Journal of Cultural Heritage 31 (2018) 133–140

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Original article

Dimensional stability and hygroscopic properties of PEG treated irregularly degraded waterlogged Scots pine wood

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ARTICLE INFO

Article history:
Received 31 July 2017
Accepted 7 December 2017
Available online 4 January 2018

Keywords:
Medieval road
Sorption isotherms
Equilibrium moisture content
Exhibition conditions
Anti-shrink efficiency (ASE)
Pinus sylvestris L

ABSTRACT

The study concerns the conservation problem of large scale elements of irregularly degraded archaeological wood being characterized by different susceptibility to agents responsible for wood consolidation and bulking. The conservation effectiveness was established for processes carried out with PEG solutions of different molecular weight with respect to dimensional stabilization, hygroscopic properties and the agent consumption. One of the investigated treatment options had concerned the application of PEG 2000, i.e. poorly studied variant of that type of consolidants. The analysis was performed for wooden elements from a Late Medieval road. The investigated artifacts were characterized by different anatomical structure and each of them included sapwood (SW) and heartwood (HW). Chemical, physical and sorption properties of SW and HW were first determined. A significant difference in the degree of degradation and the content of extractives in SW and HW was observed. The examined artifacts were then impregnated with five different PEG solutions. It was found that the highest anti-shrink efficiency (ASE) was obtained for one-stage PEG 2000 impregnation. The obtained data of sorption experiments showed that all applied impregnation options guaranteed safe exposure of wood in air relative humidity (RH) lower than 80%. Moreover, one-stage impregnation with PEG 2000 assured the lowest equilibrium moisture content (*EMC*) of wood, especially SW, at RH above 80%.

1. Introduction

Degradation of archaeological wood is a combination of processes which take place during three stages, i.e. utilization, deposition and finally awaiting for conservation. In the case of waterlogged wood, deposition conditions are usually near anaerobic ones, which makes the degradation limited. There are numerous examples of well-preserved objects reported in the literature [1,2]. Their good properties also result from the fact that they did not undergo degradation during utilization. Other definitely more unpredictable effects of degradation can be expected in wooden objects such as boats, roads, bridges or water supply systems which were exploited extensively and degraded before deposition [2–4]. Majority of wood artifacts is irregularly degraded in their cross section. The degradation process usually proceeds from outer to central zones of artifacts. In the case of pine wood sapwood is usually severely decayed while heartwood is well preserved. It results in an abrupt change in degradation at the interface between sapwood and heartwood. Therefore, such artifacts are characterized by irregular degradation in their cross section.

Scots pine (*Pinus sylvestris L.*) is the most common wood species found in archaeological sites in North-West Europe and Scandinavia. Due to its perfect technical properties and durability Scots pine wood has been widely used in building constructions. A typical application of the wood was to build roads in medieval towns [5,6]. Wooden road elements were subjected during their use to cyclic wetting and drying as well as mechanical loads. Such conditions caused alteration of chemical and mechanical properties of the wood [7,8].

The crucial features of waterlogged wood, i.e. resistance to biotic and abiotic factors, depend on hygroscopic properties, and it concerns both wood before and after impregnation processes. Hygroscopicity is a set of properties describing the wood-water system however, sorption isotherms, i.e. a relation between wood equilibrium moisture content (*EMC*) and air relative humidity (RH) at constant temperature, are the most common ones [9]. As far as

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https://doi.org/10.1016/j.culher.2017.12.002
1296-2074/

fungal durability of waterlogged wood is often concerned, the *EMC* is the most important parameter. However, due to the phenomenon of sorption phenomenon the *EMC* should be determined separately for adsorption and desorption processes [2,10].

Hygroscopic properties of the waterlogged wood, including. *EMC* values, are usually determined before the final stage of the conservation treatment, i.e. drying (seasoning). In this case the initial desorption has to be considered as the moisture content (MC) of impregnated wood is above the fiber saturation point. Such hygroscopic characteristics are especially important for the proper selection of air parameters during drying (seasoning) of impregnated wood. However, the data cannot be used for predicting MC during exposition of artifacts. For that reason the hygroscopic properties have to be determined not only for the initial desorption (i.e. after impregnation and before seasoning) but also for adsorption and desorption of already impregnated and dried wood. Hygroscopic properties of treated and dried archaeological wood are rarely analyzed substantially, e.g. [11]. The study was performed for four levels of air *RH* only. However, it was possible to find differences in *EMC* values for different phases of sorption and for treated wood as well as for treated and dried material. Moreover, there was found a significant influence of pure consolidants and their retention on the hygroscopic properties of treated waterlogged archaeological wood [11].

The degradation of wood artifacts depends among other factors on the wood species and the dimensions of its cross section. Moreover, differences in anatomical structure, chemical composition and density of sapwood (SW) and heartwood (HW) cause inevitable variations in the degradation of wood. This is a one reason of for the risk of cracking of wood elements during its drying after impregnation. Therefore, a conservation process should account for the differences in wood structure, wood species and degree of degradation. Polyethylene glycol (PEG), the substance most often used for conservation of waterlogged wood, varies significantly in terms of hygroscopicity depending on its molecular weight [12–13]. Moreover, it was pointed out that PEG in impregnated wood is prone to different factors including heat, metal ions, salts, microbial and photo-chemical degradation [14]. It was also found that wood impregnation with PEG negatively influences mechanical properties of wood including the compressive and tensile strength [15] as well as creep properties leading to significant permanent wood deformation [16]. Catalytic oxidative degradation in PEG impregnated wood has also been observed [17].

In order to ensure durability of archaeological wood one has to select the appropriate conservation agent, apply proper parameters of wood impregnation and, ensure safety of exhibition of conserved wood artifacts. The proper selection of the conservation method is especially complicated for wood elements characterized by different properties of the material, i.e. anatomical and chemical structure, physical properties and deterioration. The different characteristics of the material together with the properties of the applied conservation agent might cause cracking of impregnated wood during the last stage of conservation (i.e. drying), or lead to a risk of fungal development when exposing wood at high air RH.

2. Research aim

The objective of the study was to determine hygroscopic properties and dimensional stability of adjacent zones of waterlogged archaeological wood characterized by different anatomical and chemical structure, irregular decay as well as applied low and high molecular weight PEG. The hygroscopic characteristics of the wood zones as obtained for (a) the final stage of the conservation treatment, i.e. drying (seasoning) and (b) subsequent adsorption and desorption phases, i.e. typical for exhibition will help to determine air parameters limiting wood cracking and fungal development, respectively.

3. Materials and methods

The research was conducted for waterlogged Scots pine wood obtained from the remains of a Late Medieval road (turn of the 14th and 15th century – Fig. 1). The wood was collected during the rescue excavations being conducted in Klasztorna Street in Grudziądz [13,18]. The investigated wooden elements were dated from the turn of the 14th and 15th century. Therefore, the material was explicitly identified as Scots pine since Austrian pine (*Pinus nigra Arn.*) characterized by practically identical macroscopic properties was introduced to Poland as early as in 1759. The investigated element was deposited at a depth of 0.5–0.8 m under a pavement of a contemporary road. The samples were drawn from an element with a length of 180 cm and a diameter of 30 cm.

The cross section of the investigated element and the cutting pattern of samples are presented in Fig. 2. A wood strip of dimensions of 35·70·700 mm in tangential, radial, and longitudinal direction, respectively, was first cut from the road element. The separation of sapwood and heartwood was based on the identification of the interface between the two zones. It was explicitly made due to significantly different color of sapwood and heartwood being a result of other anatomical structure, decay and water content. The strip consisted of equal parts of SW and HW. The strip was then cut into twin SW and HW elements in order to obtain two groups of 60 samples of SW or HW only. Each group consisted of 24 samples with dimensions of 30·30·10 mm, for tangential, radial and longitudinal directions, respectively used for the dimensional stability measurements as well as 36 samples with dimensions of 1.5·30·45 mm, for tangential, radial and longitudinal directions, respectively applied for sorption experiments. The obtained 120

Fig. 1. Lining elements of a medivel road in Grudziądz.

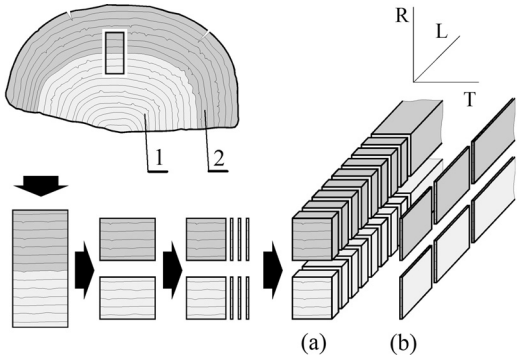

Fig. 2. Scheme of sampling: a: samples for shrinkage measurements; b: twin samples for sorption experiments; 1: heartwood (HW); 2: sapwood (SW).

samples were divided into six sets of 10 for each of SW and HW, respectively. Each set consisted of 4 twin samples for the dimensional stability measurements and six twin samples as to be used for the sorption experiments. Five sets of samples were used for PEG impregnation, while the last set consisted of untreated (control) material. Before impregnation all samples were immersed in water.

Chemical analysis of the investigated material was separately performed for SW and HW. The content of the main chemical components was determined. The holocellulose (H) content, including cellulose and hemicelluloses, was determined according to Browning [19]. The cellulose (C) content was obtained with the application of the Seifert procedure using a mixture of acetylacetone-dioxane-hydrochloric acid [20]. The TAPPI T 222 om-02 standard [21] was used to determine lignin (L) content. Ash content was determined on the basis of the TAPPI T 211 om-02 standard [22]. The extractives were determined according to the TAPPI T 204 cm-97 method [23]. The mean contents of all chemical compounds were determined on the basis of three repetitions. Due to the high amount of extractives in the examined material volatile organic compounds (VOC) were analyzed using gas chromatography combined with mass spectroscopy (GC/MS). Solid phase microextraction (SPME) was used. The GC/MS analysis was performed using the gas chromatograph coupled with a mass spectrometer TRACE 1300 from Thermo Scientific, Waltham, MA, USA, equipped with a DB5 capillary column. The temperature of the column was programmed from 50°C (hold time 4 min) to 240°C (hold time 4 min), at a rate of 10°C per minute. Helium was used as carrier gas (60 hPa). Split/splitless (split mode 1:50) inlet temperature was 200°C. Temperature of the ion source was maintained at 250°C.

The degradation of the investigated material was estimated by determining the maximum water content (MWC) and wood basic density (BD). The twin samples of SW and HW (four samples in each set with dimensions of 30·30·10 mm) were immersed in water in a vacuum chamber under pressure of 50 hPa. The saturation was obtained after 12 weeks. The mass of the saturated samples was measured and then the samples were freeze-dried. The following formula was used to determine *MWC*:

$$MWC = \frac{m_w - m_0}{m_0} \times 100 \quad (\%) \tag{1}$$

where m_w is mass of the saturated sample (kg) and m_0 is mass of the freeze-dried sample (kg). It allows one to calculate BD according to Schniewind [24].

$$BD = \frac{100000}{MMC + 66.7} (\mathrm{kg/m^3}) \tag{2}$$

The PEG impregnation was performed for five sets of SW and five sets of HW samples. It was related to four options of two-stage impregnation and 1 option of one-stage impregnation. At the first stage of two-stage impregnation the samples were treated with low molecular weight PEG (200, 300, 400, 600) in an 8% solution. In the following three stages PEG 4000 was added until the final concentration of low and high molecular PEG was 33%. The fifth one-stage option differed from the others because the concentration of PEG 2000 was increased stepwise to 8, 16, 24 and 33%, respectively. Untreated (control) samples were deposited in water.

The dimensional changes of the investigated material were determined at two different states, i.e. immediately after the impregnation, and after seasoning (drying) at a temperature of 20°C and air RH of 44%. The dimensions of the samples were measured by a digital caliper with the accuracy of 0.001 mm. Mass of the samples was determined with the accuracy of 0.001 g. The swelling/shrinkage (*S*) was determined for the tangential (T), radial (R) and longitudinal (L) anatomical directions according to the following formula:

$$S = \frac{l_0 - l_1}{l_0} \times 100 \quad (\%) \tag{3}$$

where l_0 (mm) was the dimension of a sample before or after impregnation, and l_1 (mm) was the dimension of a sample immediately after impregnation or after seasoning (drying). Positive values of *S* represented wood shrinkage while negative ones represented swelling.

The dimensional stability was estimated by the anti-shrink efficiency (ASE) for impregnated wood after seasoning:

$$ASE = \frac{S_c - S_i}{S_c} \times 100 \quad (\%) \tag{4}$$

where S_c (%) was shrinkage of untreated (control) wood, and S_i (%) was shrinkage/swelling of impregnated wood. The MWC and dimensional changes of equilibrated wood samples were calculated as mean value of four measurements. The uptake of PEG was calculated as the ratio of the mass of impregnated freeze-dried samples and untreated ones.

The experiments for determining sorption isotherms were carried out in a set-up, in which the samples were placed in a chamber while the air RH was controlled by salt solutions [25]. The air parameters were measured by a thermo-hygrometer, type LB 706 from LAB-EL, Reguły, Poland. The measurement inaccuracy for temperature was ± 0.1°C, and for air RH was ± 2.0% (in the range of 10% to 90%). The use of salt solutions enabled to achieve nine levels of RH to be achieved inside the chamber. The sorption tests were performed at 22 ± 1°C for impregnated and untreated wood. The samples were first used to determine the initial desorption (first desorption), and then adsorption as well as second desorption isotherms. All wood samples were weighed at least twice after obtaining the equilibrium. At the end of the sorption experiments, all samples were placed in a drier and their freeze-dry mass was determined. The *EMC* was calculated according to the following formula:

$$EMC = \frac{m - m_0}{m_0} \times 100 \quad (\%) \tag{5}$$

where *m* was mass at the equilibrium (g) and m_0 was the freeze-dry mass (g). The EMC values were calculated for each RH as the mean value of six measurements.

Apart from determining the isotherms, sorption hysteresis (H) was analyzed. It was estimated by the absolute difference of EMC for the second desorption and adsorption for each air RH value:

$$H = EMC_{2Des} - EMC_{Ads} (\%) \tag{6}$$

where EMC_{2Des} was the equilibrium moisture content for the second desorption and EMC_{Ads} was the equilibrium moisture content for adsorption.

The experimental data were analyzed using the Dell™ Statistica™ 13.1 software. For the PEG uptake, swelling/shrinkage and equilibrium moisture content for RH = 44%, comparisons were subjected to an analysis of variance (ANOVA) and significant differences between mean values of control and treated samples were determined using Tukey's HSD test for $\alpha = 0.05$.

4. Results and discussion

Before performing the sorption experiments the chemical analysis of the investigated material was performed. The results of the analysis are presented in Table 1. It was found that the holocellulose content in HW was considerably higher than in SW. Therefore, HW of the wooden element had to be better preserved as compared to SW. The cellulose content in HW was similar to the content in recent wood [26]. Whereas the holocellulose content in SW was

Table 1
Chemical composition and degradation estimators of the investigated sapwood (SW) and heartwood (HW) of waterlogged Scots pine wood.

	Holocellulose (%)	Cellulose (%)	Lignin (%)	H/L	C/L	Ash (%)	Extractives (%)	MWC (%)	BD (kg/m^3)
SW	22.8 ± 0.43	18.8 ± 2.03	64.8 ± 0.20	0.3	0.3	2.8 ± 0.03	10.4 ± 0.31	442.3 ± 21.0	196.8 ± 8.2
HW	67.8 ± 0.65	45.9 ± 0.72	31.4 ± 0.09	2.2	1.5	0.7 ± 0.03	28.5 ± 0.03	89.1 ± 13.7	646.1 ± 56.1

± standard deviation.

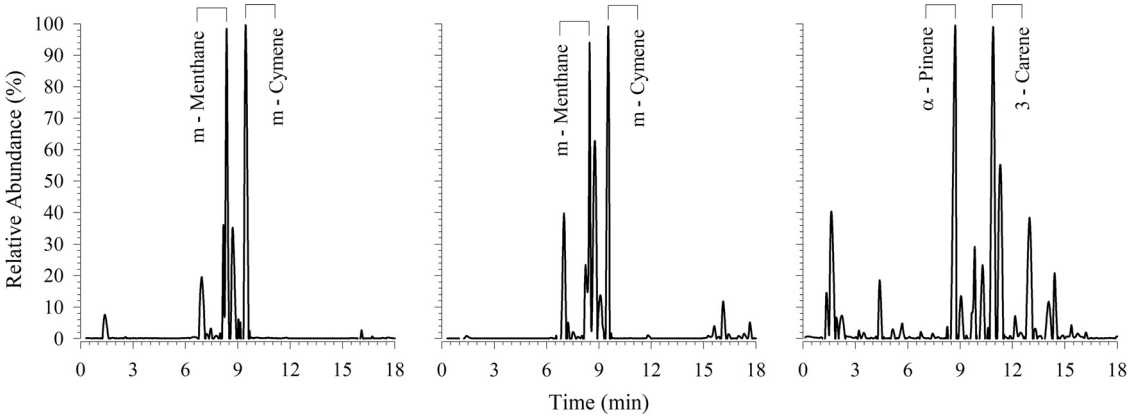

Fig. 3. The GC-MS chromatograms obtained from waterlogged archaeological sapwood (left) and heartwood (middle) as well as recent Scots pine wood (right).

dramatically low, i.e. it was only 22.8%. Moreover, it predominantly consisted of cellulose (18.8%). The result revealed high decomposition of hemicelluloses in SW. Lignin was the main component of SW as its content was as high as 65%. Also the H/L and C/L ratios were considerably different for SW and HW. It again confirmed the high decomposition of hemicelluloses in SW. Ash content amounted to was 0.7% and 2.8% in HW and SW, respectively, and it was higher than in recent wood [26]. The extractives content was high in the investigated wood (Table 1). It was especially pronounced in HW at 28.5%. According to Fengel and Wegener [26] the content of extractives in SW usually varies from 0.5 to 17.8%. The high content of extractives was also found for other artifacts, e.g. [27]. Due to such high content of extractives their main compounds were identified with GC/MS. The chromatographic analysis of VOCs released from the investigated waterlogged archaeological SW and HW as well as from recent wood revealed the presence of major compounds (Fig. 3). In the case of waterlogged archaeological SW and HW m-menthane and m-cymene were predominant. Both m-menthene and m-cymene are products of bioconversion of α- and β-pinene as well as 3-carene, which are the main components of extractives of recent wood [28–30]. It can be supposed that the main compounds identified in archeological wood were formed due to a chemical transformation of the original ingredients existing in wood before its deposition and degradation. Moreover, the detailed analysis of the obtained GC-MS chromatograms showed that other substances were not introduced into wood before or during use of the road elements.

The estimators of archaeological wood degradation are also presented in Table 1. Significant differences between SW and HW were found. The *MWC* of SW exceeded 442.3% and BD was as low as 196.8 kg/m^3. It supports the observations on wood decay and it can be interpreted that more than half of the original wood mass was degraded. In the case of HW the BD was 646.1 kg/m^3 which is similar to the average value of recent Scots pine wood. The most probable reason for good preservation of HW was its extremely high content of extractive substances identified during the chemical analysis (Table 1).

The results of PEG uptake in SW and HW are presented in Table 2. In the case of SW the uptake varied in the range of 147.0 to 153.9%. Significant differences of the uptake in SW were found between the treatment options, i.e. for PEG 400/4000 and PEG 600/4000. Much lower uptake was observed for HW, as it ranged from 18.5 to 20.0%, with insignificant differences for treatment options. The observed uptake differences for SW and HW were primarily due to different degrees of wood decay and chemical composition of the two wood zones.

Immediately after the impregnation swelling of wood was measured in all anatomical directions (Table 2). The average values of swelling were not higher than 1% for all options and each anatomical direction. Likewise, the differences between the swelling of the samples immersed in water (untreated–control material) and in the investigated PEG solution were statistically insignificant (for $\alpha = 0.05$).

The EMC values of treated and untreated SW and HW are presented in Table 3. Significantly higher values (for $\alpha = 0.05$) were found for untreated SW and HW as compared to archaeological wood treated with PEG. This advantage of the PEG treatment was previously noticed [25,31]. The differences in the EMC values of impregnated HW are insignificant (for $\alpha = 0.05$) despite different hydrophilic properties of the applied PEG. In the case of impregnated SW is observed that the highest EMC values were found for impregnation with a mixture containing low molecular weight PEG (i.e. PEG 200/4000), e.g. Hoffmann [10].

The dimensional changes of PEG treated SW and HW after drying (seasoning) were smaller than those for untreated (control) wood (Table 3) and it was observed for the tangential and radial directions. The shrinkage of well-preserved untreated HW amounted to 6.0% and 2.5% in the tangential and radial directions, respectively. The shrinkage of strongly degraded SW was lower 4.5% and 1.1% in tangential and radial directions, respectively. The influence of extractives on shrinkage of archaeological wood was reported by Borgin et al. [26,32], while the a similar influence was found by Choong and Achmadi [33] for sound recent tropical wood. The content of extractives in the investigated HW was extremely high (Table 1). Another reason for low shrinkage of the investigated material could be related to shallow deposition of the road elements and its exploitation resulting in gradual reduction of their MC and dimensions [34].

The dimensional changes of the untreated (control) HW in the longitudinal direction reached -0.6%, i.e. slight swelling was

Table 2
PEG uptake (U) and swelling in tangential (S_T) radial (S_R) and longitudinal (S_L) directions during impregnation of waterlogged Scots pine sapwood and heartwood.

		Treatment options					
		PEG 200/4000	PEG 300/4000	PEG 400/4000	PEG 600/4000	PEG 2000	Untreated (control) material
SW	U (%)	$150.5^{ab} \pm 3.4$	$153.3^{ab} \pm 1.3$	$147.0^{b} \pm 2.1$	$153.9^{a} \pm 2.1$	$152.5^{ab} \pm 3.4$	–
	S_T (%)	$-0.7^{a} \pm 0.1$	$-0.7^{a} \pm 0.1$	$-0.6^{a} \pm 0.2$	$-0.7^{a} \pm 0.2$	$-0.7^{a} \pm 0.2$	$-0.7^{a} \pm 0.1$
	S_R (%)	$-1.0^{a} \pm 0.6$	$-0.5^{a} \pm 0.2$	$-0.8^{a} \pm 0.3$	$-0.9^{a} \pm 0.3$	$-1.0^{a} \pm 0.3$	$-0.8^{a} \pm 0.3$
	S_L (%)	$-0.3^{a} \pm 0.6$	$-0.3^{a} \pm 0.2$	$-0.3^{a} \pm 0.1$	$-0.4^{a} \pm 0.2$	$-0.5^{a} \pm 0.4$	$-0.6^{a} \pm 0.3$
HW	U (%)	$19.2^{a} \pm 4.3$	$18.8^{a} \pm 4.3$	$20.0^{a} \pm 4.3$	$18.5^{a} \pm 4.3$	$20.0^{a} \pm 4.7$	–
	S_T (%)	$-0.1^{a} \pm 0.1$	$-0.4^{a} \pm 0.5$	$-0.1^{a} \pm 0.2$	$-0.1^{a} \pm 0.1$	$-0.2^{a} \pm 0.2$	$-0.3^{a} \pm 0.1$
	S_R (%)	$-0.2^{a} \pm 0.0$	$-0.2^{a} \pm 0.0$	$-0.1^{a} \pm 0.1$	$-0.1^{a} \pm 0.1$	$-0.1^{a} \pm 0.1$	$-0.1^{a} \pm 0.0$
	S_L (%)	$-1.0^{a} \pm 0.6$	$-0.8^{a} \pm 0.2$	$-0.7^{a} \pm 0.1$	$-0.7^{a} \pm 0.2$	$-0.9^{a} \pm 0.2$	$-0.7^{a} \pm 0.4$

Mean values ($n = 4$) ± standard deviations; identical superscripts (a, b, c) denote no significant difference ($P < 0.05$) between mean values in rows according to Tukey's HSD test (ANOVA) for the investigated treatment options.

Table 3
Equilibrium moisture content (EMC) for $RH = 44\%$ and swelling/shrinkage in tangential (S_R), radial (S_T), longitudinal (S_L) direction of waterlogged Scots pine sapwood and heartwood.

		Treatment options					
		PEG 200/4000	PEG 300/4000	PEG 400/4000	PEG 600/4000	PEG 2000	Untreated (control) material
SW	EMC (%)	$3.0^{b} \pm 0.2$	$2.9^{bc} \pm 0.1$	$2.6^{cd} \pm 0.1$	$2.5^{de} \pm 0.1$	$2.2^{e} \pm 0.1$	$5.2^{a} \pm 0.2$
	S_T (%)	$2.9^{bc} \pm 0.6$	$3.9^{ab} \pm 0.8$	$3.7^{ab} \pm 0.6$	$4.4^{a} \pm 0.9$	$1.9^{c} \pm 0.2$	$4.5^{a} \pm 0.5$
	S_R (%)	$0.4^{b} \pm 0.3$	$0.4^{b} \pm 0.1$	$0.4^{b} \pm 0.7$	$0.5^{b} \pm 0.3$	$0.1^{b} \pm 0.0$	$1.1^{a} \pm 0.1$
	S_L (%)	$-0.4^{b} \pm 1.2$	$0.4^{b} \pm 0.7$	$-0.4^{b} \pm 0.4$	$-0.4^{b} \pm 0.3$	$0.4^{b} \pm 1.3$	$6.5^{a} \pm 1.3$
HW	EMC (%)	$3.4^{b} \pm 0.2$	$3.3^{b} \pm 0.2$	$3.2^{b} \pm 0.2$	$3.0^{b} \pm 0.2$	$3.2^{b} \pm 0.2$	$4.4^{a} \pm 0.4$
	S_T (%)	$1.6^{b} \pm 0.2$	$1.5^{b} \pm 0.2$	$1.7^{b} \pm 0.1$	$1.6^{b} \pm 0.1$	$1.6^{b} \pm 0.1$	$6.0^{a} \pm 0.2$
	S_R (%)	$0.2^{b} \pm 0.2$	$0.3^{b} \pm 0.2$	$0.3^{b} \pm 0.2$	$0.3^{b} \pm 0.1$	$0.3^{b} \pm 0.2$	$2.5^{a} \pm 0.1$
	S_L (%)	$-0.5^{a} \pm 0.3$	$-0.8^{a} \pm 1.3$	$-0.1^{a} \pm 0.5$	$-0,8^{a} \pm 0.7$	$-0.5^{a} \pm 0.4$	$-0.6^{a} \pm 0.6$

Mean values ($n = 4$) ± standard deviations; identical superscripts (a, b, c,d,e) denote no significant difference ($P < 0.05$) between mean values in rows according to Tukey's HSD test (ANOVA) for the investigated treatment options.

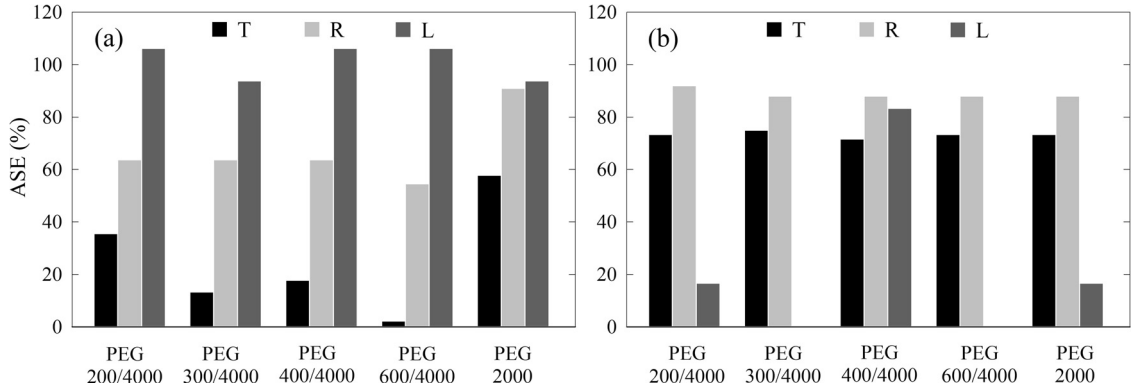

Fig. 4. Anti-shrink efficiencies in tangential, radial and longitudinal directions of waterlogged Scots pine a: sapwood and; b: heartwood seasoned at $t = 20^{\circ}C$, $RH = 44\%$.

observed. Whereas shrinkage of the untreated (control) SW in the longitudinal direction reached a very high value of 6.5%, being higher than in the tangential and radial directions. The obtained result corresponded to the earlier findings of Babiński [35], who revealed high shrinkage in the longitudinal direction for Scots pine and silver fir archaeological wood affected by degradation. Moreover, it was also suggested by Babiński [35] that shrinkage in the longitudinal direction is a better indicator of archaeological wood decay than shrinkage in the radial or tangential direction. The significant difference in the longitudinal shrinkage of SW and HW causes wide transverse cracks in untreated artifacts during drying (seasoning). The decrease of the difference is achieved by dimension stabilization (e.g. with PEG). A decrease of SW shrinkage after impregnation for all treatment options was observed (Table 3). However, the decrease of shrinkage in all anatomical directions was significantly lower than for untreated wood but only for SW impregnated with PEG 200/4000 and PEG 2000 (for $\alpha = 0.05$). In the case of impregnated HW the decrease of the shrinkage in the tangential and radial directions was observed for all applied treatment options and the differences between the impregnated samples were insignificant (for $\alpha = 0.05$). The performed statistical analysis did not confirm the effect of the impregnation on the dimensional stabilization of HW in the longitudinal direction. It was found that in the case of SW only the two-stage PEG 200/4000 and one-stage PEG 2000 impregnation caused a significant increase of dimensional stability in all anatomical directions (Fig. 4). However, the use of PEG 2000 caused a larger decrease of shrinkage than PEG 200/4000 application.

In the case of impregnated SW there was observed high reduction of shrinkage in the longitudinal direction. In all options of impregnation the ASE was nearly 100%. The ASE of HW was similar and amounted to was more than 70% and 90% for the tangential and radial direction, respectively. Simultaneously, there was observed negligibly low ASE in the longitudinal direction for HW (excluding the material treated with PEG 400/4000). The low ASE values were the result of low shrinkage of untreated HW.

The experimental sorption isotherms of the waterlogged Scots pine wood untreated and treated with PEG are presented in

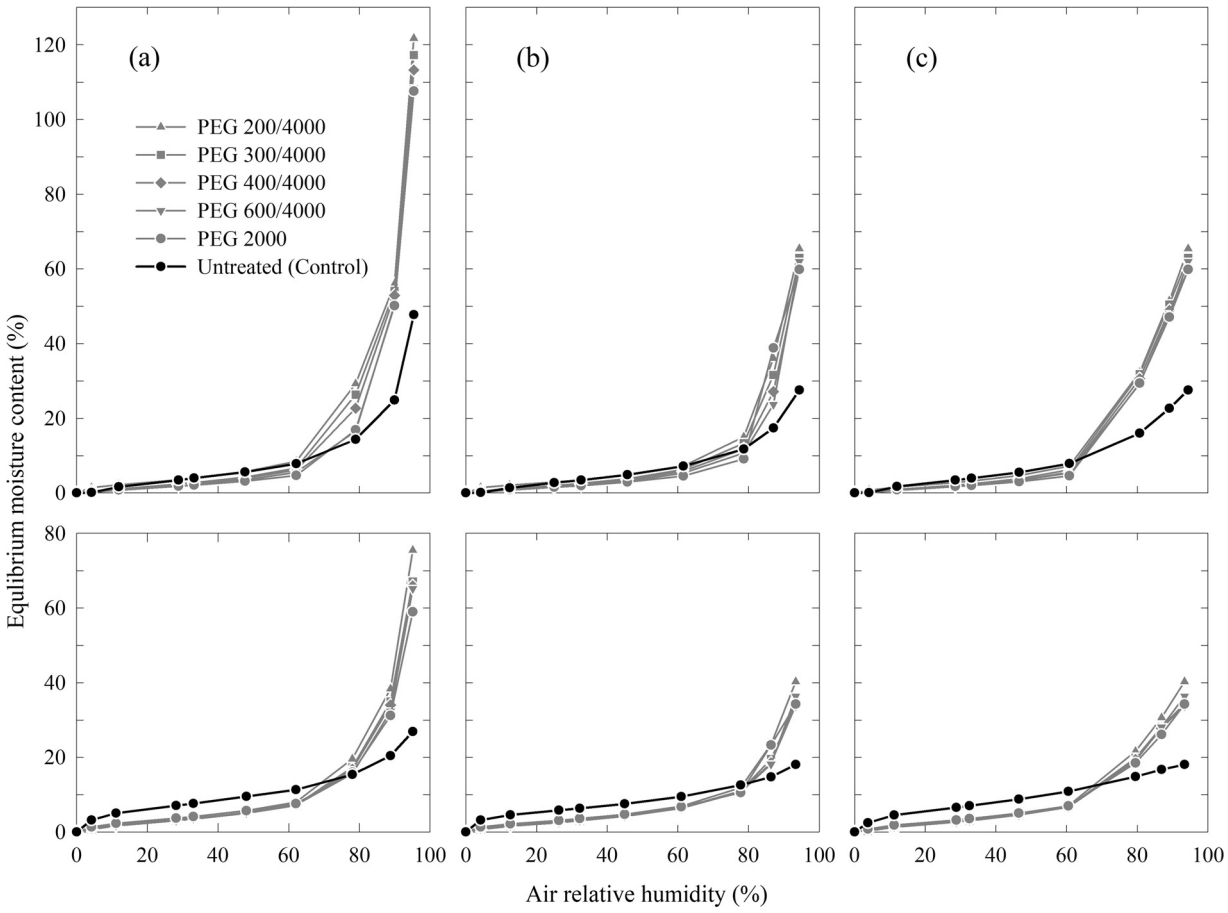

Fig. 5. Sorption isotherms of waterlogged Scots pine wood obtained at temperature of 22 ± 1 °C for: sapwood (above) and heartwood (bottom) treated with different PEG solutions, a: initial desorption; b: adsorption and; c: desorption.

Fig. 5. The isotherms were obtained at a temperature of 22°C. The isotherms were identified as the type II, i.e. sigmoid ones [9], and it was found for all phases of the sorption experiment. It was observed that the isotherms obtained for the initial sorption (i.e. the 1st desorption) significantly differed from the isotherms for further sorption phases, i.e. the 1st adsorption and the 2nd desorption. The observed differences in the isotherms inevitably resulted in obtaining different EMC values for the impregnated waterlogged wood during its drying after the treatment and for already impregnated and dried artifacts.

It has also been observed that the sorption isotherms obtained for PEG treated wood differ from the isotherms determined for untreated material. For RH below 80% the EMC of the impregnated SW and HW is significantly lower than in the case of the untreated wood. However, an unfavorable phenomenon is observed for RH values equal to or higher than 80%. There was found an anomalous increase of EMC for PEG treated wood. The phenomenon was observed for all options of the treatment, and it can pose a serious threat to artifacts due to possible development of microorganisms leading to wood decay. Wood impregnated with PEG 2000 reached lower EMC during the 1st desorption (i.e. during drying after the impregnation) than wood impregnated in the two-stage process. It is especially evident in the range of air RH above 80%. Simultaneously, shrinkage in the tangential direction (in the range below RH of 44%) of wood impregnated with PEG 2000 was significantly lower (for $\alpha = 95\%$) than in the other two-stage impregnation processes. However, the sorption hysteresis phenomenon for the 1st adsorption and 2nd desorption was observed (Fig. 6). For air RH below 60% the described phenomenon should be considered

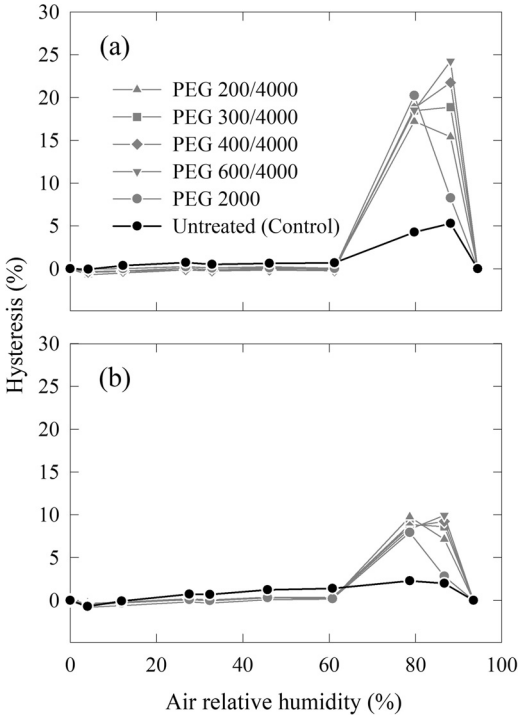

Fig. 6. Sorption hysteresis of a: sapwood; b: heartwood of waterlogged Scots pine wood.

as negligible. Anomalous high sorption hysteresis occurs for RH above 60%, and it is even more distinct for SW. The effect of wood impregnation with PEG 2000 significantly reduced the unfavorable phenomenon in comparison to other treatment options, especially in the case of SW.

The results of sorption experiments and chemical composition analysis confirmed a significant influence of wood degradation and the presence of extractives on the course and scope of sorption phenomena. With respect to untreated wood it has been observed that the EMC of more degraded SW, air-conditioned at 20°C and low air RH, i.e. 44%, is only slightly higher than the EMC of much less degraded HW, i.e. 5.2 and 4.4% respectively. For high air RH, the untreated SW obtained higher EMC as compared to untreated HW (Fig. 5). It was observed despite higher degradation and low cellulose content in SW. It is also the effect of the higher content of extractives in HW (Table 1). The influence of extractives on the sorption phenomenon was previously reported by Simón et al. [36], and it has been pointed out that high concentration of extractives causes the decrease of EMC. Spalt [37] observed that wood with a high content of extractives reveals low EMC, especially when air RH is above 50%. Moreover, Spalt [37] stated that extractives have little effect on monolayer sorption (i.e. for low RH), while their influence is significant in the case of multilayer sorption (i.e. for high RH). The comparison of sorption isotherms of SW and HW (Fig. 5) shows that at low air RH, the EMC of wood impregnated with different PEG primarily depends on the degree of decay. In contrast, EMC of wood impregnated with PEG, as the effect of higher air RH (above 80%), is determined by the content of PEG, resulting in the significant reduction of the EMC value.

5. Conclusions

- the anatomical structure, chemical composition and wood degradation are reasons for the different content of PEG in waterlogged SW and HW. It was found that the increase of dimensional stability and reduction of wood hygroscopicity depend primarily on the different properties of SW and HW. The effectiveness of impregnation processes to a lesser extent depends on PEG content and treatment option;
- a positive effect of PEG impregnation on the reduction of hygroscopicity was found for typical conditions of artifacts displayed in museums, i.e. 20°C and RH = 44%. However, for each treatment option EMC was significantly lower than in the case of untreated wood (for $\alpha = 0.05$). Moreover, the effect of impregnation had a greater influence on the EMC reduction in SW than in HW;
- PEG treatment increases wood hygroscopicity when artifacts are exposed to air of RH above 80%. This phenomenon is the result of high hygroscopicity of PEG. Moreover, the lower EMC of HW as compared to SW in air RH above 80% results from a lower degree of degradation, higher content of extractives and lower content of hygroscopic PEG;
- the sorption of waterlogged wood is characterized by hysteresis. Freshly impregnated wood has a higher EMC than in the subsequent phases of sorption. Therefore, the EMC directly after the drying phase should not be considered as the final one. During the exhibition of wood artifacts in museums EMC will be lower and sorption hysteresis will be reduced;
- the different conservation effectiveness of waterlogged SW and HW may be the reason for an increased risk of destruction during drying after the impregnation. An especially high risk occurs at the interface between SW and HW;
- the longitudinal shrinkage was closely related to the degree of wood degradation. The reduction of the shrinkage in this anatomical direction is particularly important in conservation of long, fine artifacts with irregular degradation;
- the one-stage impregnation with PEG 2000 guarantees better effectiveness of conservation than the two-stage PEG treatment that is the most popular method of impregnation of wood artifacts. Waterlogged Scots pine SW and HW treated with PEG 2000 was characterized by the best dimensional stability and hygroscopic properties, especially at higher air RH.

References

[1] S. McGrail, Ancient boats and ships, Shire Publications Limited, Buckinghamshire, 2006.
[2] P. Hoffmann, Conservation of archeological ships and boats - personal experiences, Archetype Publications, London, 2013.
[3] C.J. Bond, Walking the track and believing: the Sweet Track as a means of accessing earlier Neolithic spirituality? in: D.A. Barrowclough, C. Malone (Eds.), Cult in context: reconsidering ritual in archaeology, Oxbow Books, Oxford, 2007, pp. 158–166.
[4] R. Pukienė, in: I. García-González, M. Souto-Herrero (Eds.), The earliest water supply and sewage systems in Vilnius, Lithuania, Book of abstracts of EuroDendro 2014, Lugo, Spain, 2014, p. 20.
[5] P. Konczewski, J. Piekalski, The streets of medieval Wrocław–methods of construction and functions, in: S. Krabath, J. Piekalski, K. Wachowski (Eds.), Ulica, plac i cmentarz w publicznej przestrzeni średniowiecznego i wczesnonowożytnego miasta Europy Środkowej, Wratislavia Antiqua, University of Wrocław, Institute of Archaeology, Wrocław, 2011, pp. 155–162.
[6] J. Piekalski, Prague, Wrocław and Krakow: public and private space at the time of the medieval transition, in: K. Wachowski, J. Klápště, S. Krabath, M. Młynarska-Kaletynowa, J. Piekalski (Eds.), Wratislavia Antiqua, University of Wrocław, Institute of Archaeology, Wrocław, 2014, p. 19.
[7] G. Giachi, F. Bettazzi, S. Chimichi, S. Staccioli, Chemical characterisation of degraded wood in ships discovered in a recent excavation of the Etruscan and Roman harbour of Pisa J. Cult. Herit. 4 (2003) 75–83.
[8] H. Vurdu, H.İ. Kesík, O.Ç. Kurtulus, O.E. Özkan, Some physical and mechanical properties of antique and fresh cut Pinus sylvestris and Abies nordmanniana subsp. Bornmulleriana woods, Pro. Ligno. 9 (2013) 562–567.
[9] C. Skaar, Wood-water relations, Springer-Verlag, Berlin, 1988.
[10] P. Hoffmann, On the stabilization of waterlogged oakwood with PEG: molecular size versus degree of degradation, in: Les Bois Gorgés d'Eau : étude et conservation [Waterlogged Wood: Study and conservation], Proceedings of the 2nd ICOM Waterlogged Wood Working kroup Conference, Grenoble, 1984, pp. 95–115.
[11] G. Giachi, C. Capretti, N. Macchioni, B. Pizzo, I.D. Donato, A methodological approach in the evaluation of the efficacy of treatments for the dimensional stabilisation of waterlogged archaeological wood, J. Cult. Herit. 11 (2010) 91–101.
[12] M.N. Mortensen, H. Egsgaard, S. Hvilsted, Y. Shashoua, J. Glastrup, Characterisation of the polyethylene glycol impregnation of the Swedish warship Vasa and one of the Danish Skuldelev Viking ships, J. Archaeol. Sci. 34 (2007) 1211–1218.
[13] J. Majka, L. Babiński, W. Olek, Sorption isotherms of waterlogged subfossil Scots pine wood impregnated with a lactitol and trehalose mixture, Holzforschung (2017) 813–819, http://dx.doi.org/10.1515/hf-2017-0006.
[14] E. Hocker, G. Almkvist, M. Sahlstedt, M., The Vasa experience with polyethylene glycol: a conservator's perspective, J. Cult. Herit. 135 (2012) S175–S182.
[15] G. Almkvist, S. Norbakhsh, I. Bjurhager, K. Varmuza, Prediction of tensile strength in iron-contaminated archaeological wood by FT-IR spectroscopy – a study of degradation in recent oak and Vasa oak, Holzforschung 70 (2016) 855–865.
[16] P. Hoffmann, On the long-term visco-elastic behaviour of polyethylene glycol (PEG) impregnated archaeological oak wood, Holzforschung 64 (2010) 725–728.
[17] S. Norbakhsh, I. Bjurhager, G. Almkvist, Impact of iron (II) and oxygen on degradation of oak-modeling of the Vasa wood, Holzforschung 68 (2014) 649–655.
[18] A. Retkowska, R. Grochowski, Sprawozdanie z ratowniczych badań archeologicznych przeprowadzonych przy ul. Klasztornej w Grudziądzu, woj. kujawsko-pomorskiew roku 2013/2014 w związku z inwestycją modernizacji sieci tramwajowej (in Polish), Sprawozdanie dla WKZ, Bydgoszcz, 2014.
[19] B.L. Browning, The chemistry of wood, Interscience, New York, 1967.
[20] V.K. Seifert, Zur Frage der Cellulose-Schnellbestimmung nach der Acetylaceton–Methode, Das Papier 14 (1960) 104–106.
[21] Anon, TAPPI standard–acid insoluble lignin in wood and pulp test method T 222 om-02, 2001.
[22] Anon, TAPPI standard–ash in wood, pulp and paper and paperboard: combustion at 525°C, test method T 211 om-02, 2002.
[23] Anon, TAPPI standard–solvent extractives of wood and pulp test method T 204 cm-97, 1997.
[24] A.P. Schniewind, Physical and mechanical properties of waterlogged wood, in: R.M. Rowell, R.J. Barbour (Eds.), Archaeological wood, properties, chemistry and preservation. Advance in chemistry, 225, American Chemical Society, Washington DC, 1990, pp. 87–109.
[25] J. Majka, W. Olek, Effects of European beech (*Fagus sylvatica L.*) wood steaming on sorption properties and kiln drying intensity, *Folia Forestalia Polonica*, series B, 38, 2007, pp. 55–66.
[26] D. Fengel, G. Wegener, Wood: chemistry, ultrastructure reactions, Walter de Gruyter, Berlin, 1989.

[27] N. Macchioni, B. Pizzo, C. Capretti, G. Giachi, How an integrated diagnostic approach can help in a correct evaluation of the state of preservation of waterlogged archaeological wooden artefacts, J. Archaeol. Sci. 39 (2012) 3255–3263.
[28] S.K. Yoo, D.F. Day, K.R. Cadwallader, Bioconversion of α- and ß-pinene by *Pseudomonas sp*. strain PIN, Process Biochem. 36 (2001) 925–932.
[29] M. Dvorakova, I. Valterova, D. Saman, T. Vanek, Biotransformation of (1S)-2-carene and (1S)-3-carene by Picea abies suspension culture, Molecules 16 (2011) 10541–10555.
[30] K.A.C. Vespermann, B.N. Paulin, M.C.S. Barcelos, M.G. Pessôa, G.M. Pastore, G. Molina, Biotransformation of α- and β-pinene into flavor compounds, Appl. Microbiol. Biotechnol. 101 (5) (2017) 1805–1817.
[31] W. Olek, J. Majka, A. Stempin, M. Sikora, M. Zborowska, Hygroscopic properties of PEG treated archaeological wood from the rampart of the 10th century stronghold as exposed in the archaeological reserve genius loci in Poznań (Poland), J. Cult. Herit. 18 (2016) 299–305.
[32] K. Borgin, G. Tsoumis, C. Passialis, Density and shrinkage of old wood, Wood Sci. Technol. 13 (1979) 49–57.
[33] E.T. Choong, S.S. Achmadi, Effect of extractives on moisture sorption and shrinkage in tropical woods, Wood Fiber Sci. 23 (1991) 185–196.
[34] L.G. Esteban, J. Gril, P. de Palacios, A.G. Casasús, Reduction of wood hygroscopicity and associated dimensional response by repeated humidity cycles, Ann. Forest Sci. 62 (2005) 275–284.
[35] L. Babiński, Badanie stopnia degradacji i stabilizacji wymiarowej mokrego drewna wykopaliskowego, Acta Sci. Polonor. Silvar. Colendar. Ratio Industr. Lignar. 4 (1) (2005) 153–171.
[36] C. Simón, L.G. Esteban, P. Palacios, F.G. Fernández, Thermodynamic analysis of water vapour sorption behaviour of juvenile and mature wood Abies alba Mill, J. Mat. Sci. 50 (2015) 7282–7292.
[37] H.A. Spalt, The fundamentals of water vapor sorption by wood, Forest Prod. J. 8 (10) (1958) 288–295.