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INVESTIGATIONS OF DIMENSIONAL STABILITY OF 2700-YEAR OLD OAK WOOD FROM BISKUPIN AFTER ITS TREATMENT WITH POLYETHYLENE GLYCOLS AND FREEZE-DRYING

Leszek Babiński
Archaeological Museum in Biskupin, Conservation Department
Biskupin
Gąsawa, Poland

Magdalena Zborowska, Włodzimierz Prądzyński
Poznań University of Life Sciences, Faculty of Wood Technology
Institute of Chemical Wood Technology
Poznań, Poland

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ABSTRACT

Experiments were performed to study dimensional stability of well-preserved 2700-year old oak wood from Biskupin excavations after its treatment with polyethylen glycol (PEG) 300 and PEG 4000 solutions, freeze-drying and seasoning at air relative humidity of 52 %. The following parameters were determined: polyglycol uptake, water content, wood shrinkage in tangential, radial and longitudinal directions, as well as ASE values. The smallest changes of dimensions of freeze-dried wood were found to occur following its initial impregnation with 30 % PEG 300 solution after the uptake ranging from 32 to 42 % of absolutely dry mass of wood. Shrinkage of non-impregnated freeze-dried wood was significantly smaller than that of non-impregnated wood dried in ambient air.

KEYWORDS: Archaeological oak wood, shrinkage, dimensional stabilisation, PEG, freeze-drying.

INTRODUCTION

Preserved fragments of wooden constructions of a Lusatian culture defensive settlement in Biskupin dating back to the 8th century BC remain in conditions of a wet archaeological site. Among the recovered constructions, oak wood elements are dominant and these objects are characterised by different degrees and range of degradation. In 2003 periodical examination

of the wood preservation condition and the rate of its degradation was initiated, as well as monitoring of major environmental parameters (Babiński et al. 2007, Zborowska et al. 2007, Babiński 2009). Moreover, the research project also aims to assess the possibilities of conservation of the best preserved Biskupin wood.

In the past, Biskupin wood was treated *in situ* using phenol-formaldehyde resins (Stańczuk-Różycka 1976). The dimensional stability of oak wood of advanced degree of degradation, after its conservation by different methods, was compared at the Canadian Conservation Institute (Bilz et al. 1994). In those investigations the researchers used samples in the form of discs and the best results were reported after conservation with the two-step treatment proposed by Hoffmann (1986), as well as after pre-treatment of wood with a mixture of polyethylene glycols according to the PEGCON computer program (Cook and Grattan 1991) and freeze-drying. On the other hand, the possibilities of conservation of well-preserved oak heartwood from Biskupin were determined following its impregnation with saccharose or polyglycols and ambient air drying (Babiński 1995).

It is relatively easy to introduce into archaeological material of high degree of degradation various chemical compounds limiting its moisture deformations and strengthening its degraded wood tissue. In the case of well-preserved oak heartwood, the possibilities of its impregnation are limited to compounds characterised by small dimensions of molecules. The experiments carried out by Babiński and Poskrobko (2000, 2004) showed that, in the case of objects of large cross section, treatment lasting even several years fails to guarantee the uptake of the required quantities of polyglycol even of small molecular weight.

Freeze-drying of waterlogged archaeological wood subjected to initial impregnation with polyglycols belongs to the most effective methods of its dimensional stabilisation (Ambrose 1990). The required absorption of polyglycols into wood subjected to freeze-drying may be smaller than in the case of wood dried in ambient air (Cook and Grattan 1985, Jensen and Schnell 2005). Earlier studies, carried out at the Archaeological Museum in Biskupin, demonstrated high dimensional stability of well-preserved oak heartwood following its treatment with 20-30 % solutions of PEG 300 and freeze-drying (Babiński 2007), as well as after impregnation with 50 % solution of PEG 300 and drying in ambient air (Babiński 2005). It is worth emphasising that dimensional changes of non-treated, freeze-dried wood were smaller than dimensional changes of non-treated, air-dried wood. This may be important in the case when the degree of PEG absorption into freeze-dried wood is smaller than it was assumed before the treatment.

The objective of the presented investigations was to determine dimensional stability of the well-preserved archaeological oak wood from Biskupin subjected to initial impregnation with polyglycols and freeze-drying.

MATERIAL AND METHODS

Tests were conducted on approximately 2700-year old oak (*Quercus sp.*) heartwood obtained from a construction element found on the 71st are of site 4 in Biskupin. Two types of samples were employed in the discussed experiment: D samples (discs 15 to 20 cm in diameter and 25 mm thick) as well as T samples of the dimensions of 50×50×10 mm (T×L×R). D samples constituted the entire cross section of the excavated element, whereas T samples were cut out from the external zone of the object. The wood from which the test material was prepared was characterised on the basis of macroscopic structure features (width of annual increments, percentage of latewood), selected physical properties (maximum moisture content, conventional

density, total linear shrinkage), loss of wood substance, and results of microscopic observations.

Waterlogged samples were impregnated for the period of 28 weeks using the method of cold baths in aqueous PEG 300 solutions or in aqueous PEG 300 solutions supplemented with PEG 4000. The experimental impregnation solutions were selected on the basis of the results of earlier investigations (Babiński 2007) and PEGCON computer program (Cook and Grattan 1991). Solution concentrations and sample impregnation times are presented in

Tab. 1. Each experimental variant used one D sample and four T samples. The comparative material comprised non-impregnated control samples subjected to freeze-drying (Control FD) and non-impregnated control samples dried in ambient air (Control AD).

Tab. 1: Concentrations of polyglycols solutions and samples treatment times.

Treatment	Treatment time (weeks)							
	PEG 300 (v/v)						PEG 4000 (w/v)	
	5	10	15	20	25	30	5	10
	%							
20 % PEG 300	4	4	4	16				
25 % PEG 300	4	4	4	4	12			
30 % PEG 300	4	4	4	4	4	8		
25 % PEG 300 + 5 % PEG 4000	4	4	4	4	4		8	
25 % PEG 300 + 10 % PEG 4000	4	4	4	4	4		4	4

Samples intended for freeze-drying were frozen for a period of 14 days at the temperature of -27°C. Freeze-drying of wood samples was carried out in a chamber coupled with a laboratory freeze-dryer and a two-stage vacuum pump. Samples were dried for a period of 8 days. The final pressure in the drying chamber amounted to 5.5 Pa.

Freeze-dried samples as well as samples dried in ambient air in laboratory conditions (Control AD) were seasoned for six weeks until they reached constant mass in the air at the temperature of 20°C and relative air humidity (RH) of 52 %.

The uptake of polyglycols in wood was presented as percentage ratio of the absolutely dry mass of the introduced polyglycols to the absolutely dry wood mass (determined on the basis of a mean maximum moisture content of control samples). Water content in samples was determined directly after the termination of freeze-drying (W_{FD}) and following wood seasoning in ambient air of 52 % RH (W_{52}) as a percentage ratio of water mass found in the sample to the sum of absolutely dry wood mass and introduced impregnates. Samples were weighed with 1 g (D samples) or 0.01 g (T samples) accuracy.

Wood shrinkage was determined on the basis of changes at the distance between stainless pins. The total of 20 pins was hammered into each D sample and dimensional changes in tangential and radial directions were assessed. In the case of T samples, only 4 pins were hammered and dimensional changes in tangential and longitudinal directions were determined. Measurements were taken with the assistance of a slide calliper (with 0.01 mm accuracy) prior to impregnation, after freeze-drying as well as after sample seasoning at 52 % relative air humidity. Wood shrinkage in tangential, radial and longitudinal directions was presented from the state of

wood maximal water saturation (prior to PEG-impregnation) to the state directly after freeze-drying termination, as well as to the state of attaining equilibrium moisture content at 52 % RH.

Shrinkages of freeze-dried and seasoned wood at 52 % RH were compared with shrinkage of untreated wood dried in ambient air and seasoned at 52 % RH (Control AD) on the basis of anti-shrink efficiency (ASE).

RESULTS AND DISCUSSION

Major features and physical properties of the examined oak wood are presented in Tab. 2. On the basis of the values of determined features of anatomical structure as well as maximum moisture content and conventional density it can be stated that examined experimental material (samples D and samples T) was characterised by comparable and small degree of degradation.

Tab. 2: Selected macroscopic features and physical properties of examined oak wood.

Feature / Property	Mean value	
	D samples	T samples
Width of annual increment (mm)	1.54	1.53
Percentage of latewood (%)	62.5	65.5
Maximum moisture content (%)	132	136
Conventional density (kg.m^{-3})	513	504
Total tangential shrinkage (%)	18.6	11.1
Total radial shrinkage (%)	10.1	
Total longitudinal shrinkage (%)		0.7

Good preservation condition of examined wood tissue also was confirmed by the results of microscopic observations (Fig. 1). Distinctly greater differences between the properties of both types of examined samples were recorded when total wood shrinkage in tangential direction was compared. Considerably greater shrinkage determined in the disc-shaped samples should be attributed to differences in the size and geometry of the employed samples, as well as to the distribution of annual increments and the presence of pith in the central part of D samples.

Tab. 3 collates the results of uptake of polyglycols in both types of samples as well as the water content in non-impregnated (control) and impregnated samples after freeze-drying and seasoning at relative air humidity of 52 %.

The absorption of polyglycols by wood was found to have increased together with the increase in concentration of impregnation solutions. Despite the applied length of impregnation (28 weeks), the content of polyglycols in smaller samples (T) was markedly lower in comparison with the uptake of the polymer in the larger samples (D). This can be attributed to the fact that in the case of discs, polyglycol penetrated them almost exclusively through the cross section. Furthermore, it means that the radial direction penetration of polyglycols into oak wood from Biskupin can be limited or requires a very long period of treatment.

Directly after freeze-drying water content in D samples ranged from 1 to 2 %. The content of water in T samples was similar only in the case of drying of untreated wood (Control FD samples).

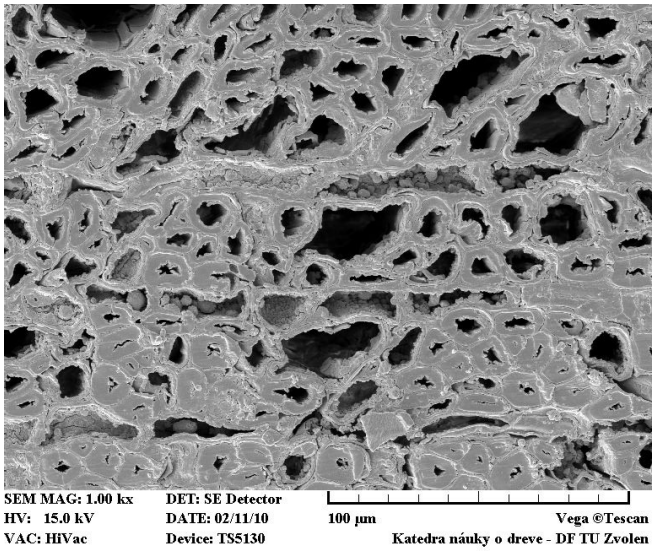

Fig. 1: Preservation condition of the cell walls of oak (Quercus sp.) heartwood from the Biskupin excavation site. Photos by: J. Kúdela

Tab. 3: Uptake of polyglycols and water content in oak wood.

Treatment	Uptake (%)		W_{FD} (%)		W_{52} (%)	
	D	T	D	T	D	T
Control AD					10.4	9.1
Control FD			1.3	1.1	9.1	8.0
20 % PEG 300	25.6	23.2	1.6	2.2	8.1	7.1
25 % PEG 300	30.4	23.8	1.8	2.5	8.4	7.7
30 % PEG 300	41.9	31.9	1.6	3.0	8.5	8.0
25 % PEG 300 + 5 % PEG 4000	36.8	30.2	1.5	3.2	8.1	7.5
25 % PEG 300 + 10 % PEG 4000	42.0	33.5	1.6	3.7	7.9	7.6

W_{FD} – water content in the samples immediately after freeze-drying
W_{52} – water content in the samples after freeze-drying and seasoning at RH 52 %
D – D samples
T – T samples

In the case of treated wood water content in T samples was distinctly higher, particularly after the treatment of samples with solutions of higher final concentrations. Slower drying of T samples was observed already in earlier investigations (Babiński 2007). After seasoning of impregnated and freeze-dried wood at 52 % RH, the content of water in relation to total amount of wood and polyglycol dry mass reached 8-9 % in D samples and 7-8 % in T samples.

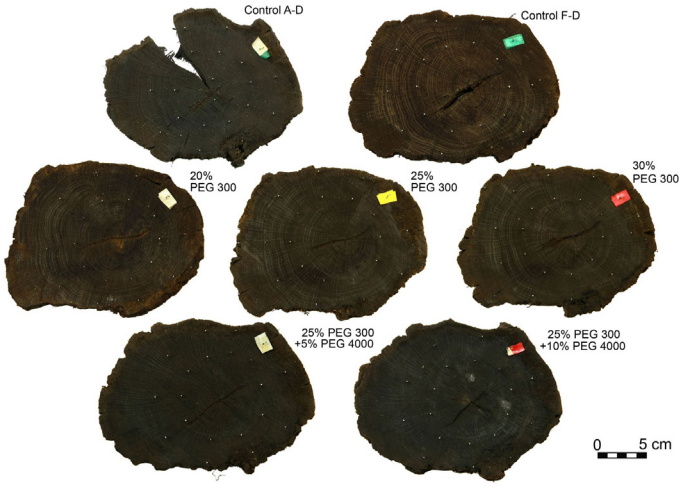

Fig. 2: Discs (D samples) after freeze-drying and seasoning in ambient air at RH 52 %.

Dimensional changes of wood following freeze-drying and seasoning are collated in Tabs. 4 and 5, while Tab. 6 shows ASE values for the two kinds of wood samples. Fig. 2 presents D samples after the phase of wood seasoning at 52 % RH.

Tab. 4: Tangential (β_T) and radial (β_R) shrinkages of oak wood determined in D samples after freeze-drying (FD) and seasoning at RH 52 % (RH52).

Treatment	β_T (%)		β_R (%)	
	FD	RH52	FD	RH52
Control AD		16.0		8.2
Control FD	3.6	2.6	4.6	3.5
20 % PEG 300	6.7	4.9	4.0	2.6
25 % PEG 300	6.0	4.0	3.2	1.7
30 % PEG 300	5.7	3.0	2.9	1.2
25 % PEG 300 + 5 % PEG 4000	6.2	4.0	3.3	1.7
25 % PEG 300 + 10 % PEG 4000	6.2	3.9	2.9	1.3

Wood shrinkage in tangential and radial directions determined on D samples dried in ambient air of 52 % RH (Control AD) was determined to have been 16.0 and 8.2 %, respectively. Following freeze-drying and seasoning of disc-shaped wood samples at RH 52 %, both types of shrinkage were reduced very significantly. Wood shrinkage in tangential direction ranged from 2.6 to 4.9 %, while determined radial wood shrinkage ranged from 1.2 to 3.5 %.
Excluding the minimal value of the tangential shrinkage of untreated samples (Control FD), the greatest reduction of both examined wood shrinkages was recorded following its earlier treatment

with 30 % PEG 300 solution. In that case the ASE_T and ASE_R values exceeded 80 % (Tab. 6). Also in another study of freeze-drying of similarly preserved oak wood from excavations in Szczecin, the best stability of wood dimensions was obtained following its initial impregnation with 30 % solution of PEG 300 (Babiński 2007). Apart from small cracks which occurred in the neighbourhood of the pith, no distinct deformations of examined samples were observed after freeze-drying. Considerable sample warping and wide crack could be observed only in the case of the control disc dried in ambient air (AD Control sample) (Fig. 2).

Tab. 5: Tangential (β_T) and longitudinal (β_L) shrinkages of oak wood determined in T samples after freeze-drying (FD) and seasoning at RH 52 % (RH52).

Treatment	β_T (%)		β_L (%)	
	FD	RH52	FD	RH52
Control AD		9.1		0.5
Control FD	4.2	3.4	0.6	0.3
20 % PEG 300	5.6	4.2	0.2	0.0
25 % PEG 300	4.5	3.1	0.2	0.0
30 % PEG 300	4.2	2.6	0.2	0.1
25 % PEG 300 + 5 % PEG 4000	4.5	3.6	0.2	0.0
25 % PEG 300 + 10 % PEG 4000	4.3	3.4	0.1	0.1

Tab. 6: ASE values for freeze-dried and seasoned oak wood.

Treatment	D samples		T samples	
	ASE_T	ASE_R	ASE_T	ASE_L
	(%)			
Control FD	84	57	63	40
20 % PEG 300	69	68	54	100
25 % PEG 300	75	79	66	100
30 % PEG 300	82	85	71	80
25 % PEG 300 + 5 % PEG 4000	75	79	60	100
25 % PEG 300 + 10 % PEG 4000	76	84	63	80

Tangential and longitudinal shrinkages of T control samples dried in ambient air amounted to 9.1 and 0.5 %, respectively (Tab. 5). The tangential shrinkage of freeze-dried wood seasoned at 52 % RH was comparable with the tangential shrinkage determined on D samples and ranged from 2.6 to 4.2 %. It turned out that the optimal method of initial wood impregnation before freeze-drying was treatment of samples with 30 % PEG 300 solution. In that case wood stability index in tangential direction (ASE_T) exceeded 70 %. The longitudinal shrinkage of impregnated wood subjected to freeze-drying following the seasoning of T samples at RH 52 % did not exceed 0.1 %.

The smallest linear shrinkages of freeze-dried wood were observed in the case of experimental material treated with PEG 300 when the uptake amounted to about 42 % (sample D) and 32 % (samples T) of absolutely dry mass of wood. It is quite probable that introduction of such quantities of polyglycol into deeper parts of objects of large cross section and small degree of heartwood degradation will turn out to be impossible (Babiński and Poskrobko 2000, 2004). However, the comparison of dimensional changes of freeze-dried Biskupin wood shows that smaller uptake of polyglycol resulted only in slightly greater shrinkage of examined samples. When no polyglycol was introduced into wood prior to freeze-drying (samples Control FD), its linear shrinkage was not very different from the shrinkage of wood which was treated with the experimental solutions and significantly smaller in comparison with the untreated wood shrinkage dried in ambient air (samples Control AD).

CONCLUSIONS

The following conclusions were drawn on the basis of the investigations:

1. Linear shrinkage of well-preserved oak heartwood from Biskupin which was subjected to freeze-drying was considerably smaller in comparison with the shrinkage observed for untreated material dried in ambient air at atmospheric pressure.
2. The smallest dimensional changes of examined oak wood occurred when the process of its freeze-drying was preceded by treatment with PEG 300 solution and the uptake of polyglycol amounted to about 32-42 % of absolutely dry wood mass. Oak heartwood of small degree of degradation can also be effectively stabilised dimensionally in the case when the absorption of polyglycol is less than optimal.
3. The scope of performed investigation makes it only possible to conclude that freeze-drying is useful for conservation of small-sized objects. The possibility of achieving high dimensional stability in the case of much larger fragments of Biskupin constructions, including wood of varying degree of penetration with polyglycol, requires further investigations.

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Leszek Babiński
Archaeological Museum in Biskupin
Conservation Department
Biskupin 17
88-410 Gąsawa
Poland
Coresponding author: leszek.babinski@wp.pl

Magdalena Zborowska, Włodzimierz Prądzyński
Poznań University of Life Sciences
Faculty of Wood Technology
Institute of Chemical Wood Technology
Wojska Polskiego 38/42
60-627 Poznań
Poland