

SOME ASPECTS OF ESTIMATION OF THE CRYSTALLINITY OF GAMMA RADIATION WOOD CELLULOSE BY FTIR SPECTROSCOPY AND X-RAY DIFFRACTION TECHNIQUES

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Abstract. Changes in crystallinity of wood cellulose *in situ* under gamma radiation were investigated with infrared (FTIR) spectroscopy and X-ray diffraction technique. The correlation between degree of crystallinity determined by X-ray diffraction and crystallinity index calculated with normal and second-derivative IR spectra were studied. Good correlation obtained only for ratio A_{1373}/A_{2885} . It has been shown that absorbance/valley ratio: $A_{1373 \text{ cm}^{-1}}/A_{1350 \text{ cm}^{-1}}$ or $A_{1160 \text{ cm}^{-1}}/A_{1148 \text{ cm}^{-1}}$ with FTIR spectra can be used for estimation crystallinity of wood cellulose *in situ*.

Key words: wood cellulose, crystallinity, gamma radiation, FTIR spectroscopy, X-ray diffraction

INTRODUCTION

Gamma radiation is the most penetrating form of radiation. It is known that gamma radiation has destructive influence on both physical and chemical properties of wood [Raczkowski and Fabisiak 1987, Suchorski 1999, Csupor et al. 2000].

Gamma radiation on wood contributes to degradation of its constituents (namely cellulose, hemicellulose and lignin) and changes the crystallinity in wood cellulose. There is evidence that the changes of cellulose crystallinity importantly influence the elasticity, absorptive capacity, and other industrially valuable physical properties of the wood fibres.

To characterize crystallinity changes of cellulose, the degree of crystallinity, that is the ratio between the crystalline and amorphous areas of cellulose, has been assumed.

Estimation of cellulose crystallinity has been studied with different techniques as: X-ray diffraction [Segal et al. 1959, Cutter et al. 1980, Kim et al. 2001], differential scanning microcalorimetry (DSC) (Malutan et al. 1999), ^{13}C NMR spectroscopy [New-

man and Hemmingson 1990, Newman et al. 1993], and IR spectroscopy [O'Connor et al. 1958, Nelson and O'Connor 1964, Schultz et al. 1985].

The infrared spectroscopy is a valuable and easy method for obtaining precise information related to the structure of cellulose molecules such as the nature of hydrogen bonding or crystallinity. It has been shown that infrared absorption spectra of cellulose has been applied successfully to investigations of crystallinity and crystalline modifications of pure celluloses [O'Connor et al. 1958, Liang and Marchessault 1959, Nelson and O'Connor 1964, Ferrús and Pagés 1977, Krutul 1990, Richter et al. 1991, Fengel and Strobel 1994].

However, there are only very few studies on changes of crystallinity of celluloses in wood or pulp [Ebringerová et al. 1993, Evans et al. 1995].

The intensities of the certain bands in IR spectra have been found to be sensitive to variations in cellulose crystallinity or crystalline form. Such variations may be determined by the use of the ratio of IR bands: those which are affected by cellulose crystallinity to these bands which intensity is a result of crystallinity changes. The ratios of the peaks at 1429 to 894 cm^{-1} (A_{1429}/A_{894}) [O'Connor et al. 1958, Ferrús and Pagés 1977] and A_{1372}/A_{2900} [Nelson and O'Connor 1964, Ferrús and Pagés 1977] have been used to measure relative cellulose crystallinities. Transformation of cellulose I into cellulose II was determined by comparing the absorbance at 3333, 1163 and 900 cm^{-1} [Hurtubise and Krässig 1960].

Richter et al. [1991] proposed the ratio of the peaks areas at 1370 and 670 cm^{-1} (A_{1370}/A_{670}) as IR index for the lattice transformation cellulose I to cellulose II.

Ebringerová et al. [1993] characterized cellulose crystallinity changes in beech- and aspen wood upon steaming determined the three absorbance/valley ratio: 1108/1091 cm^{-1} , 1430/1403 cm^{-1} and 1459/1403 cm^{-1} .

Amorphousation of cellulose leads both to disappearance of differences between bands and to its broadening in IR spectra. Therefore IR spectra of native cellulose are resultant of narrow absorption bands of ordered fraction and wide absorption bands of amorphous fraction of cellulose [Maslov and Suhov 1988]. Moreover, absorption bands from other components of wood overlap some absorption bands of *in situ* cellulose in wood.

The introduction of the Fourier transformation technique improved and widened the possibilities of infrared spectroscopy. The formation of spectra by multiple scanning very small samples can be analysed, while the mathematical potential of the computer provides an improvement of spectra and an increase in resolution. One of the mathematical methods, which are part of the computer software of any FTIR spectrometer, is "deconvolution" or derivative spectra. By this method the bands become more clearly separated. The increased selectivity in derivative spectrophotometry results from the fact that bands, which overlap in normal absorption spectra, appear as separated bands in the derivative spectra.

In this work, there are presented results of studies carried out with FTIR spectroscopy method on crystallinity changes of *in situ* cellulose in wood irradiated by gamma radiation. With normal and second derivative spectra there were determined three crystallinity index (A_{1427}/A_{896} , A_{1373}/A_{2885} and A_{1373}/A_{667}) that were most often used in studies of cellulose crystallinity and there were also proposed new indexes measured from absorbance/valley ratio: A_{1373}/A_{1350} and A_{1160}/A_{1148} .

The obtained values of index were correlated with results of crystallinity degree, which were determined by X-ray diffraction method.

EXPERIMENTAL

Irradiation of pine wood

The experimental samples were selected from sapwood part of a log and produced as the prismatic beams in which the grains direction was exactly parallel to the longest edge of each sample (10(R) x 5(T) x 150(L) mm³).

Samples of pine wood *Pinus sylvestris* were treated by different doses of γ -radiation: 20, 60, 120, 300, 500, 1500, 4500, 9000 kGy in room temperature. The samples were exposed to gamma radiation in apparatus type RChM-Gamma-20 with cobalt Co⁶⁰ as a source of radiation.

Infrared spectra

The samples of wood were ground to pass about 1mm screen. Screened wood were dried overnight first in an oven at 60°C and further over P₂O₅ in vacuum desiccator. About 200 mg of dry wood were milled in vibratory ball mill. FTIR spectra were obtained using the KBr pellet technique. The pellets were prepared by mixing 2mg of the wood powder with 400 mg of dry KBr in a vibratory ball mill. The 13 mm diameter pellets were prepared in standard device. The portion 200 mg was pressed under vacuum to about 19.6 Mpa for 15 min. Transmission spectra in (MIR) were recorded on the Mattson Infinity spectrophotometer in range from 550 to 4000 cm⁻¹ with 2 cm⁻¹ resolutions. The number of scans was 128, and the sample spectra were rationed against a blank reference. The absorbance spectra were standardized: a base line correction was performed between 1887 to 766 cm⁻¹ and 4000 to 2400 cm⁻¹. The spectra were normalized by the y axis expansion algorithm of the spectrometer in such a way that the absorption of the dominant band equalled 1.0. The intensities of 5 bands (2885, 1427, 1373, 896 and 667 cm⁻¹) on the normal spectra in these regions were determined by the baseline method as suggested by Faix [1986].

With the normal spectra the second derivative spectra were generated and smoothed. The area of the peaks on second derivative spectra were determined electronically (the integrated area was measured) using WinFIRST software.

The ratios of absorption bands (crystallinity index -CI):

$$CI = A_{1427 \text{ cm}^{-1}}/A_{896 \text{ cm}^{-1}} \text{ [O'Connor et al. 1958],}$$

$$CI = A_{1373 \text{ cm}^{-1}}/A_{2885 \text{ cm}^{-1}} \text{ [Ferrús and Pagés 1977],}$$

$$CI = A_{1373 \text{ cm}^{-1}}/A_{667 \text{ cm}^{-1}} \text{ [Richter et al. 1991],}$$

have been assumed as a comparative criterion of the "crystallinity degree" of cellulose. This ratios were determined with the normal spectra and second derivative spectra. Crystallinity indexes were calculated from both height and integrated area of normal spectra and only from integrated area for second derivative spectra. Baselines were drawn individually for each peaks in agreement with method introduced by Faix (1986).

The absorbances/valley (A/V) ratio:

$$CI = A/V \text{ Ratio} = A_{1373 \text{ cm}^{-1}}/A_{1350 \text{ cm}^{-1}},$$

CI = A/V Ratio = $A_{1160\text{cm}^{-1}}/A_{1148\text{cm}^{-1}}$
 were determined with the normal spectra.

X-ray diffraction

The X-ray diffraction patterns of unirradiated and irradiated pinewood were recorded by a diffractometer in the angle range of $5-30^\circ 2\theta$. Ni-filtered Cu- K_α radiation (1.5418 Å) generated at 30 kV and 25 mA was used. The degree of crystallinity of pine wood cellulose *in situ* was analysed using wide-angle X-ray scattering (WAXS) technique. The degree of crystallinity (x_c) was calculated from the ratio of the integral intensity of crystalline portions to the total intensity of the sample [Kasprzyk et al. 2004]. The degree of crystallinity was calculated as average values from three measurements for each irradiation dose group.

RESULTS AND DISCUSSION

Figure 1 shows FTIR spectra of pine wood before and after gamma radiation and Klason lignin and cellulose isolated from unirradiated wood of *Pinus sylvestris*. Lignin in pine wood has significant absorbance in the regions being used for cellulose crystallinity determination (particularly about 1427 and 2885 cm^{-1}) so lignin absorptions bands interfere the area of the crystalline cellulose peaks. Second-derivative spectra let to show distinctly superimposition cellulose and lignin bands (Fig. 2 a, b, c)

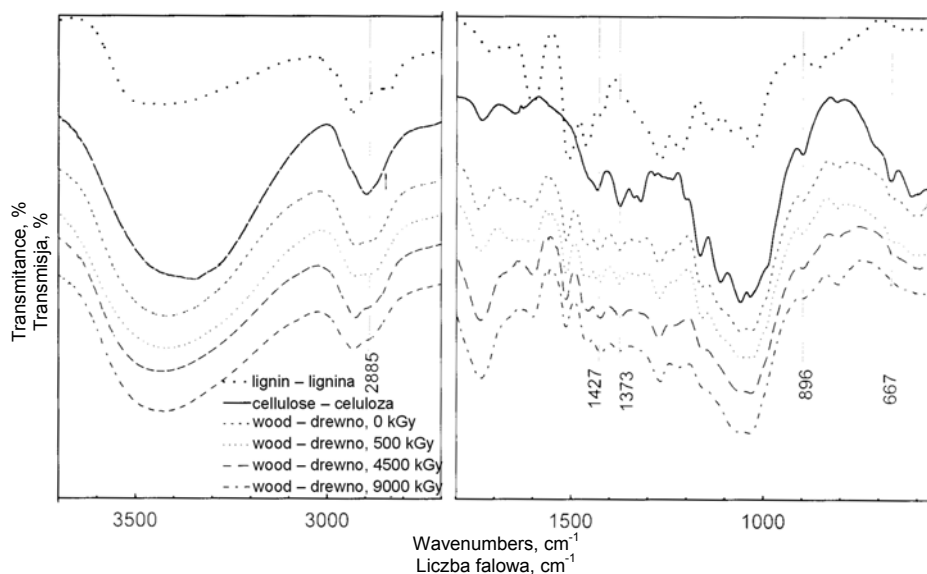


Fig. 1. FTIR spectra of pine wood before and after gamma irradiation and isolated wood components (lignin and cellulose)

Rys. 1. Widma FTIR drewna sosnowego przed i po napromieniowaniu promieniowaniem gamma oraz wyizolowane składniki drewna (lignina i celuloza)

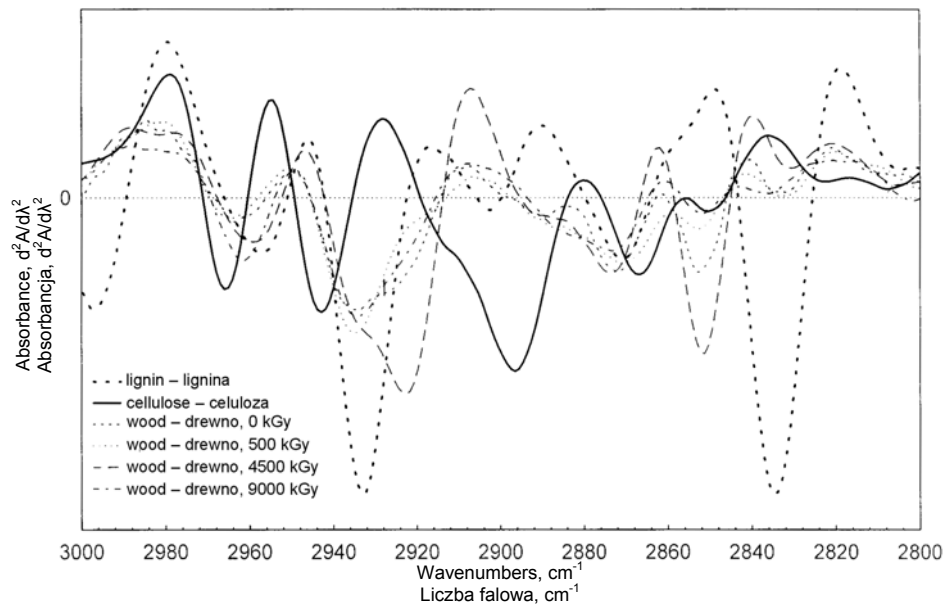


Fig. 2 a. Expanded second derivatives of the FTIR pine wood spectra in Figure 1 over the range 3000-2800 cm^{-1}

Rys. 2 a. Druga pochodna widma FTIR drewna sosnowego z rysunku 1 w zakresie 3000-2800 cm^{-1}

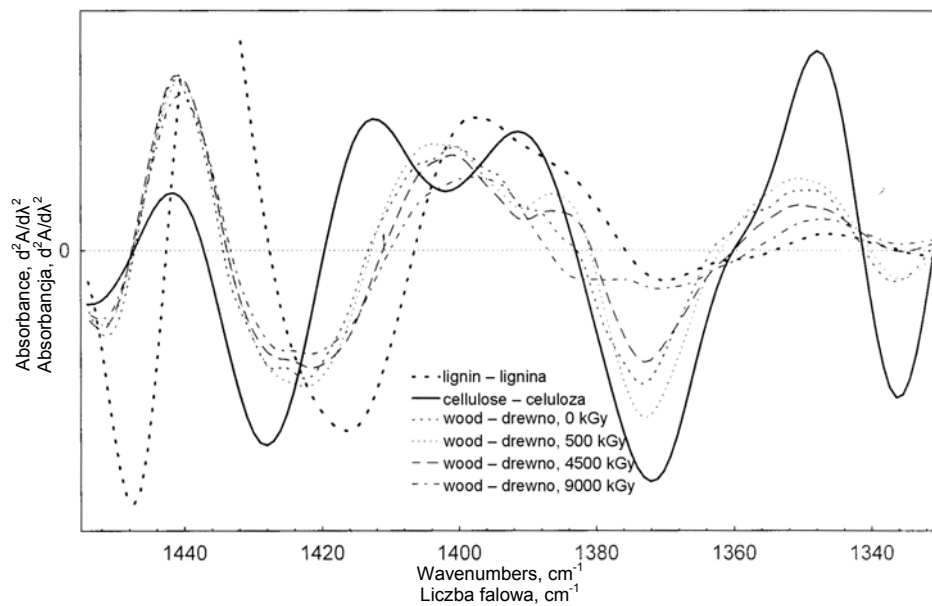


Fig. 2 b. Expanded second derivatives of the FTIR pine wood spectra in Figure 1 over the range 1455-1330 cm^{-1}

Rys. 2 b. Druga pochodna widma FTIR drewna sosnowego z rysunku 1 w zakresie 1455-1330 cm^{-1}

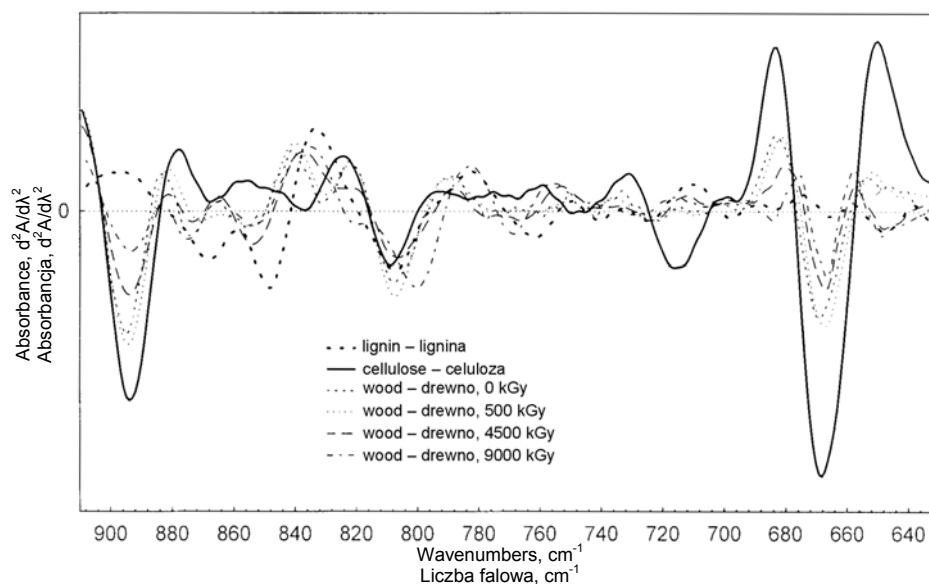


Fig. 2 c. Expanded second derivatives of the FTIR pine wood spectra in Figure 1 over the range 910-630 cm^{-1}

Rys. 2 c. Druga pochodna widma FTIR drewna sosnowego z rysunku 1 w zakresie 910-630 cm^{-1}

For estimation of cellulose crystallinity many authors have been used absorption bands that occur at about 2885, 1427, 1373, 896 and 667 cm^{-1} .

The absorption band at 2885 cm^{-1} is caused by stretching vibration of C-H groups [Harrington et al. 1964].

The band at 1427 cm^{-1} resulted from CH_2 symmetrical bending should respond to changes in the environment of the C_6 group, such as the formation (or breaking) of an intramolecular hydrogen bond involving O_6 [Nelson and O'Connor 1964] but there is also a contribution the CH bonds from methoxyl groups in lignin [Harrington et al. 1964] and C = C stretching in aromatic ring of lignin [Evans et al. 1992].

The band near 1373 cm^{-1} arises from CH bending vibration in cellulose and hemicelluloses [Kondo and Sawatari 1996].

The band at 896 cm^{-1} is the anomeric carbon group frequency in cellulose and hemicelluloses [Evans et al. 1992]. This band is assigned to motions of atoms attached to C_1 , would be expected to reflect changes in molecular conformation due to rotation about the $\text{C}_1\text{-O-C}_4$ (glucosidic) linkage [Nelson and O'Connor 1964].

The band at 667 cm^{-1} is caused by OH out-of plane bending [Kondo and Sawatari 1996].

The changes in absorbance of the peaks that are used for determination of crystallinity index were monitored during irradiation (Fig. 3). The intensity of bands were compared to the intensity of the 1506 cm^{-1} band that is used as an internal standard, assigned to benzene ring stretching in lignin. Lignin is used as an internal standard because its high resistance to degradation by gamma radiation [Seifert 1964, Kasprzyk and Wichlacz 2003 a]. Moreover the absorption coefficient of peak at 1506 is not influenced by substitution [Kimura et al. 1992].

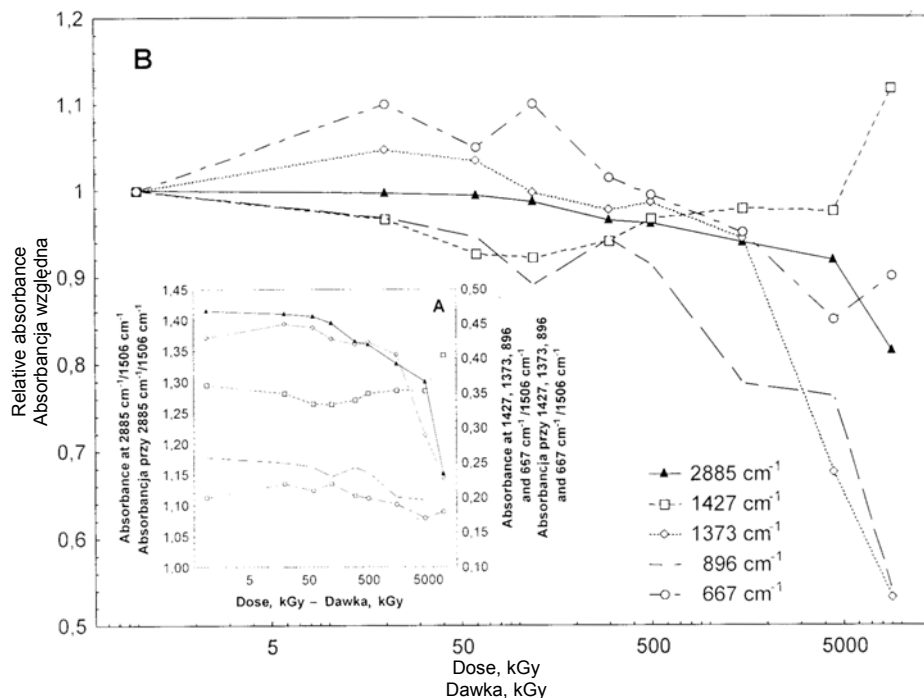


Fig. 3. The change in absorbance (A) and relative absorbance (B) of band using in MIR crystallinity index of wood cellulose depend of dose gamma radiation
 Rys. 3. Zmiana absorbancji (A) i absorbancji względnej (B) pasm stosowanych do oznaczeń indeksów krystaliczności cellulozu w drewnie metodą MIR w zależności od dawki promieniowania gamma

The relative absorbance of studied peaks decreases (except band at 1427 cm^{-1}) with increasing of gamma irradiation. It is worth to notice that the pattern of decrease is different (Fig. 3 a). The decrease of the bands at 1373 cm^{-1} and 896 cm^{-1} occurred rapidly particularly when the dose of irradiation overcome 500 kGy . These changes mean that wood's carbohydrates were destroyed. This observation is confirmed by chemical analysis of samples, where significant destruction of cellulose by high doses of gamma radiation were measured [Seifert 1964, Kasprzyk and Wichłacz 2003 a]. The relative absorbance of band at 1427 cm^{-1} does not change significantly till 4500 kGy and then increase to about 10% at 9500 kGy dose gamma irradiation. This observation is in opposition to changes of intensity of bands at 1373 and 896 cm^{-1} . This discrepancy is caused by the fact that the band at 1427 cm^{-1} descends not only from vibrations of CH cellulose and hemicelluloses but also from lignin, as it was mentioned above. Although the lignin is not destroyed by gamma radiation, we observed the increase of condensation index of lignin [Kasprzyk and Wichłacz 2003 b]. The increase of lignin condensation lead to increase of absorption coefficient of this band.

The intensities of peaks at 2885 cm^{-1} and 667 cm^{-1} changed insignificantly.

Table 1. Correlation between the degree of crystallinity of wood cellulose determined by X-ray diffraction and crystallinity index measured by FTIR spectroscopy for different calibration methods

Tabela 1. Korelacja między stopniem krystaliczności celulozy w drewnie oznaczonym metodą dyfrakcji promieni X a indeksem krystaliczności oznaczonym metodą spektroskopii FTIR dla różnych metod kalibracji

Dose Dawka kGy	Degree of crystallinity* Stopień krystaliczności* %	Absorbance ratio (crystallinity index) – Iloraz absorbancji (indeks krystaliczności)						Absorbance/valley ratio Iloraz absorbancji w maks. do absorbancji w min.				
		1427 cm ⁻¹ /896 cm ⁻¹		1373 cm ⁻¹ /2885 cm ⁻¹		1373 cm ⁻¹ /667 cm ⁻¹		1373 cm ⁻¹ /1350 cm ⁻¹	1160 cm ⁻¹ /1148 cm ⁻¹			
		height wysokość	integration integracja	D2	height wysokość	integration integracja	D2	height wysokość	integration integracja	D2		
0	67	1.460	0.870	3.500	0.320	0.053	3.200	2.215	2.903	0.904	1.201	1.040
20	65	1.449	0.865	3.311	0.297	0.050	3.052	2.200	2.832	0.825	1.195	1.037
60	65	1.456	0.723	2.915	0.318	0.053	2.534	2.273	3.039	0.643	1.190	1.038
120	63	1.446	0.826	3.300	0.276	0.040	2.660	2.463	2.578	0.661	1.197	1.038
300	57	1.381	0.793	3.683	0.293	0.049	1.845	1.993	2.130	0.734	1.180	1.035
500	58	1.310	0.755	3.696	0.328	0.056	1.905	2.131	2.256	0.777	1.158	1.036
1 500	52	1.903	1.031	4.662	0.308	0.051	1.851	1.592	1.792	0.142	1.142	1.025
4 500	39	1.898	0.950	3.640	0.222	0.037	1.561	1.853	1.657	0.077	1.091	1.003
9 000	0	2.549	1.331	2.860	0.187	0.037	0.617	1.716	1.930	0.049	1.065	0.982
Correlation coefficient, r Współczynnik korelacji, r		-0.935	-0.900	0.235	0.882	0.677	0.887	0.665	0.635	0.782	0.924	0.972

*Kasprzyk et al. 2004.

Height – height of peak was calculated with respect to a baseline drawn between: 3021-2600 cm⁻¹ [H(2885)]; 1443-1400 cm⁻¹ [H(1427)]; 1400-1348 cm⁻¹ [H(1373)]; 913-843 cm⁻¹ [H(896)] and 640-694 cm⁻¹ [H(667)] on normal spectra. Integration – area of peak on normal spectra measured by integrated method. D2 – integrated area of peak on second-derivative spectra.

*Kasprzyk i in. 2004.

Wysokość – wysokość piksu zmierzonego względem linii podstawowej wykresu (linie między: 3021-2600 cm⁻¹ [H(2885)]; 1443-1400 cm⁻¹ [H(1427)]; 1400-1348 cm⁻¹ [H(1373)]; 913-843 cm⁻¹ [H(896)] i 640-694 cm⁻¹ [H(667)] na widmie normalnym. Integracja – pole powierzchni piksu na widmie normalnym oznaczonym metodą integracji. D2 – powierzchnia integralna piksu na widmie drugiej pochodnej.

Table 1 shows the crystallinity index (CI) determined by FTIR spectroscopy using different methods of calibration and their correlation with degree of crystallinity measured by X-ray diffraction technique.

Crystallinity index $A_{1427 \text{ cm}^{-1}}/A_{896 \text{ cm}^{-1}}$ calculated from normal spectra give high negative correlation with degree of cellulose crystallinity determined by X-ray diffraction technique. When second derivative spectra have been used, we obtained slightly improved correlation, however its' value is still low ($r = 0.235$). Negative correlation of crystallinity index can be explained by the fact that samples of wood treated by high doses of radiation (above 1500 kGy) showed significant increase in crystallinity index whereas the values of degree of crystallinity measured by X-ray diffraction distingly decrease.

Moreover, high negative correlation of ratio $A_{1425 \text{ cm}^{-1}}/A_{898 \text{ cm}^{-1}}$ for wood samples obviously results from intensity changes of used absorption bands; (the increase of absorption at 1425 cm^{-1} and large decrease at 898 cm^{-1} particularly for samples irradiated by high doses (Fig. 2). O'Connor et al. (1958) indicated for cotton direct proportional dependence of ratio $A_{6.9\mu}/A_{11\mu}$ ($A_{1449 \text{ cm}^{-1}}/A_{909 \text{ cm}^{-1}}$) to degree of crystallinity from X-ray diffraction.

It is known that cotton contains cellulose in more than 90%, while in wood cellulose content is only 45%. Moreover, high doses of radiation cause not only decrease of degree of crystallinity of wood cellulose and its decay but also changes of chemical composition of wood which is revealed by IR spectra.

The obtained results show that the ratio $A_{1427 \text{ cm}^{-1}}/A_{896 \text{ cm}^{-1}}$ used for the measurement of crystallinity index in studies of pure cellulose cannot be used for assays of the wood cellulose *in situ*.

On the contrary, the ratio $A_{1427 \text{ cm}^{-1}}/A_{896 \text{ cm}^{-1}}$ crystallinity index obtained from both normal and second derivative spectra gives the positive correlation with degree of crystallinity measured by X-ray diffraction for ratio: $A_{1373 \text{ cm}^{-1}}/A_{2885 \text{ cm}^{-1}}$ and $A_{1373 \text{ cm}^{-1}}/A_{667 \text{ cm}^{-1}}$. However, only the ratio A_{1373}/A_{2885} calculated from hight of bands of normal spectra and integrated area of bands of second derivative spectra have analytical value (coefficient of correlation about 0.88) for estimation of changes of crystallinity cellulose of irradiated wood.

Richter et al. [1991], using the ratio A_{1370}/A_{670} , have obtained a good correlation between changes in this ratio and the conversion of cellulose I to cellulose II in alkali solutions by X-ray diffraction.

The similar results were obtained for changes in cellulose crystallinity during Kraft pulping studied by X-ray and IR (A_{1370}/A_{670}) methods [Evans et al. 1995].

In our studies correlation between the IR ratio A_{1370}/A_{670} and X-ray diffraction method was only about 0.66 for normal spectra and 0.78 for second derivative spectra.

Schultz et al. [1985] found that the sharpness of cellulose IR peaks increases with increasing cellulose crystallinity.

Therefore, decrease in the intensity of bands characterised of cellulose ($1373, 1160 \text{ cm}^{-1}$) may be attributed to most amorphous carbohydrates, which in turn, tends to decrease crystallinity of residual cellulose.

The absorption band at 1160 cm^{-1} is assigned to the C-O-C antisymmetric bridge stretching in cellulose and hemicelluloses [Harrington 1964].

To characterize cellulose crystallinity changes upon irradiation, we propose additional two absorbance/valley ratio: $1160/1148 \text{ cm}^{-1}$ and $1373/1350 \text{ cm}^{-1}$. Results of

these crystallinity indexes changes measured with proposed absorbance/valley ratio are presented in Table 1. These indexes show high positive correlation ($r = 0.97$ and 0.92 respectively) with degree of crystallinity measured by X-ray diffraction. Therefore suggested absorbance/valley ratio: $1160/1148 \text{ cm}^{-1}$ or $1373/1350 \text{ cm}^{-1}$ let us to estimate crystallinity of cellulose even in significantly degraded wood by gamma-radiation.

CONCLUSIONS

1. Degree of crystallinity of wood cellulose significantly decrease when the dose of radiation is above 1500 kGy.

2. With three IR ratio: A_{1427}/A_{896} , A_{1373}/A_{2885} and A_{1373}/A_{667} that are used for measurement of crystallinity index of pure cellulose only A_{1373}/A_{2885} can be used for estimation of crystallinity changes in wood cellulose *in situ* irradiated by high dose of gamma radiation.

3. The ratio A_{1427}/A_{896} has negative correlation with degree of cellulose crystallinity determined by X-ray diffraction method.

4. Absorbance/valley ratio: $1160/1148 \text{ cm}^{-1}$ or $1373/1350 \text{ cm}^{-1}$ calculated with FTIR spectra can be used to estimate changes of wood cellulose crystallinity even in strongly degraded wood by high gamma-radiation.

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**NIEKTÓRE ASPEKTY OCENY KRystalICZNOŚCI CELULOZY
W DREWNIENAPROMIENIOWANYM PROMIENIAMI GAMMA
METODĄ SPEKTROSKOPII FTIR I DYFRAKCJI PROMIENI X**

Streszczenie. Zmiany krystaliczności celulozy *in situ* w drewnie napromieniowanym promieniami gamma badano metodą spektroskopii w podczerwieni (FTIR) i dyfrakcji promieni X. Oceniono korelację między stopniem krystaliczności, oznaczanym z dyfrakcji promieni X a indeksem krystaliczności wyznaczonym metodą spektrofotometryczną w podczerwieni wykorzystując widma normalne i ich drugie pochodne. Otrzymano wysoką korelację jedynie dla stosunku A_{1373}/A_{2885} . Wykazano, że stosunek absorbancji w maksimum do absorbancji w minimum $A_{1373\text{ cm}^{-1}}/A_{1350\text{ cm}^{-1}}$ oraz $A_{1160\text{ cm}^{-1}}/A_{1148\text{ cm}^{-1}}$ mogą być stosowane do oceny zmian stopnia krystaliczności celulozy *in situ* w drewnie.

Słowa kluczowe: celuloza z drewna, krystaliczność, promieniowanie gamma, spektroskopia FTIR, dyfrakcja promieni X

Accepted for print – Zaakceptowano do druku: 24.03.2004 r.