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QUALITATIVE CHARACTERISTICS OF CELLULOSE FROM ARCHAEOLOGICAL OAK (*QUERCUS* SP) WOOD

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ABSTRACT

The article compares changes taking place within the cellulose systems of four wooden archaeological objects differing with regard to the conditions and length of deposition in the natural environment. In order to characterise the changes concerning the analysed component, its percentage proportion as well as mean weight and number molecular mass, polydispersity and polymerisation degree were determined. On the basis of the obtained results, a significant impact was demonstrated of the deposition environment of wood on the condition of cellulose preservation. In addition, the authors demonstrated a correlation between the age of wood and cellulose polydispersity and degree of polymerisation.

KEY WORDS: archaeological wood, cellulose, degree of polymerisation, oak (*Quercus* sp), polydispersity, waterlogged wood

INTRODUCTION

Oak wood is the most frequently found wood species during archaeological excavations. It was widely applied in the past centuries to build houses, bridges, mounds etc. This is why archaeological objects made from oak wood provide today very useful materials for comparative research allowing to present degradation processes that this raw material had undergone in the course of centuries in different environments.

Although oak belongs to the most durable wood species which occur in our climatic conditions (Prosiński 1984), just like all other species, it is sensitive to degradation resulting from the infestation by insects and microorganisms such as fungi and bacteria (Blanchette et al. 1990, Passialis 1997, Solar et al. 1987, Schmitt and Hoffmann 1998, Wróblewska 1999).

One of the wood components undergoing the degradation process is cellulose – a structural constituent whose percentage proportion can influence significantly the mechanical properties of wood. Structural changes as well as the reduction in the percentage proportion of cellulose taking place during the deposition of wood in the natural environment occur as a result of slow hydrolysis and biological degradation (Passialis 1997). These processes are well recognised and described in literature (Bujak 1998, Eriksson et al. 1990). Depolymerisation of cellulose chains causes that they occur in the form of smaller molecules which are more easily available for microorganisms. This leads to a decline in the percentage content of this constituent (Grattan and Mathias 1986, Iiyama et al. 1988, Zborowska 2004). There are significantly fewer reports concerning problems associated with cellulose structural changes in the archaeological wood. Values which characterise cellulose structure include, among others: mean molecular weight and number, polydispersity and the degree of polymerisation. A decrease in the above-mentioned values leads to a deterioration in the strength of this constituent and, consequently, of the entire material.

When investigating oak wood derived from different archaeological objects, Hoffmann and Parameswaran (1982) found that factors dominating degradation processes include: physical and chemical properties of the environment, whereas the age of the sample was treated as less important. According to Dzbeński (1970a), wood covered with soil behaves best in peat, layers of clay or sand in conditions of constant levels of moisture content. On the other hand, repeated alternating periods of exposure and immersion of wood in water or fluctuations in the water level result in accelerated wood degradation and the deterioration of wood properties. Conditions existing in the wet environment prevent wood tissue decomposition by the fungi of white and brown rot as well as by insects. Strong supersaturation of wood by water accompanied by a simultaneous limitation of oxygen access frequently may prevent its degradation even by soft rot fungi. However, in the case of the archaeological objects investigated in the past, a distinct decomposition of wood tissue was always observed. In many situations, the biological decomposition could have started before the wood had been used by man (Nilsson and Daniel 1992) or before it had been waterlogged (Blanchette et al. 1990).

The objective of the performed experiments was to compare changes in the cellulose systems of archaeological oak wood derived from different historical periods and various environments.

MATERIAL AND METHODS

Four different oak archaeological raw materials whose characteristics are presented in Tab. 1 were subjected to analyses.

Tab. 1: List of the investigated archaeological objects

Century	Origin	Environment	Depth [cm]	Function when utilised
8^{th} BC	Archaeological Museum in Biskupin	Wet peat	100	Constructional element
$9\text{-}10^{th}$	Ostrów Tumski in Poznań	River mud	300-400	Constructional element of a wooden-earth rampart
$9\text{-}10^{th}$	Museum of the First Piasts in Lednica	Lake mud	1500	Timber bridge pile
13^{th}	Castle of Pomeranian Princes in Szczecin	Wet soil	600-700	Constructional element of house
20^{th}	Zielonka Forest Experimental Station		-	-

The oldest of the investigated wood (8th c. B.C.) derived from the Archaeological Museum in Biskupin and was deposited horizontally in a layer of wet peat. A clear differentiation between the degree of degradation of the external (sapwood) and internal (heartwood) zones of the object made it possible to separate the material and to conduct individual comparative analyses for the sapwood and heartwood. This approach allowed to control the intensity of the degradation processes which had taken place inside one object. Two other oak materials dated back to the end of the 9th and beginning of the 10th centuries were also analysed. The first of them was obtained from Ostrów Tumski in Poznań and was found at the depth of 300-400 cm in a layer of mud deposited by the Warta River. The second specimen, derived from the Museum of the First Piasts in Lednica, was extracted from the bottom of the Lednica Lake. The last object dated back to the 13th century was unearthed from the depth of 600-700 cm during excavation work conducted in the Castle of the Pomeranian Princes in Szczecin. For comparative purposes, identical analyses were carried out on contemporary wood of the same species.

The analyses carried out to characterize changes taking place in cellulose comprised: the determination of the percentage proportion of this wood constituent (PN 92/P-50092), mean molecular and number weight, polydispersity as well as the degree of polymerisation using for this purpose gel chromatography (Ekmanis 1987).

The chromatographic analysis was performed with the assistance of a system which consisted of the Isocratic Pump HP 1050, Manual Injector (Model 7125-Rheodyne Inc.), Differential Refractometer Detector HP 1047A, Column Set: 3 x PL gel Mixed A, 20µm + guard (Polymer Laboratories Ltd.), PL Calibre GPC Software Ver. 5.1. (Polymer Laboratories Ltd.). The following conditions of the chromatographic separation were applied: solvent DMAC/0.5% LiCl, flow rate 1 ml/min, concentration 0.05%, injection volume 100 ml, temperature 80° C.

RESULTS

Tab. 2 shows cellulose percentage proportions in the compared archaeological oak wood. It was demonstrated that the percentage proportion of cellulose in the wood derived from 8th century BC from the Biskupin settlement amounted to 19.25% and was by over 50% lower than that determined in contemporary and sound wood. The division into the external and internal zones allowed to reveal significant differences in the content of this constituent in the sapwood and heartwood. The proportion of cellulose in the internal zone reached 21.73%, while in the external one only 16.78%. It can be presumed that the conditions in which the examined wood lay in Biskupin were similar to anaerobic and, therefore, aerobic organisms, i.e. fungi, had limited conditions for their activities. In the above-described conditions, the only organisms whose activities could be taken into account were bacteria (Björdal et al. 1999).

In the case of specimens dated from the end of the 9th and beginning of the 10th centuries, the content of cellulose amounted to: 33.30% in the object extracted from the mud deposited by the Warta River and 41.74% in the material retrieved from the bottom of the Lednickie Lake. Different conditions in which the individual examined specimens were deposited explain differences in the intensity of the degradation process of the cellulose constituent. The first of them, a fragment of a mound constructional element from Ostrów Tumski in Poznań was exposed to the action of changing environmental conditions (changing moisture content and, hence, altering activities of aerobic microorganisms). This type of environment supports the presence of numerous microorganisms, both bacteria as well as very active fungi. That is why the content of cellulose was considerably lower in comparison with the other specimen derived from the same historic period but extracted from water environment which restricted to availability to many microorganisms. In the case of the examined object dated back to the 13th century, the proportion of cellulose did not differ from values typical for recent wood. This specimen was extracted from considerable depth which must have restricted the destructive activities of aerobic microorganisms. The elapsed period of 700 years was too short for the changes which may have been caused by bacteria active in these conditions to be noticed in the determined cellulose content.

Tab. 2: Percentage proportion and mean molecular and number weight, polydispersity (Mw/Mn) and polymerisation degree (DP) of cellulose obtained from oak wood objects subjected to analyses

Century	Origin		Cellulose proportion [%]	Mn	Mw	Mw/Mn	DP
8th BC	Archaeological Museum in Biskupin	Sapwood	16.78	21966	60981	2.8	377
		Heartwood	21.73	40008	119568	3.0	518
9-10th	Ostrów Tumski in Poznań		33.20	20865	110127	5.3	676
9-10th	Museum of the First Piasts in Lednica		41.74	21499	128198	6.0	786
13th	Castle of Pomeranian Princes in Szczecin		45.50	21038	136840	6.5	845
20th	Zielonka Forest Experimental Station		44.00	26952	191139	7.1	1173

The comparison of the percentage proportion of cellulose from the examined experimental objects showed a significant impact of the environment in which the specimens were deposited on the quantity of the carbohydrate constituent of the archaeological wood.

In order to illustrate better cellulose structural changes, mean molecular and number weight as well as polydispersity and polymerisation degree were determined.

The lowest polydispersity, i.e. the value indicating the degree of variability of the molecular weights of this polymer was found in the cellulose which derived from the wood excavated in Biskupin. Cellulose polydispersity of this raw material in its sapwood amounted to 2.8, while in its heartwood to 3.0. The next cellulose raw material which derived from wood extract in Ostrów Tumski in Poznań was characterised by polydispersity of 5.3. The cellulose obtained from the second 9th-10th century object, which was characterised by a higher proportion of this constituent, showed the Mw/Mn value of 6.0. The highest degree of variability of molecular weights in the cellulose polymer reaching 6.5 was determined in the wood specimen dated back to the 13th century which derived from Szczecin. Nevertheless, this value is lower than that recorded in the cellulose derived from the contemporary oak wood. Despite the fact that the percentage proportion of this component in the materials derived from the 13th century and recent wood was similar, yet the different values of polydispersity point to the degradation processes which had caused qualitative changes in cellulose. It is quite probable that part of the molecules of high degree of polymerisation was 'cut' into shorter pieces and this caused differences in molecular weights but the process failed to lead to cellulose losses. This assumption appears to be corroborated by lower values of the polymerisation degree (PD) obtained for this material (845), in comparison with the DP of cellulose derived from sound wood (1173). In the case of the remaining, 'older' specimens, the DP value was even lower. In the case of the material from the end of the 9th and beginning of the 10th century extracted from the bottom of the Lednickie Lake, the DP value was 786 and in the other material derived from this period – 676. The lowest DP value was determined in the wood from Biskupin; for the heartwood the DP value was 518, whereas for the strongly degraded sapwood – only 377.

Fig. 1 illustrates the relationship between the degree of cellulose polymerisation and the time of wood deposition in the natural environment. This relationship shows that together with the lengthening of the time of wood deposition, the degree of polymerisation of cellulose decreased. A similar correlation was found between polydispersity of this component and the time of wood deposition (Fig. 2) where a distinct decline of the polydispersity value with the passage of time is quite visible.

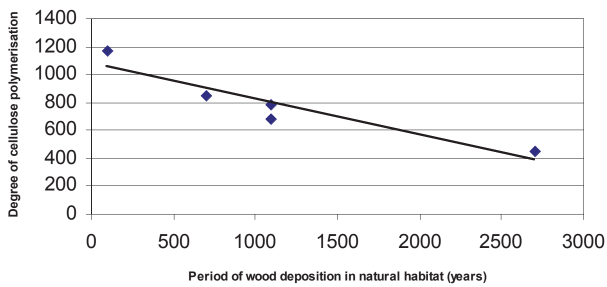

Fig. 1: Dependence of the degree of polymerisation of cellulose on the period of deposition of oak wood in the natural habitat

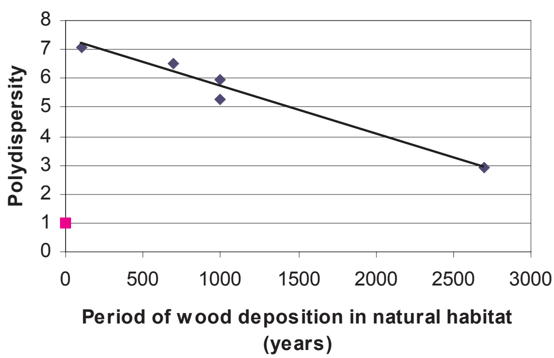

Fig. 2: Dependence of the polydispersity of cellulose on the period of deposition of oak wood in the natural habitat

DISCUSSION

The comparison of the percentage proportion of cellulose in the analysed archaeological objects revealed a significant impact of the deposition environment on the behaviour of the carbohydrate components of wood. The importance of this factor is confirmed by the observed differences in the response of cellulose in the compared objects derived from the end of the 9th and beginning of the 10th century. One, which remained in unchangeable conditions of maximum moisture at the bottom of the lake, was characterised by cellulose preserved in very good condition – its percentage proportion did not differ much from values typical for recent wood. Changes which did occur in this wood constituent became apparent only after chromatographic analyses; its DP was lower than in the cellulose of contemporary wood. The second object derived from the end of the 9th and beginning of the 10th century, subjected to changing environmental conditions was degraded more strongly as indicated by the percentage proportion of cellulose and additionally corroborated by values of polydispersity and degree of polymerisation.

On the other hand, it would be wrong to confine the analysis only to the impact of the environment on the degradation process. The oldest of the examined objects, the specimen from Biskupin, exposed only to the activity of bacteria, underwent the strongest degradation because it was deposited much longer than the remaining objects. However, even though environmental conditions exert the most important influence on the degradation processes occurring in wood, the effect of the time factor cannot be underestimated. Frequently, archaeological objects which remained in seemingly safe conditions undergo processes which cause their break up and degradation.

What is even more important, the obtained results showed a clear correlation between the age of the examined wood and cellulose polydispersity and DP; the older the examined material, the lower the polydispersity and DP of the cellulose it contained. The material derived from 8th century BC was characterised by the lowest polydispersity and DP of its cellulose constituent. The highest values were recorded in the case of the cellulose derived from the recent material from the 20th century.

Furthermore, the obtained results showed that, apart from the determination of the percentage proportion of cellulose, it is also necessary to conduct the analysis which makes it possible to determine structural changes. The youngest of the analysed archaeological specimens dated back to the 14th century underwent processes which did not lead to quantitative changes, hence the performed analysis of the percentage proportion failed to record them. It was only when chromatographic separation was conducted, that these processes became apparent. They caused the deterioration of cellulose quality by decreasing the polymerisation degree and this initiated the degradation of the object.

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