

**THE INFLUENCE OF METHOD OF CELLULOSE
ISOLATION FROM WOOD ON THE DEGREE AND INDEX
OF CRYSTALLINITY**

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ABSTRACT

An attempt was made to find the correlation between the crystallinity index, as determined by FTIR, and the crystallinity degree, as determined with the WAXS technique. Analyzed cellulose was isolated from pine and poplar woods with the Kirschnner-Hoffer method, while the number of cycles varied from 1 to 9. The degree of cellulose crystallinity changed depending on the number of cycles. The degree of cellulose contamination by lignin influenced the quality of results obtained regarding the crystallinity index. Lignin content was the highest after 1 to 3 cycles, but then significantly decreased (especially in pine wood). Vibrations of the C-H group originated from lignin and cellulose overlap, causing the overestimation of the crystallinity index after these cycles. For the rest of the cycles, the correlation between the crystallinity index and crystallinity degree (measured with WAXS) was different for pine and poplar woods and appeared to be caused by effects related to the presence of lignin.

KEYWORDS: Cellulose, crystallinity index, crystallinity degree, FTIR, lignin, WAX.

INTRODUCTION

Any attempt at cellulose isolation or its modification leads to a crystallographic structure change (O'Sullivan 1997). Crystallinity degree, along with the polymerization degree, is a very important parameter that is connected with the strength properties of fibrous materials. A material with a high amount of ordered areas is less hygroscopic, swells to a lesser degree, has increased tension strength and hardness, and is much more resistant to chemical factors. This arises from strong connections between cellulose chains because of hydrogen bonds and Van der Waals forces. The crystallinity degree of wood cellulose is about 50 %.

Many analytical techniques can be used for the structural analysis of cellulose (Zborowska et al. 2007, Kim et al. 2013, Zawadzki et al. 2011). The following direct methods of cellulose structural analysis are most often used: Wide angle X-ray diffraction (WAXD), nuclear magnetic resonance spectroscopy (^{13}C NMR), Fourier transform infrared spectrophotometry (FTIR), size exclusion chromatography (SEC-HPLC). WAXD analysis is performed using diffraction maxima originating from crystalline cellulose and areas connected to X-ray scattering in the structure of amorphous cellulose. The FTIR technique is often used for wood analysis (Müller et al. 2009), but it may also be applied for crystallinity index (CI) determination, based on the measurement of height or area of bands appearing at specific wave number values that originate from crystalline and amorphous cellulose (Åkerholm et al. 2004). It is a straightforward method, but obtained values are relative because analyzed bands are connected with both structural forms of cellulose. For this reason, CI calculated using this method is often compared with the results of crystallinity degree measurements performed with WAXD.

The aims of this paper are to find the optimal conditions of cellulose isolation from wood using the Kürschner-Hoffer method and to determine the crystallinity degree of cellulose isolated in these conditions using FTIR. To realize this second task, the possibility of FTIR calibration by applying the WAXD method was examined.

MATERIAL AND METHODS

Wood of Scots pine (*Pinus sylvestris* L.), as a representative of coniferous species, and poplar (*Populus tremula* L.), as a representative of deciduous species, were analyzed. These two species are common in Poland. Material was collected from 200-mm-thick discs that were cut from the stem at a height of 130 cm.

Samples of cellulose that differed from one another by the number of cycles (boiling in ethanol – nitric (V) acid mixture), from 1 to 9, were analyzed. Each cellulose sample was analyzed to determine residual lignin using a Shimadzu UVmini 1240 UV-VIS spectrophotometer (Rodrigues et al. 1999).

The primary cellulose measurements were performed with a Thermo Fisher Scientific Inc. Nicolet 6700 FTIR spectrometer. Samples of cellulose obtained with the Kürschner-Hoffer method were mixed with KBr at a ratio of 1:200. The FTIR spectrometer performed 32 scans at 4 cm^{-1} resolution for each measurement.

Crystallinity degree was determined using wide angle X-ray diffraction (WAXD) with a Carl Zeiss AG TUR M-62 apparatus. The obtained roentgenograms are functions of X-ray intensity with the diffraction angle 2θ (range of $2\theta = 5^\circ$ to 30° , counting rate $0.04^\circ/3\text{ s}$). Peaks were separated with the method used by Rabiej (1991). Crystallinity degree was calculated after peak separation based on the ratio of areas that originated from crystalline parts to the total of areas that originated from both crystalline and amorphous parts (Isogai and Usuda 1990).

RESULTS AND DISCUSSION

Example FTIR spectra are presented in Fig. 1. Analyzed cellulose was isolated in an optimal manner (after the third cycle) with the Kürschner-Hoffer method from both pine and poplar wood.

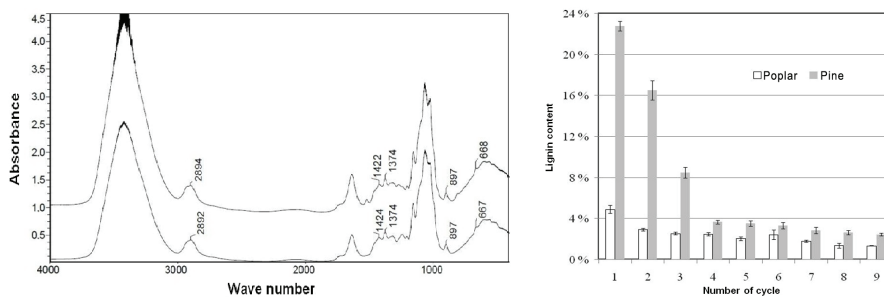


Fig. 1: Example FTIR spectra of the cellulose isolated with Kürschner-Hoffer method from pine (upper curve) and poplar wood (lower curve) after the third cycle of isolation.

The obtained spectra of cellulose isolated from pine and poplar woods are difficult to interpret due to the significant content of impurities such as hemicelluloses and lignin. The proper ratio of areas or heights of chosen bands must be calculated to determine the crystallinity index (Åkerholm 2004). Bands with the wave numbers 2900 (strong band of C-H bonds stretching vibrations), 1429, 1370, 895 (deforming vibrations of C-H bonds), and 670 cm^{-1} (deforming vibrations of C-OH bonds), connected with crystalline and amorphous cellulose, were analyzed.

These vibrations may have originated from the rest of the wood's components. Superposition of similar atom group vibrations originated from other carbohydrates and lignin may cause a change in band intensity.

The crystallinity index was calculated by applying ratios of proper FTIR band heights ($H_{1429 \text{ cm}^{-1}} / H_{895 \text{ cm}^{-1}}$, $H_{1370 \text{ cm}^{-1}} / H_{2900 \text{ cm}^{-1}}$) or surfaces ($A_{1370 \text{ cm}^{-1}} / A_{670 \text{ cm}^{-1}}$), according to Åkerholm (2004). The results, depending on the number of Kürschner-Hoffer cycles, are presented in Tab. 1.

The results given in Tab. 1 are repeatable for analyzed ratios of band heights for pine wood. Coefficients ($H_{1429 \text{ cm}^{-1}} / H_{895 \text{ cm}^{-1}}$, $H_{1370 \text{ cm}^{-1}} / H_{2900 \text{ cm}^{-1}}$) for the first two isolation cycles from pine wood were the highest. This may be caused by cellulose pollution with lignin. This thesis is confirmed by spectrophotometric tests (UV-VIS) that were performed on cellulose pulp isolated from pine and poplar woods. Results of these measurements are presented in Fig. 2.

After the first Kürschner-Hoffer cycle, the lignin content in pine wood decreased to 22.5, and the second cycle caused a further decrease to the level of 16.5 %. Lignin content following two cycles equaled about 3.5 %. The change in the absorbance for the 1429 cm^{-1} band may be caused, among others, by the superposition of vibrations originating from carbohydrates (cellulose

Tab. 1: The results of crystallinity index calculations based on FTIR measurements.

Rates of bands heights or surfaces	Number of cycles in K.-H. method								
	1	2	3	4	5	6	7	8	9
Pine H_{1370}/H_{2900}	5.909	4.654	0.454	0.506	1.008	2.776	2.176	3.229	–
Pine H_{1429}/H_{895}	0.652	0.629	0.431	0.451	0.615	0.504	0.627	0.888	–
Pine A_{1370}/A_{670}	89	115	94	165	122	149	117	12	–
Poplar H_{1370}/H_{2900}	1.592	0.078	0.429	0.477	0.477	1.000	0.951	0.401	1.067
Poplar H_{1429}/H_{895}	0.464	0.550	0.420	0.473	0.673	0.508	0.607	0.599	1.067
Poplar A_{1370}/A_{670}	484	2	187	181	124	219	69	158	192

and hemicelluloses) and lignin C-H bonds (Evans et al. 1995). That is why the crystallinity index was initially high, much higher than for the cellulose pulp isolated from poplar wood.

Lignin content in the cellulose isolated from poplar wood decreased to 5 % after the first cycle of isolation. Consecutive cycle caused a further decrease of this parameter to 3 %.

In further Kürschner-Hoffer cycles (both in pine and poplar), the lignin content consequently decreased and cellulose (mainly the amorphous part) may have degraded under the influence of nitric (V) acid. Changes in the cellulose structure may have caused an observable increase in the crystallinity index.

Crystallinity degree values obtained using wide angle X-ray scattering (WAXD) were compared with the crystallinity index (H_{1429}/H_{895}) to evaluate its utility. Results of WAXD experiments are presented in Tab. 2.

Tab. 2: Crystallinity degree (calculated with WAXD method) of cellulose isolated from pine and poplar woods.

Number of cycle	0	1	2	3	4	5	6	7	8	9
Crystallinity degree (pine) (%)	53	61	65	67	67	67	69	69	71	73
Crystallinity degree (poplar) (%)	50	69	71	68	69	68	68	68	69	70

The continuous action of the ethanol-acid mixture caused the increase in crystallinity of the cellulose isolated from pine wood. This indicates that amorphous cellulose is the primary recipient of the influence of the mixture used. Degradation of the crystalline part of cellulose would have caused the crystallinity degree to decrease. The increase in crystallinity degree for poplar wood was detected only after the first cycle of mixing, and its value remained on the level of 68 to 69 %.

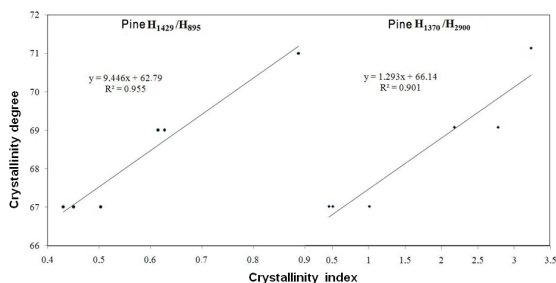


Fig. 3: Linear correlations between crystallinity degree of pine cellulose and crystallinity index based on coefficients $H_{1429\text{ cm}^{-1}}/H_{895\text{ cm}^{-1}}$ and $H_{1370\text{ cm}^{-1}}/H_{2900\text{ cm}^{-1}}$.

Fig. 3 presents the obtained linear correlations between the crystallinity degree of pine cellulose and the crystallinity index based on the coefficients $H_{1429\text{ cm}^{-1}} / H_{895\text{ cm}^{-1}}$ and $H_{1370\text{ cm}^{-1}} / H_{2900\text{ cm}^{-1}}$. The dependence is presented starting from the third cycle (because of the influence of the high lignin content on the crystallinity index value). Both values are characterized with quite high correlation coefficients. This seems to allow for the application of the WAXD method to calibrate FTIR results to obtain crystallinity degree values based only on this second technique. However, results obtained for poplar wood raise significant doubts in this matter. What is the difference between pine and poplar that causes such a difference in the crystallinity degree results? According to Fig. 2, lignin content is the factor to consider. Does decreasing lignin content interfere with the X-ray intensity in the WAXD method and cause the increase in crystallinity degree? The connection between the decrease in lignin content after the first K-H cycle for poplar wood and the corresponding decrease in crystallinity degree suggest that the answer is yes.

The differences in the results obtained for pine and poplar are probably caused by one of several reasons (or by a few of them). First, the wood structure is different for both species, and the relations between lignin and carbohydrates are not the same. Second, poplar wood density is lower because of its more developed porous structure. Nitric (V) acid is then able to penetrate the wood structure better and, in consequence, most lignin is removed after the first cycle. The collapse of bonds between lignin and carbohydrates (creating the so-called LCC: lignin-carbohydrates complex) causes the hydrolysis of part of the cellulose (especially the amorphous content); this is why the crystallinity degree changes with decreasing lignin content. Third, there may be different types of cellulose (triclinic I_α , monoclinic I_β) in coniferous and deciduous species, as stated by Yildiz and Gümüşkaya (2007). The I_α/I_β ratios in pine and poplar wood samples changed with the action of the acid used. According to these results, it can be seen that the crystalline structure of cellulose in pine wood samples is more affected by acid than it is in poplar wood samples.

The strength of LCC bonds probably differs depending on the cellulose type (I_α or I_β), which influences the FTIR results. Moreover, the lower strength of LCC bonds allows for faster lignin elimination. LCCs are hydrolysis-proof. In pine wood, the decrease in lignin content is gradual, as is the process of amorphous cellulose hydrolysis. In poplar wood, almost all the lignin is removed, and amorphous cellulose with a low polymerization degree is hydrolyzed, after the first cycle. This, then, is why the crystallinity degree remains almost constant.

CONCLUSIONS

1. Results from cellulose isolated from wood with the Kirschner-Hoffer method show that the long-lasting influence of the ethanol-acid mixture causes an increase in the cellulose crystallinity in the case of pine wood.
2. Amorphous areas of cellulose in an acidic environment may undergo depolymerization first.
3. The crystallinity degree and crystallinity index may be successfully correlated. However, determination of the crystallinity degree seems to be interrupted by the presence of lignin.
4. More studies must be performed to determine whether the crystallinity degree could be calculated based on the crystallinity index.

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