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CELLULOSE CRYSTALLINITY INDEX EXAMINATION IN OAK WOOD ORIGINATED FROM ANTIQUE WOODWORK

The influence of oak wood age on the crystallinity index of cellulose was determined. Antique wood originating from Warsaw woodwork from the middle of the 18th century, the turn of XIXth and 20th century and the middle of the 20th century was analysed. It was reported, using FTIR spectrometry, that the crystallinity index increases with wood age. It is consistent with previous examinations in other papers and shows that the chosen method of crystallinity index analysis is correct.

Keywords: crystallinity degree, cellulose crystallinity, antique wood, *Quercus* sp.

Introduction

The process of natural wood ageing is a very complicated issue. Specialized literature presents unspecified, often contradictory, opinions about it. The negative influence of UV radiation, temperature and humidity variations or changes in static and dynamic stresses on wood ageing in residential areas is a commonly known fact. Seifert [1972] states that the degradation of wood structure is the effect of natural wood ageing in a closed space. First of all, the destruction of the polysaccharide chains takes place, as well as in the cellulose, both in ordered and disordered areas.

Kohara and Okamoto [1955], based on chemical analyses carried out on wood originating from old Japanese sanctuaries (300–1300 years old), reported that the degree of crystallinity in the cellulose (calculated using the Battist

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method) increases with the age of the wood. This was explained by the creation of new cross-bonds between cellulose chains which leads to an increase incrystalline areas.

A knowledge of the degree of crystallinity, meaning the ratio of ordered (crystalline) and disordered (amorphous) cellulose configuration, is very useful to the evaluation of wood properties. An increase in cellulose crystallinity causes a lower value of swelling and water sorption, and higher values of density, hardness and compression strength. The determination of the degree of cellulose crystallinity may be important for the proper usage of wooden components in woodwork.

The Crystallinity Index measures the degree of crystallinity. It is easier to determine with such a common instrumental technique as FTIR. It has been widely used in different papers to define the influence of cellulose crystallinity on a series of wood and cellulose properties [Mansfield, Meder 2003; Park et al. 2010; Kataoka, Kondo 1998].

The aim of this paper is to determine the influence of natural wood ageing on cellulose crystallinity. The results obtained will extend previous knowledge about the changes in wood during ageing. This will enable a prediction of the behaviour of wood nowadays and the effective protection of wood, especially antique woodwork.

Materials and methods

Oak wood (*Quercus* sp.) was examined. It was chosen because of the fact that oak wood together with pine wood (*Pinus* sp.) were the main materials available for wooden constructions in previous centuries. Samples were gained from renovated or pulled down antique buildings built in Warsaw in the middle of the 18th century, at the turn of 19th and 20th century and in the middle half of 20th century. This is a unique collection of wood in the shape of furnishing components (floor boards, paneling, stairs and balustrade components).

Samples were prepared in several stages. In the first stage, the samples were cut from antique wood fragments. Their dimensions were compatible with standards concerning the determination of basic wood parameters (moisture content – PN-77/D-4100, density – PN-77/D-04101). The samples were divided into three groups:

- group 1: wood from the 20th century (1960),
- group 2: wood from the turn of 19th and 20th century (1895),
- group 3: wood from the 18th century (1750).

Then samples of recent wood (group 0 – control samples, 2005 year) with a similar density and annual increment width were matched to selected samples from group 1, 2 and 3 (table 1). The next stage consisted of sample disintegration and fractioning. Afraction of air-dry sawdust, passing through a 0.6 mm and remaining on a 0.5 mm mesh sieve was taken for analysis. The cellulose which was used for crystallinity index examination was isolated according to the Seifert method (PN-92/P-50092).

The crystallinity index was determined with the FTIR method (Thermo Fisher Scientific Inc. Nicolet 6700). The cellulose samples were dried in a vacuum dryer before FTIR analysis. 0.6 g KBr was added to 0.003 g of cellulose (1:200 ratio) and the mixture was homogenized in a Retsch MM400 ball grinder (120 s, 30 Hz). Samples of 0.3 g mixture were pelletized with a bench press (10000 kG, 5 minutes). The pellets obtained (with 13 mm diameter) were analysed within the range of wave length between 400 and 4000 cm^{-1} (64 scans, 2 cm^{-1} resolution, every 60 minutes background measurement). Each pellet was measured five times at different points. OMNIC 8.1 software was used for spectral analysis. 2900, 1429, 1370, 895, 670 cm^{-1} absorption bands were taken for crystallinity index calculations. The following ratios of values were applied:

$CI = H1429\ cm^{-1}/H895\ cm^{-1}$

$CI = H1370\ cm^{-1}/H2900\ cm^{-1}$

$CI = A1370\ cm^{-1}/A670\ cm^{-1}$

where: CI – crystallinity index, A – peak area, H – peak height.

Table 1. Characteristics of analyzed wood
Tabela 1. Charakterystyka analizowanego drewna

Group *Grupa*	Density (ρ) [$kg{\cdot}m^{-3}$] *Gęstość (ρ) [$kg{\cdot}m^{-3}$]*		Width of annual increments (S) [mm] *Szerokość przyrostów rocznych [mm]*	
	ρ_{av}	sd	S_{av}	sd
0	671	18	2.2	0.4
1	675	20	2.1	0.3
2	680	25	2.1	0.3
3	677	12	1.9	0.4

Results and Discussion

A comparison of exemplary FTIR spectra of samples from each group is presented in fig. 1. There are no visible differences between them but the values of CI calculated based on particular ratios (presented in the table 2) indicatethat distinctions might be noted. There are visible tendencies for $H1429cm^{-1}/H895cm^{-1}$ and $A1370cm^{-1}/A670cm^{-1}$. The standard deviation for this second ratio is so high that changes in character may be aberrant. The CI value increases with the age of the analysed wood. There is no unequivocal dependence for the third ratio ($H1370cm^{-1}/H2900cm^{-1}$). However, all three ratio values indicate a gradual increase of CI with wood age which is clearly visible in fig. 2.

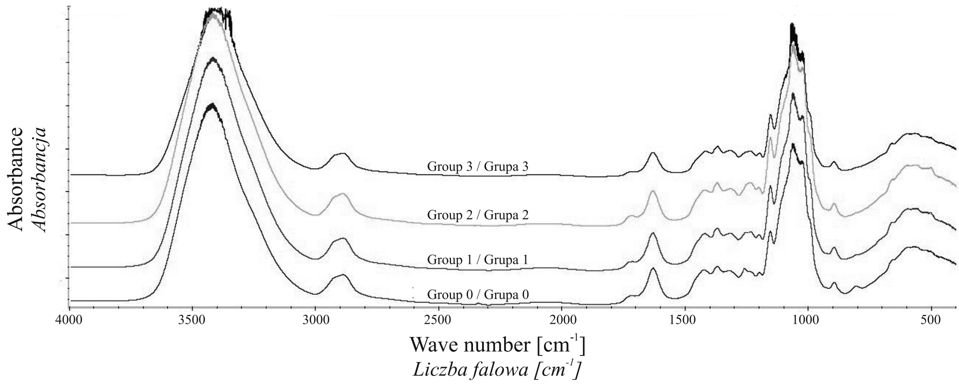

Fig. 1. Comparison of exemplary FTIR spectra of samples from each group (roman numbers means the century of sample origin)
Rys. 1. Porównanie przykładowych widm FTIR otrzymanych dla próbek z wszystkich grup (cyframi rzymskimi zaznaczono wiek pochodzenia drewna)

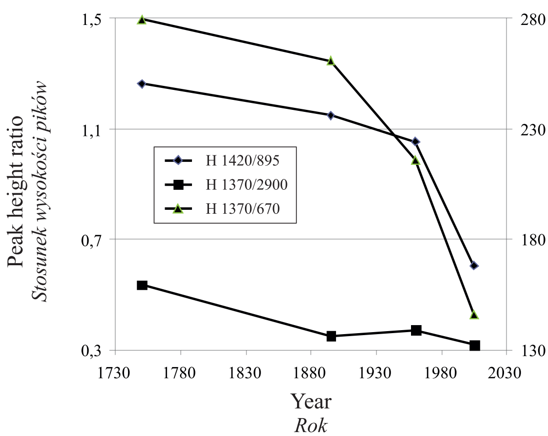

Fig. 2. Dependence of calculated ratios of FTIR peaks height and area on the wood age
Rys. 2. Zależność obliczonych stosunków liczbowych wysokości i powierzchni pików FTIR od wieku drzewa

A higher CI value also means ahigher degree of crystallinity [Drożdżek 2011] which is equivalent to higher crystalline area volume in cellulose. The observed phenomenon may be caused by the effect described in the above mentioned paper of Kohara and Okamoto [1955]. Faster decomposition of the amorphous part of the cellulose which is more susceptible to degrading factors than crystalline cellulose could be another reason. This has been reported, for example by Gehlen [2010]. Formerly decomposed chains of cellulose are easily removed during cellulose isolation. It cannot be excluded that both of these explanations are correct.

Conclusion

The crystallinity index changes with the age of the wood. Its values are higher in antique wood in relation to recent wood. The highest CI value was obtained for the woodwork from 18th century, the lowest difference compared with recent wood was denoted for components from the middle of 20th century.

Data from literature cited above confirm such a dependence indicating that the presented method of determining the crystallinity index is the correct one. The possibility of wood age determination using the crystallinity index cannot be excluded but the further experiments should be performed.

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List of standards:

PN-77/D-04101 Drewno. Oznaczanie gęstości

PN-77/D-4100 Drewno. Oznaczanie wilgotności

PN-92/P-50092 Surowce dla przemysłu papierniczego. Drewno. Analiza chemiczna

BADANIE INDEKSU KRYSTALICZNOŚCI DREWNA DĘBOWEGO POCHODZĄCEGO Z ZABYTKOWEJ STOLARKI BUDOWLANEJ

Streszczenie

Wraz z upływem czasu stare drewniane okna, drzwi, podłogi podobnie jak i inne elementy stolarki budowlanej nabierają wartości muzealnej i dlatego, jako świadectwo kultury materialnej minionych stuleci powinno zostać zachowane dla przyszłych pokoleń. Za pozostawieniem tych elementów, poza argumentami dotyczącymi wartości zabytkowych i estetycznych, przemawiają właściwości samego drewna, które pomimo upływu czasu często nie ulegają istotnym zmianom, a materiał ten zachowuje pełne funkcje użytkowe. Wobec panujących obecnie niejednoznacznych poglądów na temat skutków długotrwałego starzenia się drewna, istnieje potrzeba podejmowania możliwie wielostronnych badań zmierzających do określenia właściwości zabytkowego drewna.

Celem niniejszych badań było określenie indeksu krystaliczności celulozy w drewnie pochodzącym z zabytkowej warszawskiej stolarki budowlanej z połowy 18, przełomu 19 i 20 wieku, a także z połowy 20 wieku w porównaniu do drewna pozyskanego współcześnie. Analizę stopnia krystaliczności celulozy przeprowadzono metodą spektrometrii w podczerwieni FTIR przy użyciu modelu *Nicolet 6700, Thermo Fisher Scientific Inc.*

Wyniki przeprowadzonych badań pozwalają stwierdzić, że w zabytkowym drewnie, w porównaniu do drewna pozyskanego współcześnie, następuje zmiana indeksu krystaliczności celulozy. Wielkość zmian uzależniona jest od wieku drewna. Największym indeksem krystaliczności celulozy charakteryzuje się drewno elementów stolarki budowlanej z 18 wieku, a najmniejszą różnicę wykazało drewno pochodzące z zabytkowych elementów z połowy 20 wieku. Obserwacje te potwierdzają z fachowej literatury, co świadczy także na korzyść wybranej metody określania indeksu krystaliczności.

Słowa kluczowe: stopień krystaliczności, krystaliczność celulozy, zabytkowe drewno, *Quercus* sp.