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ORIGINAL ARTICLE

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Crystallinity of wood and the size of cellulose crystallites in Norway spruce (*Picea abies*)

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Abstract X-ray diffraction was used to study variations in the crystallinity of wood and the average thickness and length of the crystallites of cellulose as a function of the number of the year ring in Norway spruce [*Picea abies* (L.) Karst.]. The crystallinity increased from ring 4 to ring 10 from the pith and was constant after ring 10. The crystallinity of mature wood was about 30% ± 5%. The average thickness and average length of the crystallites were 3.2 ± 0.1 nm and 28 ± 2 nm, respectively; and no systematic variation of these values with the number of the year ring was observed. The mean microfibril angle decreased near the pith but was constant in the mature wood.

Key words Cellulose · Crystallinity · Microfibril angle · *Picea abies* (L.) Karst. · Wood

Introduction

The walls of wood cells (tracheids in conifers) consist mainly of cellulose, hemicellulose, and lignin. Cellulose occurs in the helically wound reinforcing microfibrils, and lignin and hemicellulose serve as a gluing and stiffening matrix.[1] Hemicellulose and lignin are amorphous, but cellulose has both amorphous and crystalline regions. Cellulose crystallites are small. For instance, values between 25 Å and 36 Å for the thickness of the crystallites in Norway spruce and other softwoods have been reported.[2–5] The small thickness of the cellulose crystallites and a large portion of amorphous material in wood make distinction of the amorphous background from the intensity arising from the cellulose crystallites difficult. This diminishes the precision of determining the thickness of the crystallites by X-ray diffraction (XRD). Values between 65 Å and 311 Å have been reported for the length of the crystallites in Norway spruce and other softwoods.[2–6] The accuracy of the length depends strongly on how carefully the instrumental broadening has been considered. Furthermore, the relation of the size of the crystallites with, for example, growth stress and climate, has not been thoroughly studied.

The crystallinity of wood is defined as the weight fraction of crystalline material – crystalline cellulose – in wood. XRD is a well-established method for determining the crystallinity of partially crystalline materials.[7,8] Hermans and Weidinger[9] conducted the first quantitative investigation into the crystallinity of cellulose fibers by means of XRD. XRD patterns of crystalline cellulose show reflections superimposed on a diffuse background, and the ratio of the sum of the relative integrated intensities and the total intensity provides a measure of the degree of crystallinity.[7] XRD has been widely applied to study the crystallinity of pulp and cellulose fibers (e.g., Teeäär et al.,[10] Paakkari et al.,[11] Stubičar et al.[12]), and there are also some studies on the relative crystallinity of wood.[2–4,6,13,14]

By means of carbon-13 nuclear magnetic resonance with cross polarization and magic angle sample spinning (^{13}C-NMR CP/MAS) it is possible to determine the intrinsic crystallinity of cellulose.[15,16] For pure cellulose samples the crystallinities that were determined by NMR and XRD were in good agreement.[10] The crystallinity of wood determined by XRD is smaller than the crystallinity of cellulose determined by NMR, as the portion of lignin and hemicellulose affect the XRD value.

The crystallinity has an effect on the mechanical properties of cellulose fibers.[17] For instance, Young's modulus and the hardness increase and flexibility decreases with increasing crystallinity.[17] Structural studies are needed for tailoring the properties of wood products. It has been observed that crystallinity and the size of the crystallites are among parameters that change during thermal modification of wood. For example, it has been found that crystallinity increases with steaming treatment but decreases with heat treatment.[13,18]

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The orientation of the cellulose microfibrils in the cell walls of Norway spruce [*Picea abies* (L.) Karst.] has been studied as a function of the number of the year ring.[19–22] It has been found that the mean microfibril angle (MFA) of normal wood of Norway spruce decreases with the distance from the pith. The same samples as those used by Sarén et al.[22] were used in our research to study variations in the crystallinity of wood and the size of cellulose crystallites in Norway spruce as a function of the number of the year ring by means of XRD. The fiber texture of wood complicates the crystallinity determination. We used solid wood samples that have about the same MFA for studying variations in the relative crystallinity with the distance from the pith. Absolute crystallinity values were also determined.

Experimental

Samples

Early wood samples were cut in the tangential direction from normal wood of four Norway spruce trees, grown in Ruotsinkylä, Finland (lat 66°57′36″N, long 33°53′24″E) (Table 1). The samples were obtained at a height of 1.3 m. The dimensions of the samples were 1.0 mm in the radial direction, about 15 mm in the tangential direction, and about 15 mm in the growth direction; and their tangential face was exposed to the X-ray beam. The samples were dry. Before the crystallinity measurements the samples were stored under normal room conditions for several months. The mean MFAs of the samples[22] are presented as a function of the number of the year ring in Fig. 1. The samples used for crystallinity determination (Table 1) are marked with asterisks in Fig. 1. Two additional samples taken from the 4th and 10th year rings at a height of 17 m are marked with ×'s in Fig. 1. The characteristics of the samples are presented in Table 1.

Three reference samples were also prepared; they were obtained from the 2nd, 6th, and 21st year rings at a height of 1.3 m. These three samples (ca. 1 g) were cut into matchstick size and milled (Analytical mill A-10; Kinematica, Lucerne, Switzerland) to fine wood powder in 60 s. Heating the sample was avoided. Wood powder (ca. 0.1 g) was pressed in the shape of a tablet whose diameter was 15 mm and thickness 1.0 mm. For estimating the MFA of the reference samples, solid samples were also cut from the same-year

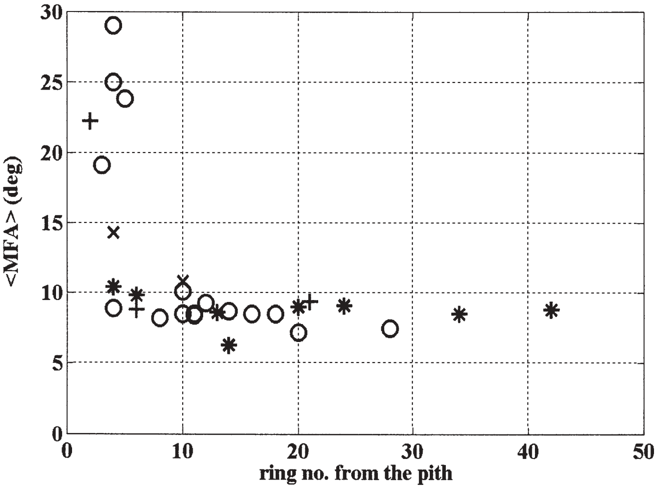

Fig. 1. Mean microfibril angle (*MFA*) as a function of the number of the year ring. Samples marked by asterisks (*) and plus signs (+) were taken at a height of 1.3 m and were used for crystallinity measurements. Samples marked by plus signs were also measured in powdered form. Samples marked by ×'s were taken at a height of 17 m. Samples marked by circles were not used for crystallinity measurements

Table 1. Characteristics of the measured samples

Ring	*d* (mm)	*h* (m)	ρ (g/cm^3)	μ (cm^{-1})	μ/ρ (cm^2/g)	MFA (degrees)	Cri (%)	B_{200} (Å)	B_{004} (Å)
Tree 1									
2	7	1.3	0.318	2.36	7.42	22		31.0	
4	18	1.3	0.278	2.13	7.66	10	39.6	32.8	264
6	27	1.3	0.293	2.30	7.85	9	47.8	31.9	281
10	45	1.3	0.275	1.88	6.83	9			225
14	59	1.3	0.277	2.28	8.23	6	50.2	32.0	
24	89	1.3	0.283	1.98	7.00	9	47.5	32.1	238
34	114	1.3	0.279	2.06	7.38	9	47.6	33.1	302
42	132	1.3	0.360	2.28	6.33	9	43.6	32.6	303
Tree 2									
4	10	17	0.367	2.52	6.87	14		31.1	
10	27	17	0.344	2.40	6.98	11	48.0	31.8	
Tree 3									
6	23	1.3	0.371	2.57	6.93	10	41.8	32.6	
13	47	1.3	0.311	2.62	8.42	9	48.1	31.9	
Tree 4									
5	13	1.3	0.300	1.94	6.47	24			304
20	62	1.3	0.295	2.32	7.86	9	47.1	32.1	301
21	50	1.3	0.307	2.01	6.55	9	48.2	31.6	

Ring, ring number from the pith; *d*, distance from the pith; *h*, height; ρ, density; μ, linear absorption coefficient; μ/ρ, mass absorption coefficient; MFA, mean microfibril angle; Cri, relative crystallinity; B_{200}, average thickness of crystallites; B_{004}, average length of crystallites

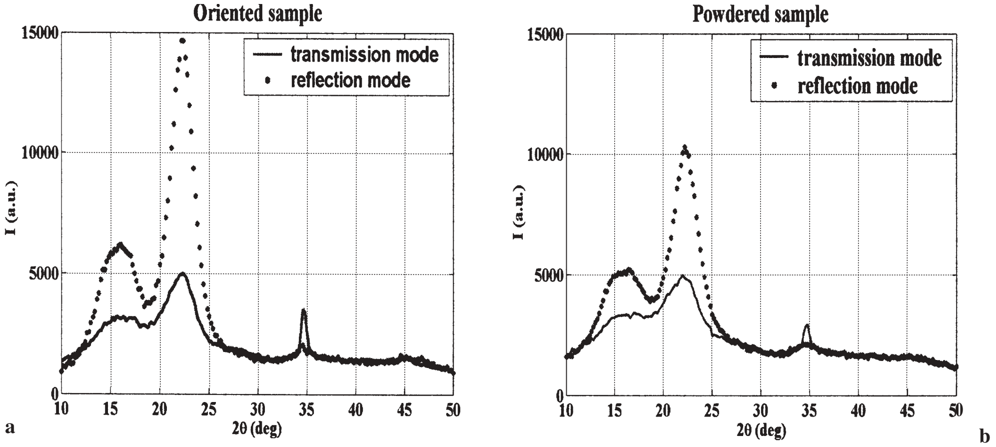

Fig. 2. Comparison of diffraction patterns of a solid oriented sample (**a**) and a powdered sample (**b**). Patterns were measured in the symmetrical reflection mode and the symmetrical transmission mode. Samples were taken from the 6th year ring. *I(a.u.)*, intensity in arbitrary units

rings as the powder samples. These solid samples are marked with plus signs in Fig. 1.

X-ray diffraction measurements

Measurements were performed with Cu $K\alpha_1$ 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 (45 kV, 20 mA). The scattered photons were detected by a NaI (Tl) scintillation counter. The radius of the goniometer was 180 mm. The instrumental broadening was measured as the full width at half maximum (FWHM) of two reflections of a sample with large crystallites. In this case the sample was made from a mixture of lithium fluoride (LiF) and microcrystalline cellulose, and the reflections 111 ($2\theta \approx 38.8$ degrees) and 200 ($2\theta \approx 45.1$ degrees) of LiF were used.

For determining the crystallinity of wood, the diffractometer was used in the symmetrical reflection and transmission modes. The divergence and receiving slits were both rectangular (width 0.6 mm × height 6.0 mm, width 0.3 mm × height 6.0 mm, respectively). The intensity was measured as a function of the scattering angle 2θ by θ-2θ scan. The angle range was 10–50 degrees and the step was 0.2 degree (Fig. 2). The measuring time was chosen so the maximum intensity was about 10 000 counts, and it was typically 60 s per point.

The average thickness of the cellulose crystallites was determined by measuring the FWHM of the reflection 200 in the pattern measured in the symmetrical reflection mode. The instrumental broadening at the reflection 200 ($2\theta \approx$ 22.4 degrees) was estimated to be 0.21 degree.

The average length of cellulose crystallites was determined by measuring the FWHM of the reflection 004 in the symmetrical transmission mode. The divergence and receiving slits were both rectangular (width 0.3 mm × height 6.0 mm, width 0.1 mm × height 6.0 mm, respectively). The angular range was 34.1–35.1 degrees, and the step was 0.04 degree. The measuring time was chosen so the maximum intensity was circa 10 000 counts, and the time was typically 300 s per point. The background was assumed to be linear around the reflection 004, and it was determined by measuring the intensity at two angular ranges in which there are no significant reflections. The angular ranges were 32–33 degrees and 37–38 degrees with steps of 0.1 degree. The measuring time was chosen so the number of counts is circa 1000 per point. To ensure the reliability of this method, one sample was cut in the cross-sectional direction, and the reflection 004 was measured in the symmetrical reflection mode. The same length of the crystallites was obtained as in the case of the tangentially cut samples. The instrumental broadening at the reflection 004 ($2\theta \approx$ 34.6 degrees) was estimated to be 0.30 degree and 0.24 degree for the transmission and reflection modes, respectively.

Results

Figure 2a presents diffraction patterns of a solid oriented sample and Fig. 2b the diffraction patterns of a powdered sample in the symmetrical reflection mode and the symmetrical transmission mode. The measured intensities were corrected for sample absorption and background scattering. In the case of the powdered sample the difference between patterns measured in the reflection and transmission modes is smaller than for the solid oriented sample. Thus, the powder samples are more isotropic than the solid-oriented samples.

To determine the crystallinity, the experimental intensity curve was presented as a linear combination of a calculated diffraction pattern of crystalline cellulose and an experimental model intensity for amorphous material in wood. Because cellulose crystallites are small, distinguishing the amorphous background from the intensity of the cellulose crystallites is a problem and cannot be done reliably, for example with Ruland's method, which is applied for synthetic polymers with larger crystallites.[8] The diffraction pattern of crystalline cellulose was calculated on the basis of the unit cell of Sugiyama et al.[23] It consisted of 14 reflections of cellulose, which were presented as Gaussian functions. The most intensive reflections were chosen based on the structure factors of Gardner and Blackwell[24] and by calculating a powder diffraction pattern from the atomic coordinates of Gardner and Blackwell using the program PowderCell.[25] The model was fitted to the experimental intensity curve of the wood sample. The fitting parameters were the intensities and widths of the Gaussian functions and a scaling factor for the amorphous background. In the fit, 26 Å was set as the lower limit for the size of the crystallites. The crystallinity was calculated as a ratio of the integral of the fitted intensity of crystalline cellulose and the integral of the experimental intensity of the wood sample.

Relative crystallinities were determined by measuring solid wood samples using the symmetrical reflection mode. Absolute crystallinities were estimated by measuring powdered wood samples. The absolute crystallinity was calculated as a weighted mean of crystallinities determined from diffraction patterns measured by the symmetrical reflection and transmission modes. The weights one-third and two-thirds for the reflection and transmission data, respectively, were used according to Paakkari et al.[11] The absolute error in the value of crystallinity of wood was estimated to be ±5%.

When calculating the diffraction pattern for crystalline cellulose, only the Iβ crystal structure was considered in order to reduce the number of fitting parameters. The model of Sugiyama et al.[23] (alga *Microdictyon tenuius*) predicted the positions of the most intensive reflections better than did the models of, for example, Gardner and Balckwell[24] (alga *Valonia ventricosa*) and Nishiyama et al.[26] (*Halocynthia roretzi*). The reason may be the contribution of cellulose Iα in wood, as the position of the intensive reflection 200 of cellulose Iβ of Sugiyama et al.[23] is close to the position of the reflection 110 of cellulose Iα.[23]

Sulfate lignin was chosen as an amorphous standard. Microcrystalline cellulose was also amorphized by ball milling (60 h); but the sample was still partially crystalline, and its intensity curve did not fit an amorphous background as well as that of the sulfate lignin sample. Substances chemically close to native hemicellulose, xylan and mannan, tend also to be too crystalline.[27] We tried to estimate the portion of lignin in wood using a linear combination of intensities of sulfate lignin and milled microcrystalline cellulose as an amorphous background but failed to get stable values. The shapes of the amorphous patterns are too similar to be distinguished by fitting. The choice of amorphous background did not affect the crystallinity value significantly.

The effect of integration limits on the crystallinity were studied by measuring one of the powdered samples at a scattering angle range of 10–90 degrees in both reflection and transmission modes. The crystallinities determined from data measured by the reflection mode decreased 2%, and the crystallinities determined from data measured by the transmission mode increased 2% when the upper limit of integration was increased from 50 to 90 degrees. The increase in the upper limit of integration from 50 to 90 degrees did not affect the weighted mean of the crystallinities determined by the transmission and reflection modes. Therefore, the integration limits were chosen to be from 13 to 50 degrees, in agreement with the work by Stubičar et al.[12]

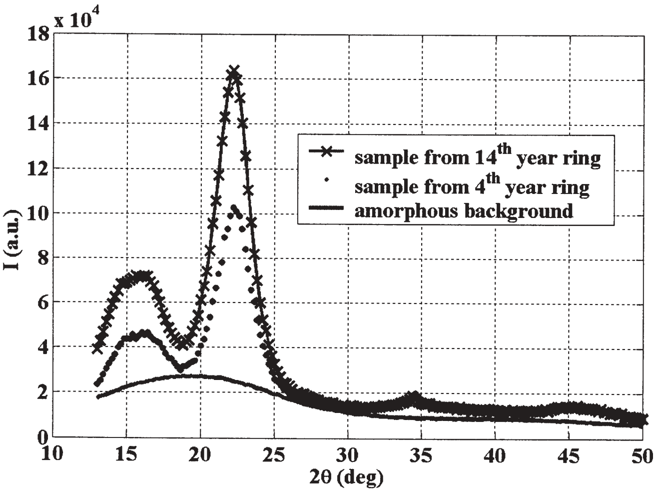

Fig. 3. Diffraction patterns of samples from the 4th and 14th year rings measured in the reflection mode

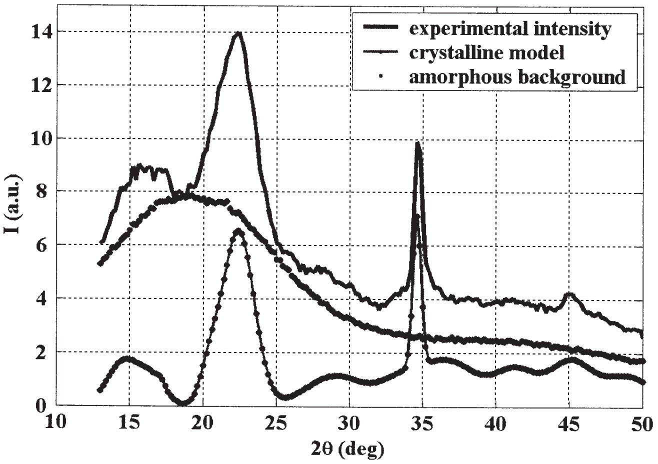

Fig. 4. Diffraction patterns of a sample from the 6th year ring measured in the transmission mode, the crystalline model, and the amorphous background

Figure 3 presents diffraction patterns of two solid oriented samples measured in the reflection mode and the amorphous background. One was taken from the 4th year ring and the other from the 14th year ring. Although both samples have about the same MFAs, their diffraction patterns differ considerably. This is caused by the differences in the crystallinities of the samples. The sample from the 14th year ring has greater crystallinity than the sample from the 4th year ring. Figure 4 presents diffraction patterns of one solid oriented sample measured in transmission mode, the crystalline model, and the amorphous background. The sample was taken from the 6th year ring.

In Fig. 5 the relative crystallinity of wood (Table 1) is presented as a function of the number of the year ring from the pith. The mean MFAs of all samples are small, indicating that the orientation of the crystallites is about the same (Fig. 1). The crystallinity increases near the pith, from the 4th year ring to the 6th year ring. The crystallinity is then

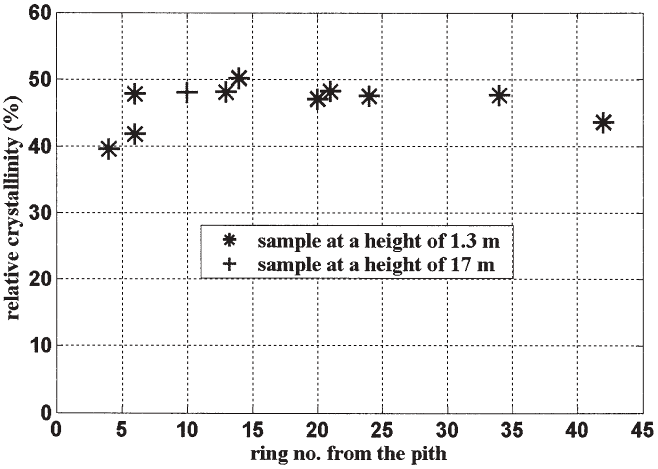

Fig. 5. Relative crystallinity of wood presented as a function of the ring number from the pith. Measurements were made by the symmetrical reflection mode from solid oriented samples with the same mean microfibril angle

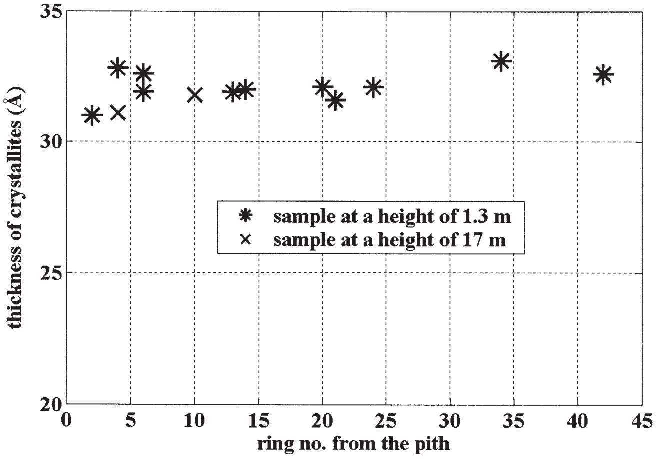

Fig. 6. Thickness of the crystallites presented as a function of the number of the year ring from the pith

Table 2. Crystallinity of powdered samples

Year ring	Crystallinity (%)		
	Reflection mode	Transmission mode	Weighted average
2nd	29.1	20.3	23
6th	32.8	24.7	27
21st	38.8	28.2	32

quite constant from the 10th year ring to the 42nd year ring. The crystallinities of three powdered samples are presented in Table 2.

The average thickness of the crystallites of the powdered samples was also determined to ensure that the crystallinity did not diminish during powdering. It was observed to be the same as that of the solid oriented samples.

The average size of crystallites, B_{hkl}, was estimated from the widths of the reflections *hkl* by using the well-known Scherrer formula

$$B_{hkl} = \frac{0.9\lambda}{\Delta 2\theta \cos\theta} \tag{1}$$

where $\Delta 2\theta$ is the FWHM of the reflection in radians. The effect of instrumental broadening on the width of the reflections was included by assuming that the shapes of both the reflection and the instrumental function are approximately Gaussian, and the value of $\Delta 2\theta$ was calculated using the formula

$$\Delta 2\theta = \left(b_s^2 - b_i^2\right)^{1/2} \tag{2}$$

where b_s is the measured FWHM of the reflection 200 or 004, and b_i is the instrumental broadening.

The FWHM of the reflection was determined by fitting after subtracting the amorphous background. The Gaussian curve was fitted to the top of the peak for determining the maximum intensity and the position of the reflection. The values where the intensity has diminished to half its maximum value were found by linear interpolation. Because the reflection 102 ($2\theta \approx 20.5$ degrees) is close to the reflection 200 ($2\theta \approx 22.4$ degrees), the 2θ value where the intensity has diminished to half of its maximum value was determined only from the high angle side of the reflection.

The FWHM of the reflection 200 was used to determine the thickness of the cellulose crystallites (Table 1). The thickness of the crystallites is presented in Fig. 6 as a function of the number of the year ring from the pith. The thickness appears to be constant for the whole year ring range. The calculated average ± SD thickness of the cellulose crystallites was 32 ± 0.6 Å. The average length of the cellulose crystallites was 280 Å. Only the average is given, as the accuracy of the determination of the length of the cellulose crystallites by the nonfocusing transmission method is diminished owing to the fluctuations of the density and the absorption coefficient of the samples. Correspondingly, the accuracy of the determination of the thickness and length of the crystallites is estimated to be ±1 Å and ±20 Å, respectively.

Discussion

The results for the solid and powder samples show that the mass fraction of crystalline cellulose in the cell wall changes with the ring number and distance from the pith. The crystallinity increases as a function of the number of the year ring (Fig. 5) similar to the tracheid length and the diameter of the cells.[21,22,28,29] Marton et al.[2] obtained similar dependence between the crystallinity index and the year ring number; but because the MFAs varied both the fraction of crystalline cellulose and fiber texture affected their results. The relative crystallinity values of the solid samples, determined by the reflection mode, are clearly too high (Table 1) owing to the oriented fiber structure compared to the crystallinities determined from the powdered samples (Table 2). However, these relative crystallinity results are correlated with the crystallinities determined using powdered samples. Therefore this method was chosen here for the set of samples with the same fiber texture. The crystallinities obtained using the solid samples and the transmission mode are close to absolute crystallinities, but the fitting is not easy because of the small average size of the crystallites and the strongly overlapping reflections (Fig. 4). It is crucial to have a good amorphous model and to choose the reflections included in the fit properly.

The crystallinities of powdered samples varied between 23% and 32%. The values obtained by the reflection mode (Table 2) are smaller than those obtained by Tanaka et al.[4] for wood meal of *Pinus densiflora* using a different method to determine the amorphous background and a shorter angular range. According to Sjöström[30] the dry weight fraction of cellulose in Norway spruce is 42%, and according to Anttonen et al.[31] it is 48%. If the weight fraction of cellulose was 45%, the crystallinity of cellulose would vary between 51% and 71%. This is in good agreement with the NMR result for Norway spruce, 62%, found by Newman and Hemmingson.[16]

The average size of the crystallites did not change as a function of the number of year ring. However, Leary et al.[32] observed for *Pinus radiata* that the intrinsic crystallinity of cellulose was almost constant in mature wood but lower in earlywood of the first ring. Therefore, the observed increase in crystallinity (Fig. 5) may be due to decreased lignin[32,33] content, increased cellulose content,[33] and the increase of the order of cellulose chains as a function of the year ring.[32]

The thickness of the crystallites was about 32 Å, which is consistent with the value obtained by Marton et al.[2] for Norway spruce grown in Syracuse, NY, USA but considerably larger than the 25 Å obtained by Jakob et al.[5] for Norway spruce grown in Austria. The average length of the cellulose crystallites was 280 Å, which is about twice as long as those reported by Marton et al.[2] and Jakob et al.[5] for Norway spruce. Reasons for the different results may be the genetic origin, the climate, and the estimation of the instrumental broadening. The value is larger than that obtained earlier for a compression wood sample of Norway spruce (200 Å).[34] Tanaka et al.[4] obtained also different lengths of crystallites for compression and opposite wood samples of *Pinus densiflora*.

Conclusions

It was observed that the crystallinity of wood increased as a function of the year ring near the pith and was nearly constant in the mature wood. No change in the average thickness of the crystallites as a function of the number of the year ring was observed. The crystallinity of wood could be determined reliably using powdered wood samples and both reflection and transmission modes. When only relative crystallinities are needed and the fiber texture of the samples is the same, it is easiest to measure solid oriented wood samples with the reflection mode.

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