were obtained for both 45° and 90° intensity curves indicates that the size distribution of crystallites is about the same for S_1 and S_2 layers. This result agrees well with the average diameter of the crystallites from reflection 200 determined from the WAXS intensity curve (29 Å).

Discussion

The average MFA of all the layers of the cell wall determined by WAXS was previously compared with those obtained by other methods by several authors,[26–29] and good agreement or correlation between the results was obtained. However, some of the determinations have not been independent because in the analysis of WAXS data other methods have been used to calibrate the angular range. In this study the X-ray scattering data have been analyzed independently, and the calculated average of the whole MFA distribution was found to be in agreement with the value determined by polarizing microscopy. Similar comparisons are being made for normal wood of Norway spruce.[28] WAXS results were also in good agreement with SAXS results. Such good agreement between WAXS and SAXS results was previously obtained also by Lichtenegger et al.[16]

The MFAs of the S_2 and S_1 layers of the compression wood sample were determined by both WAXS and SAXS.

Compression wood is a good example, because it has two thick cell walls with large, but clearly different, MFAs. In normal wood the S_1 and S_3 layers can be thin and contribute little to the measured intensity curve, which makes determination of the MFAs of the individual cell wall layers difficult.[30]

The MFAs of compression wood vary considerably, depending, for instance, on growing conditions.[20] Thus results can be compared only roughly with those in the literature because the samples are different. Sahlberg et al.[29] recently obtained about 22° and Reiterer et al.[17] about 40° for MFA of the S_2 layer of a compression wood sample of Norway spruce, which is similar to the MFA of 39° (from reflection 004) determined in this work.

The use of both reflections 200 and 004 for WAXS measurements is recommended. Using reflection 004 alone, only small MFAs can be determined reliably because of the reflections of other nearby lattice planes. The use of reflection 200 does not include this problem. However, information on the shape of the cell cross section is needed for analysis of the results. By comparing the 200 and 004 data the rectangular shape can be recognized directly. The assumption of circular shape can be tested by fitting a model to 200 data. The SAXS result is also influenced by the shape of the cross section of the cells,[14] and the MFA distribution and SAXS results cannot be analyzed without information on the shape of the cells.

The average diameter of cellulose crystallites determined from SAXS results (30 Å) agreed well with the average size of the crystallites determined from reflection 200 of the WAXS intensity curve (29 Å). The successful fits with both normal and uniform distributions show that one cannot reliably determine the shape of the distribution of the diameters. The determined length of the crystallites was 200 Å. Both dimensions of the crystallites are larger than those obtained by Jakob et al.[18] for normal wood of Norway spruce of diameter 25 Å and length 110 Å. The thickness is about the same as observed for flax.[25] The difference between their results and those in this study can be seen from the shapes of the SAXS intensity curves: The SAXS intensity in this study shifted to smaller values of k than that reported by Jakob et al.[18] which is in agreement with the larger particle size.

In principle, information on the amount of the cellulose crystallites in the S_2 and S_1 layers is obtained by comparing the areas of the peaks of the MFA distribution.[7] On the basis of SAXS and the 200 data, the height of the S_1 peak is half that of the S_2 peak. The S_1 peak is lower and broader in the 004 data. This broadening is caused by scattering from the other lattice planes; thus in this case the 200 data are more reliable for estimating the amount of cellulose crystallites in the cell wall layers.

Sometimes the fibrils of the outer cell wall (S_1) are not as nicely parallel as those of the S_2 layer, and the electron density of the S_1 layer can be close to that of the surrounding material. In such a case the S_1 layer may not be seen by SAXS. One advantage of using WAXS of reflections 004 and 200 and SAXS is that by comparing the results it is possible to obtain information also on the homogeneity and density of the cell wall layers. For the studied sample WAXS and SAXS results agreed with each other, indicating that the cellulose crystallites of both cell wall layers are well separated from the matrix.

Conclusions

The mean MFAs of different cell wall layers of compression wood were obtained simultaneously. It is advantageous to use both 200 and 004 reflections, because information on both the MFA distribution and the shape of the cross section of the cells is obtained. SAXS gives the same information as the WAXS experiment using reflection 200 and may additionally reveal differences in the average electron densities due to possibly by different degrees of crystallinity of cell wall layers. The average diameter of cellulose crystallites was determined from SAXS intensity curves, and the result agreed well with the average size of the crystallites determined by WAXS from reflection 200. No difference between the diameters of crystallites in S_1 and S_2 layers were observed.

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References

1. Harris JM, Meylan BA (1965) The influence of microfibril angle on longitudinal and tangential shrinkage in *Pinus radiata*. Holzforschung 19(5):144–153
2. Cave ID (1968) The anisotropic elasticity of the plant cell wall. Wood Sci Technol 2:268–278
3. Leney L (1981) A technique for measuring fibril angle using polarized light. Wood Fiber 13(1):13–16
4. Donaldson LA (1991) The use of pit apertures as windows to measure microfibril angle in chemical pulp fibers. Wood Fiber Sci 23:290–295
5. DeLuca LB, Orr RS (1961) Crystallite orientation and spiral structure of cotton. J Polym Sci 54:457–470
6. Cave ID (1966) Theory of X-ray measurement of microfibril angle in wood. For Prod J 16(10):37–42
7. Boyd JD (1977) Interpretation of X-ray diffractograms of wood for assessments of microfibril angles in fibre cell walls. Wood Sci Technol 11:93–114
8. Sobue N, Hirai N, Asano I (1971) Studies on structure of wood by X-ray. II. Estimation of the orientation of micells in cell wall. J Jpn Wood Res Soc 17(2):44–50
9. Paakkari T, Serimaa R (1984) A study of the structure of wood cells by X-ray diffraction. Wood Sci Technol 18:79–85
10. Cave ID (1997) Theory of X-ray measurement of microfibril angle in wood. Wood Sci Technol 31:225–234
11. Wardrop AB (1952) The low-angle scattering of X-rays by conifer tracheids. Textile Res J 22:288–291
12. Kantola M, Seitonen S (1961) X-ray orientation investigations. Ann Acad Sci Fenn A VI Phys 80:1–15
13. Kantola M, Kähkönen H (1963) Small-angle X-ray investigation. Ann Acad Sci Fenn A VI Phys 137:1–14
14. Kantola M, Kähkönen H, Seitonen S (1965) On the correspondence of the small-angle and wide-angle X-ray diffraction patterns of wood fibers. Ann Acad Sci Fenn A VI Phys 220:1–9
15. Jakob HF, Fratzl P, Tschegg SE (1994) Size and arrangement of elementary cellulose fibrils in wood cells: a small-angle X-ray scattering study of *Picea abies*. J Struct Biol 113:13–22

16. Lichtenegger H, Reiterer A, Tschegg S, Fratzl P (1998) Determination of spiral angles of elementary fibrils in the wood cell wall: comparison of small-angle X-ray scattering and wide-angle X-ray diffraction. In: Butterfield BG (ed) Microfibril angle in wood. University of Canterbury, Christchurch, pp 140–156
17. Reiterer A, Jakob HF, Stanzl-Tschegg SE, Fratzl P (1998) Spiral angle of elementary cellulose fibrils in cell walls of *Picea abies* determined by small-angle X-ray scattering. Wood Sci Technol 32:335–345
18. Jakob HF, Fengel D, Tschegg SE, Fratzl P (1995) The elementary cellulose fibril in *Picea abies*: comparison of transmission electron microscopy, small-angle X-ray scattering, and wide-angle X-ray scattering results. Macromolecules 28:8782–8787
19. Heyn ANJ (1955) Small particle X-ray scattering by fibers; size and shape of microcrystallites. J Appl Phys 26:519–526
20. Timell TE (1986) Compression wood in gymnosperms (vol 1). Springer, Berlin, pp 157–167, 195–198
21. Sugiyama J, Vuong R, Chanzy H (1991) Electron diffraction study on the two crystalline phases occurring in native cellulose from algal cell wall. Macromolecules 24:4168–4175
22. Franklin GL (1945) Preparation of thin sections of synthetic resins and wood resin composites and a new macerating method for wood. Nature 155:51
23. Jakob HF, Tschegg SE, Fratzl P (1996) Hydration dependence of the wood-cell wall structure in *Picea abies*: a small-angle X-ray scattering study. Macromolecules 29:8435–8440
24. Schmidt PW (1991) Small-angle scattering studies of disordered, porous and fractal systems. J Appl Cryst 24:414–435
25. Müller M, Czihak C, Vogl G, Fratzl P, Schober H, Riekel C (1992) Direct observation of microfibril arrangement in a single native cellulose fiber by microbeam small-angle X-ray scattering. Macromolecules 31:3953–3957
26. Prud'homme RE, Noah J (1975) Determination of fibril angle distribution in wood fibers: a comparison between the X-ray diffraction and the polarized microscope methods. Wood Fibers 6:282–289
27. Huang C-L, Kutscha NP, Leaf GJ, Megraw RA (1998) Comparation of microfibril angle measurement techniques. In: Butterfield BG (ed) Microfibril angle in wood. University of Canterbury, Christchurch, pp 177–205
28. Saranpää P, Serimaa R, Andersson S, Pesonen E, Suni T, Paakkari T (1998) Variation of microfibril angle of Norway spruce (*Pinus abies* (L.) Karst.) and Scots pine (*Pinus sylvestris* L.) – comparing X-ray diffraction and optical methods. In: Butterfield BG (ed) Microfibril angle in wood. University of Canterbury, Christchurch, pp 240–252
29. Sahlberg U, Salmén L, Oscarsson A (1997) The fibrillar orientation in the S2-layer of wood fibres as determined by X-ray diffraction analysis. Wood Sci Technol 31:77–86
30. Saranpää P, Pesonen E, Sarén M, Andersson S, Siiriä S, Serimaa R, Paakkari T (in press) Variation on the properties of tracheids in Norway spruce (*Picea abies* (L.) Karst). In: Savidge R, Barnett J, Napier R (eds) Cambium: the biology of wood formation. BIOS Scientific, Oxford