forests

MDPI

Article

Dimensional Stability of Waterlogged Scots Pine Wood Treated with PEG and Dried Using an Alternative Approach

Mariusz Fejfer [1,2], Jerzy Majka [3,*] and Magdalena Zborowska [1]

1 Department of Chemical Wood Technology, Faculty of Forestry and Wood Technology, Poznań University of Life Sciences, Wojska Polskiego 38/42, 60-637 Poznań, Poland; mariusz.fejfer@biskupin.pl (M.F.); magdalena.zborowska@up.poznan.pl (M.Z.)
2 Archaeological Museum in Biskupin. Biskupin 17, 88-410 Gąsawa, Poland
3 Department of Wood Science and Thermal Technics, Faculty of Forestry and Wood Technology, Poznań University of Life Sciences, Wojska Polskiego 38/42, 60-637 Poznań, Poland
* Correspondence: jerzy.majka@up.poznan.pl; Tel.: +48-61-848-7442

Received: 21 October 2020; Accepted: 24 November 2020; Published: 26 November 2020



Abstract: Low-intensity drying is widely believed to protect waterlogged archeological wood against the adverse effects of dimensional alteration and cracking. However, slow drying generates substantial costs for the conservation process. This study compares the effects on conservation of highly-degraded sapwood (SW) and slightly-degraded heartwood (HW) from waterlogged archeological Scots pine wood treated with polyethylene glycol either as a mixture of polyethylene glycol (PEG) 400/4000 or PEG 2000 solution and air-dried using different approaches. The reference air-drying approach, using gradually decreasing air relative humidity (RH), i.e., 96, 86, 75, 66, and finally 44% (multi-stage schedule), was compared to an alternative approach, using constant RH of 44% (single-stage schedule). The Fourier-transform infrared spectroscopy (FTIR) analysis confirmed the decomposition of hydrophilic chemical wood components and revealed differences in the degree of degradation of waterlogged SW and HW. The drying time of PEG-treated waterlogged wood air-dried using a one-stage schedule was shorter compared to the drying time using multi-stage drying. Multivariate analysis (ANOVA) revealed that the drying schedule used after impregnation of waterlogged wood with PEG can have a beneficial effect on wood hygroscopicity and dimensional stability. The drying schedule significantly affected the equilibrium moisture content (*EMC*) of SW and HW and reduced tangential (S_T) shrinkage of SW. These results show the positive effect of the single-stage alternative drying approach on the dimensional stability of highly-degraded Scots pine SW impregnated with PEG 2000. In the case of slightly-degraded HW, the drying approach did not affect wood preservation. These results can be useful for the conservation of highly-degraded waterlogged Scots pine wood.

Keywords: single and multi-stage drying schedule; equilibrium moisture content; anti-shrink efficiency (ASE); FTIR analysis; ANOVA analysis; *Pinus sylvestris* L.; sapwood; heartwood; archaeological wood

1. Introduction

Wood residues found in soil or water, of natural or anthropogenic origin, referred to as waterlogged wood, are a valuable source of information about historical material and human culture and its interaction with the environment, as well as about past environmental conditions. The study of annual growth rings, the width of which indicate the seasonal response of growing trees to climate, is used in chronological, geological, ecological, and climatic studies [1]. In anaerobic conditions,

wood can survive thousands of years in a state of complete or partial water saturation. The anoxia of the environment limits the development of highly-destructive white and brown decay fungi [2]. However, even in anaerobic conditions there is a slow course of decomposition, mainly of cell wall polysaccharides by anaerobic microorganisms, altering wood physical and mechanical properties, i.e., reducing wood density and tensile strength [3]. Wooden elements may be well or poorly preserved, corresponding to a low and high degree of degradation of the wood tissue, respectively. However, it is common for waterlogged wood to have internal differentiation of the tissues, i.e., some of the tissues will have high and some will have low degree of degradation. Waterlogged archaeological wood is often at high risk of cracking immediately following excavation. The risk of cracking is increased by large anisotropic desorption shrinkage perpendicular to the wood grain, i.e., tangential and radial shrinkage (larger than that for contemporary wood) and the loss of wood strength, making it susceptible to collapse [4]. The risk of cracking of excavated wood can be eliminated by means of conservation procedures. The main purpose of conservation is to achieve dimensional stability of the wood (reducing the hygroscopicity and desorption shrinkage of the wood). A high coefficient of anti-shrink efficiency (ASE) is a recognized measure of the effectiveness of conservation [5].

Conservation of excavated wood requires, first of all, its saturation with an impregnating agent (impregnation stage) and then decreasing the moisture content of the wood (drying stage) [6,7]. Drying should take place in strictly-controlled conditions. The selection of an appropriate method of impregnation of waterlogged wood requires taking into account the species of wood, the degree of degradation, and the dimensions of the object. Polyethylene glycols (PEGs) with molecular weights ranging from 200 to 4000 are commonly used as an impregnant in conservation. PEG has hygroscopic properties, which varies with its molecular weight. The hydroxyl value of low-molecular weight, strongly hygroscopic, PEG 400 is approximately 10 times higher than high molecular weight PEG 4000 [8]. At the same time, low molecular weight PEGs (PEG 200–PEG 1000) is characterized by high retention in wood and, as a result, they hold great promise for providing dimensional stability of wood with a low degree of degradation. On the other hand, the advantage of using high molecular weight PEGs (i.e., from PEG 1500 to PEG 4000) is better dimensional stabilization of wood with a high degree of degradation and lower hygroscopicity than in the case of PEGs with low molecular weight [6,9].

Intensive freeze-drying and long-lasting controlled air-drying are the two most common approaches for drying waterlogged archaeological wood. The applicability of these methods mainly depends on the anatomy and chemical composition of wood, the degree of degradation, and the dimensions of the objects to be treated. Freeze-drying can avoid wood collapse caused by capillary forces [10]. However, freeze-drying of excavated wood is less suitable for large pieces. In such cases, controlled air-drying [3] or so-called "slow drying" of wood may be carried out [11]. According to Jensen and Gregory [12], the drying of degraded wood can be optimized by taking into account wood density. For example, highly-degraded wood with low density has a tendency to suffer severe collapse, and therefore impregnation with high molecular weight PEG followed by freeze-drying is a more suitable conservation method. In comparison, slightly-degraded wood with higher wood density can be treated with low molecular weight PEG, followed by controlled air-drying, as the samples are at less risk of tissue collapse. Freeze-drying is considered intensive, requires specialized equipment, and is most often used for drying small objects. Therefore, tests have been undertaken to speed up air drying, e.g., using acetone-containing consolidants, which make controlled air-drying competitive with fast freeze-drying [13]. Controlled air-drying as a method of preservation of waterlogged wood has also been investigated [14]. Drying time of slightly-degraded waterlogged oak wood was shortened using super-heated steam–vacuum drying [15].

Impregnation and drying of waterlogged wood are long-term processes that are affected by wood properties. Shortening the time of conservation procedures not only provides measurable logistic and economic benefits, it also reduces the risk of bacterial and fungal growth. The aim of the present research was to test the hypothesis that the method of drying following waterlogged wood impregnation

affects the conservation of archeological wood, i.e., hygroscopicity and dimensional stability. In addition, the research evaluated the effect of the degree of degradation of waterlogged wood and the use of different impregnation methods.

2. Materials and Methods

2.1. Sampling

A wood strip of waterlogged Scots pine with dimensions of 35 × 70 × 700 mm in tangential (T), radial (R), and longitudinal (L) directions, respectively, was firstly cut from the remains of a late Medieval road sign of the 14th and 15th century [16] (Figure 1). The strip consisted of similar zones of sapwood (SW) and heartwood (HW). The strip was then cut to obtain two groups of 12 samples of SW and 12 samples of HW with dimensions of 30 × 30 × 10 mm, for tangential, radial and longitudinal directions, respectively, which were used for dimensional stability and equilibrium moisture content (EMC) measurements. The 12 samples of SW and HW obtained were divided into three sets of four samples. Two sets of samples were used for PEG impregnation (400/4000 or 2000), while the last set was untreated (control). Before impregnation, all samples were immersed in water. This procedure was caused by the necessity to bring all tested wood samples to the state of maximum water content (MWC), on the basis of which the wood density is calculated. The samples were immersed in water in a vacuum chamber at a pressure of 50 hPa and then left in cold water for 12 weeks.

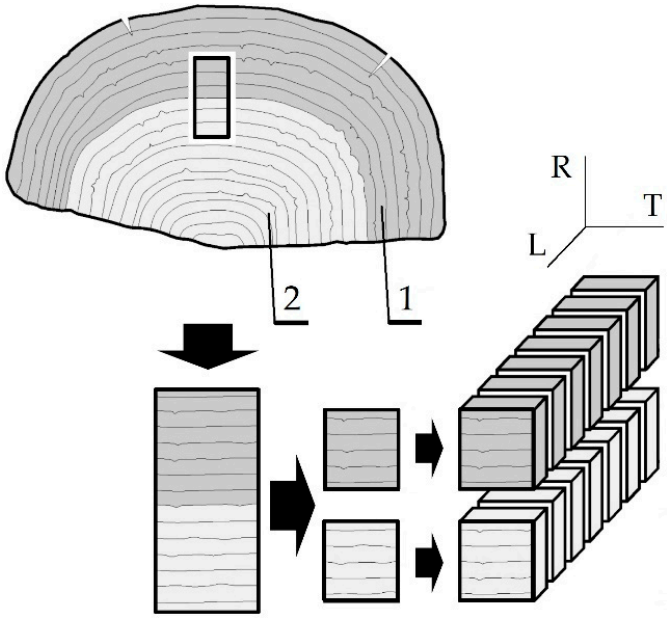


Figure 1. Cutting scheme of waterlogged Scots pine wood samples: 1, sapwood (SW) and 2, heartwood (HW), T, R, L—tangential, radial and longitudinal anatomical direction, respectively.

The results of a previous investigation indicated higher degradation of the SW than HW, with basic wood density of 197 and 646 kg/m^3, respectively [16].

2.2. PEG Impregnation

Two impregnation schedules for conserving wood samples were assessed—multi-stage impregnation and single-stage (alternative) impregnation. In multi-stage impregnation, samples were treated with low molecular weight PEG 400 in an 8% solution, followed by three stages with PEG 4000 added until the final concentration of low and high molecular weight PEG mixture amounted to 33%. In the case of the single-stage (alternative) impregnation option, the concentration of PEG 2000 was gradually increased to 8, 16, 24, and finally 33%. The single-stage method of excavated wood

impregnation with PEG 2000 solution included in the study is currently considered an alternative to the two-stage method of wood preservation with PEG 400/4000 mixture, due to the possibility of shortening treatment time and reducing maintenance costs [17,18]. Untreated (control) wood samples were submerged in distilled water.

2.3. Drying

Immediately after impregnation of the prepared wood samples, one of two drying schedules was implemented, one being multi-stage drying (reference approach) and the other single-stage drying (alternative approach) (Figure 2). In the first case, the reference approach, untreated and PEG-treated SW and HW samples were air-dried with gradually-decreasing air relative humidity (RH), i.e., 96, 86, 75, 66, and finally 44%. In the second case (the alternative approach), twin wood samples were dried using single-stage drying at a constant RH of 44%. The drying experiments were performed at 20 ± 1 °C in containers provided with air circulation. The RH of the air was controlled during the experiments using salt solutions [19]. Drying times of PEG-treated and untreated (control) waterlogged wood samples were 42 weeks and 10 weeks, respectively, for the multi-stage and single-stage air-drying schedules.

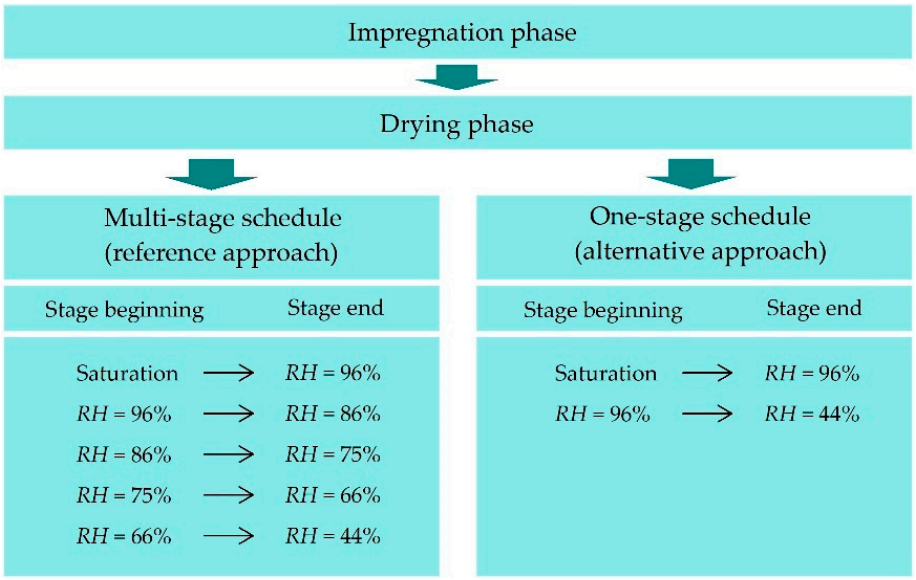


Figure 2. Conservation scheme of waterlogged Scots pine wood sample using different drying approaches.

2.4. Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

An FTIR analysis was performed to examine differences in the chemical composition of waterlogged Scots pine SW and HW. Three untreated samples of each type (SW and HW) were separately grounded and sieved. Before the measurements, the wood and KBr were dried in an oven for 24 h at 40 °C and palletized. The measurements were performed at 20 °C and 50% RH. Spectra of prepared samples were recorded by obtaining 32 scans from 400 to 4000 cm^{-1} (resolution of 4 cm^{-1}), using an FTIR IRPrestige 21 spectrometer (Shimadzu Corp., Tokyo, Japan). Scans were accumulated in transmission mode. The IR spectra were used for the calculation of the lateral order index (LOI, A1422/A899) and total crystallinity index (TCI, A1370/A2921) [20]. To make these calculations, the spectra were normalized at a wavelength of 1030 cm.

2.5. Equilibrium Moisture Content and Dimensional Stability

The equilibrium moisture content (*EMC*) was calculated as follows [21]:

$$EMC = \frac{m - m_0}{m_0} \cdot 100, \quad (1)$$

where m is the mass of wood at equilibrium (g) and m_0 is the freeze-dried mass of wood (g). The mass of the samples was determined with an accuracy of 0.001 g. The *EMC* values were calculated for each RH as a mean value of four measurements.

The dimensional changes of the investigated material were determined at two different states, i.e., immediately after impregnation and after air-drying (seasoning) at a temperature of 20 °C and air RH of 44%. The dimensions of the samples were measured by a digital flat-bed micrometer caliper with an accuracy of 0.001 mm. The swelling/shrinkage (S) was determined for the tangential (T) and radial (R) anatomical directions according to the following formula [22]:

$$S = \frac{l_0 - l_1}{l_0} \cdot 100, \quad (2)$$

where l_0 (mm) is the dimension of the sample before seasoning immediately after impregnation and l_1 (mm) is the dimension of the sample after seasoning. Positive values of S indicate wood shrinkage while negative values indicate swelling.

Dimensional stability was estimated by the anti-shrink efficiency (*ASE*) for impregnated wood after air-drying (seasoning), according to the following formula [23]:

$$ASE = \frac{S_c - S_i}{S_c} \cdot 100, \quad (3)$$

where S_c (%) is the shrinkage of untreated (control) wood and S_i (%) is the shrinkage/swelling of impregnated wood.

2.6. Statistical Analysis

The experimental data were statistically analyzed using STATISTICA 13.3 software (TIBCO Software Inc., Palo Alto, CA, USA). A two-factor analysis of variance (ANOVA) was performed to determine whether the impregnation method and drying schedule affected the equilibrium moisture content and tangential and radial shrinkage of the waterlogged wood. Significance was established at $p < 0.05$. Tukey's HSD significance test was applied to find significant differences between mean values of examined properties of waterlogged wood.

3. Results

3.1. Chemical Composition of Wood

The FTIR spectra differed between SW and HW of waterlogged Scots pine (Figure 3). Peaks visible in spectra were evident between 1800 and 800 cm^{-1} and are attributable to the selective absorption of infrared radiation by functional groups of the chemical components in the wood, i.e., carbohydrates, lignin, and extractable compounds. For many species of wood, these peaks are well defined [24–28].

The SW spectrum was characterized by peaks from lignin-related chemical groups (region 1604–1590 cm^{-1}—benzene ring stretching, skeletal vibrations, and C=O stretch; 1510 cm^{-1}—benzene ring stretching and skeletal vibrations; 1464 cm^{-1}—C–H skeletal plane deformations; 1422 cm^{-1}—benzene skeletal vibrations and C–H deformations; 1267 cm^{-1} and 1222 cm^{-1}—C–O vibrations in guaiacyl rings; 1140 cm^{-1}—C–H deformations in guaiacyl; 1034 cm^{-1}—C–O of primary alcohol, guaiacyl C–H; and 857 cm^{-1}—C–H out-of-plane in guaiacyl units). In contrast, the peaks typical of carbohydrates are characteristic of waterlogged Scots pine HW (region between 1383 and 1368 cm^{-1}—deformations of C–H bonds, 1315 cm^{-1}—deformations of CH_2, 1162 cm^{-1}—C–O–C asymmetric vibration, 1107 cm^{-1}—glucose ring stretch, 1058 cm^{-1}, 1033 cm^{-1}—C–O stretch, and 901 cm^{-1}—glucose ring stretch and C–H deformation).

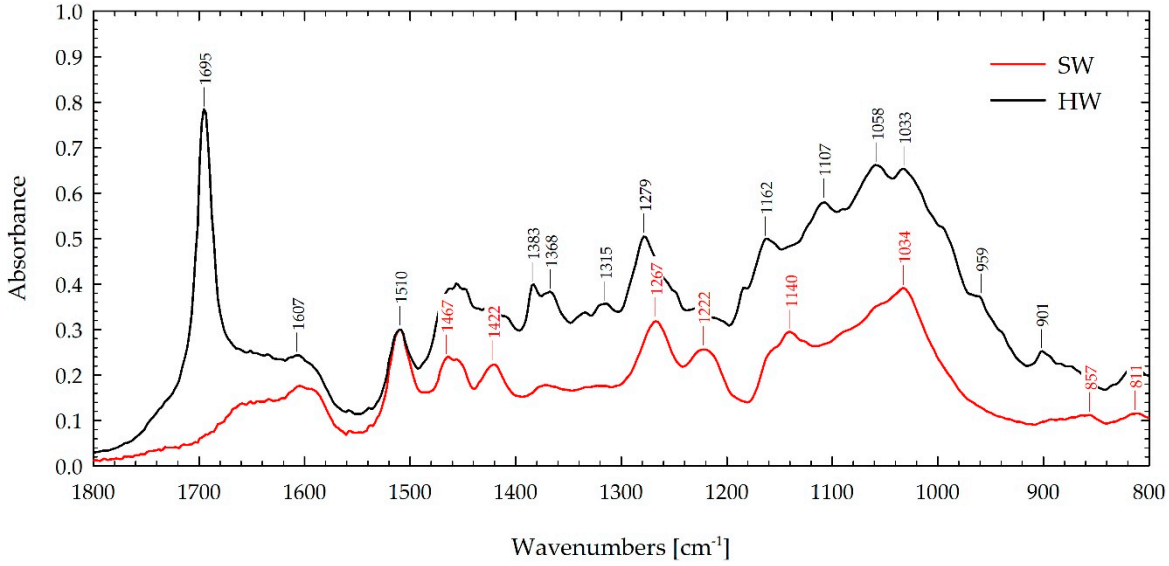


Figure 3. FTIR spectra of sapwood (SW) and heartwood (HW) waterlogged Scots pine wood corrected and normalized at a wavelength of 1510 cm^{-1}.

The calculated LOI index was higher for HW than for SW. The LOI values for HW and SW were 0.77 and 0.56, respectively. The TCI index was higher for HW and amounted to 1.76 compared to 1.30 for SW.

A clear representation of lignin-related peaks in SW samples indicated the advanced degradation of carbohydrate compounds. The spectrum of the HW sample contained more cellulose peaks, which indicated that HW is less degraded than SW. The spectra of waterlogged Scots pine wood lacked a peak in the 1731 cm^{-1} region associated with the C=O (acetyl) in xylans, resulting from early biodegradation of hemicelluloses. On the other hand, the visible, very strong, narrow peak with a maximum at 1695 cm^{-1} in the HW of recovered wood was characteristic for carboxylic groups of resin acids [29]. Additionally, the occurrence of peaks associated with deformation vibrations at 1279 cm^{-1} (O–H) and 959 cm^{-1} (C–H) in the HW spectrum indicated the presence of diterpenoids in the resin—abietanes and pimmaranes and the products of their isomeration and ageing [30,31]. The FTIR analysis of untreated wood corresponded well with the results of previous chemical analysis [16].

3.2. Equilibrium Moisture Content and Dimensional Stability

The two-factor ANOVA of highly-degraded waterlogged Scots pine sapwood (SW) (Table 1) indicated the statistically significant effect of impregnation on all investigated parameters, i.e., *EMC* as well as S_T and S_R ($p < 0.05$). Additionally, the drying schedule influenced the *EMC* and S_T ($p < 0.05$). There was also a statistically-significant interaction between impregnation and drying schedule (a × b) for sapwood *EMC*, S_T and S_R.

Table 1. Two-factor ANOVA tables for equilibrium moisture content (*EMC*) for RH = 44%, tangential (S_T) and radial shrinkage (S_R) of waterlogged Scots pine sapwood (SW) taking into account impregnation and drying schedule.

	Effect	SS	df	MS	F Value	*p*-Value
EMC	Intercept	368.56	1	368.56	19,775.1	0.0000
	Impregnation (a)	60.411	2	30.206	1620.69	0.0000
	Drying schedule (b)	4.8330	1	4.8330	259.32	0.0000
	a × b	2.7852	2	1.3926	74.721	0.0000
	Error	0.3355	18	0.0186		
S_T	Intercept	223.99	1	223.99	1136.04	0.0000
	Impregnation (a)	40.683	2	20.341	103.17	0.0000
	Drying schedule (b)	3.9204	1	3.9204	19.883	0.0003
	a × b	21.138	2	10.569	53.604	0.0000
	Error	3.5490	18	0.1972		
S_R	Intercept	6.1712	1	6.1712	830.98	0.0000
	Impregnation (a)	5.3935	2	2.6968	363.13	0.0000
	Drying schedule (b)	0.0084	1	0.0084	1.1362	0.3006
	a × b	0.5021	2	0.2510	33.803	0.0000
	Error	0.1337	18	0.0074		

SS—a sum of squares, df—degrees of freedom, MS—mean squares, F—Fisher's F-test, *p*—probability value.

The two-factor ANOVA of slightly-degraded waterlogged Scots pine heartwood (HW) (Table 2) indicated statistically-significant effects of impregnation on *EMC*, S_T, and S_R ($p < 0.05$). Moreover, the results of ANOVA indicated a statistically-significant effect of drying schedule only on *EMC* of HW. With regard to *EMC* of HW, a statistically-significant interaction between impregnation and drying schedule (a × b) was also found.

Table 2. Two-factor ANOVA tables for equilibrium moisture content (*EMC*) for RH = 44%, tangential (S_T), and radial shrinkage (S_R) of waterlogged Scots pine heartwood (HW) taking into account impregnation and drying schedule.

	Effect	SS	df	MS	F Value	*p*-Value
EMC	Intercept	377.39	1	377.39	3981.0	0.00000
	Impregnation (a)	14.200	2	7.1000	74.895	0.00000
	Drying schedule (b)	2.9190	1	2.9190	30.792	0.00003
	a × b	1.1323	2	0.5661	5.9720	0.01025
	Error	1.7064	18	0.0948		
S_T	Intercept	234.44	1	234.44	6292.5	0.0000
	Impregnation (a)	105.78	2	52.890	1419.6	0.0000
	Drying schedule (b)	0.1218	1	0.1218	3.2702	0.0873
	a × b	0.0133	2	0.0067	0.1785	0.8380
	Error	0.6706	18	0.0373		
S_R	Intercept	25.979	1	25.979	1334.8	0.0000
	Impregnation (a)	23.286	2	11.643	598.23	0.0000
	Drying schedule (b)	0.0165	1	0.0165	0.8497	0.3688
	a × b	0.0556	2	0.0278	1.4277	0.2657
	Error	0.3503	18	0.0195		

SS—a sum of squares, df—degrees of freedom, MS—mean squares, F—Fisher's F-test, *p*—probability value.

Mean values of *EMC*, S_T, and S_R of untreated and PEG-treated SW and HW of waterlogged Scots pine, dried according to single and multi-stage schedules, were significantly lower for samples treated with either PEG solution, i.e., 400/4000 mixture or 2000, than untreated wood samples (Table 3). This means that impregnation with PEG solutions had positive conservation effects, because waterlogged wood samples were more dimensionally stable. However, there were differences between SW and HW. Results of post-hoc Tukey analysis indicated that, in the case of SW, the mean values of *EMC*, S_T, and S_R were significantly dependent ($p < 0.05$) on the PEG solution used. This means that in the case

of highly-degraded SW, the preservation effect depended on the molecular weight of the preservative. In comparison, molecular weights of the preservative PEG solution did not significantly affect the properties of HW.

Table 3. Equilibrium moisture content (*EMC*) for RH = 44% and tangential (S_T) and radial shrinkage (S_R) of untreated (control) and PEG-treated waterlogged Scots pine sapwood (SW) and heartwood (HW) taking into account the drying approach after impregnation.

Wood Samples	Treatment Options	Multi-Stage Drying Schedule			Single-Stage Drying Schedule		
		EMC (%)	S_T (%)	S_R (%)	*EMC* (%)	S_T (%)	S_R (%)
Sapwood (SW)	Untreated (control)	7.1 ± 0.2^{c}	5.3 ± 0.3^{c}	1.3 ± 0.1^{c}	5.2 ± 0.2^{c}	4.5 ± 0.5^{b}	1.1 ± 0.1^{c}
	PEG 400/4000	3.4 ± 0.1^{b}	0.5 ± 0.1^{a}	-0.1 ± 0.1^{b}	2.9 ± 0.1^{b}	3.9 ± 0.8^{b}	0.4 ± 0.1^{b}
	PEG 2000	2.7 ± 0.1^{a}	2.2 ± 0.4^{b}	0.2 ± 0.1^{a}	2.3 ± 0.1^{a}	1.9 ± 0.2^{a}	0.1 ± 0.1^{a}
Heartwood (HW)	Untreated (control)	5.7 ± 0.5^{b}	6.2 ± 0.3^{b}	2.4 ± 0.2^{b}	4.4 ± 0.4^{b}	6.0 ± 0.2^{b}	2.5 ± 0.1^{b}
	PEG 400/4000	3.5 ± 0.2^{a}	1.6 ± 0.1^{a}	0.3 ± 0.1^{a}	3.3 ± 0.2^{a}	1.5 ± 0.2^{a}	0.3 ± 0.2^{a}
	PEG 2000	3.7 ± 0.2^{a}	1.8 ± 0.1^{a}	0.5 ± 0.1^{a}	3.2 ± 0.2^{a}	1.6 ± 0.1^{a}	0.3 ± 0.2^{a}

Mean value ($n = 4$) ± standard deviation; identical superscripts (^{a,b,c}) denote no significant difference ($p < 0.05$) between mean values according to post-hoc Tukey's HSD test.

Figures 3 and 4 compare *EMC*, S_T, and S_R of SW and HW from waterlogged Scots pine wood, respectively, dried using a multi-stage versus a single-stage schedule. In all samples, drying schedule affected *EMC*. Moreover, the value of *EMC* was always lower for both highly- and slightly-degraded SW and HW wood when dried using a single-stage schedule. In the case of untreated (control) samples the difference between *EMC* for the two drying schedules was much higher than in PEG-treated samples. The shrinkage of waterlogged Scots pine SW and HW in tangential (S_T) and radial directions (S_R) were different (Figures 4 and 5). In most cases SW dried according to different schedules, the mean shrinkage differed significantly ($p < 0.05$), indicating the importance of drying schedule to SW wood conservation. In comparison, S_T and S_R of HW in most cases did not differ significantly, indicating that HW can be dried using a single- or multi-stage drying schedule with similar results.

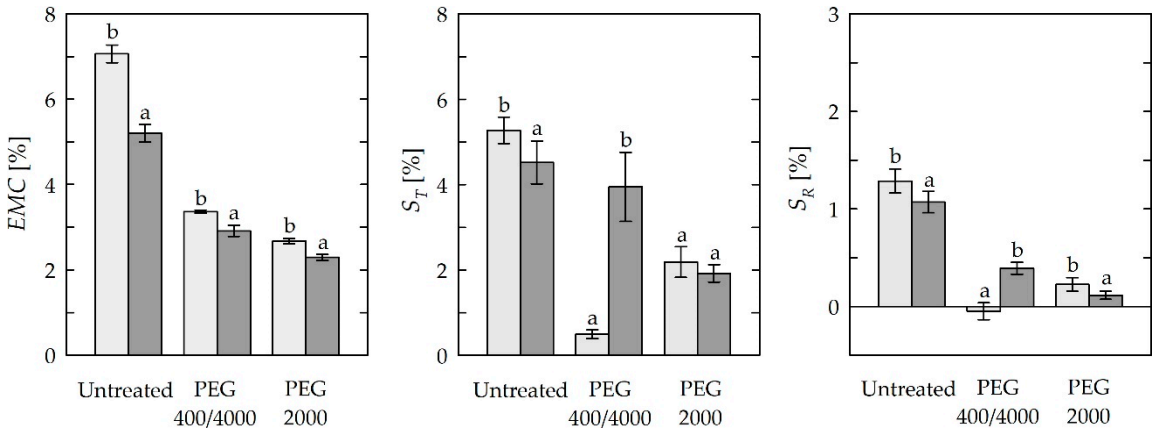


Figure 4. Comparison of the mean value of equilibrium moisture content (*EMC*) for RH = 44%, tangential (S_T), and radial shrinkage (S_R) of untreated and PEG-treated waterlogged Scots pine sapwood (SW) dried according to different approaches (gray and dark gray bar—multi-stage and single-stage (alternative) drying schedule, respectively; error bars denote ± standard deviation; identical superscripts (a, b) denote no significant difference ($p < 0.05$) between mean values according to post-hoc Tukey's HSD test).

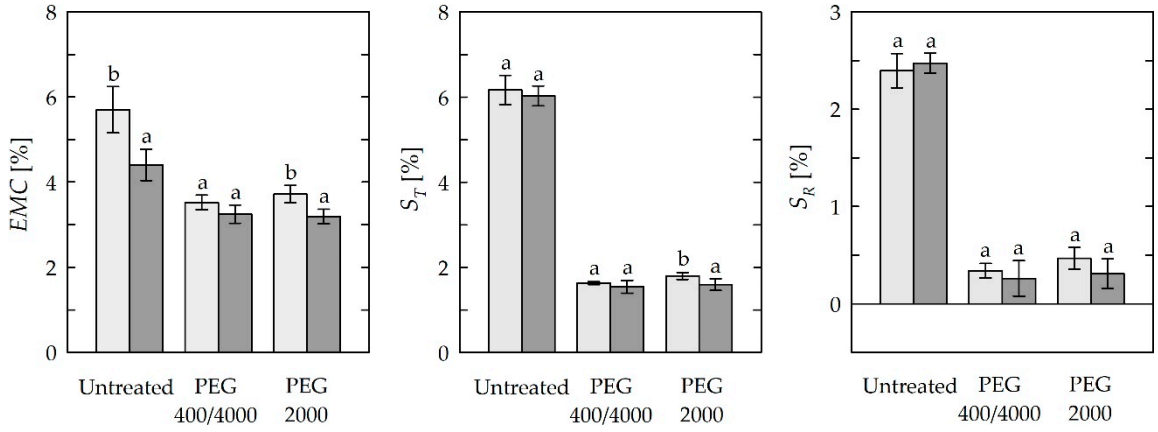


Figure 5. Comparison of the mean value of equilibrium moisture content (*EMC*) for RH = 44%, tangential (S_T), and radial shrinkage (S_R) of untreated and PEG-treated waterlogged Scots pine heartwood (HW) dried according to different approaches (gray and dark gray bar—multi-stage and single-stage (alternative) drying schedule, respectively; error bars denote ± standard deviation; identical superscripts (a, b) denote no significant difference ($p < 0.05$) between mean values according to post-hoc Tukey's HSD test).

Figure 6 show the *ASE* coefficient for SW and HW, respectively. These results confirm the influence of drying schedule on the conservation of highly-degraded SW impregnated with PEG 400/4000. Both ASE_T and ASE_R were higher after multi-stage drying, indicating its superiority for tissue conservation. In contrast, for samples impregnated with PEG 2000 solution, *ASE* values were comparable, which means that the drying approach had no effect. In the case of slightly-degraded HW, the effects of conservation as shown by *ASE* values were comparable, regardless of PEG solution and drying method.

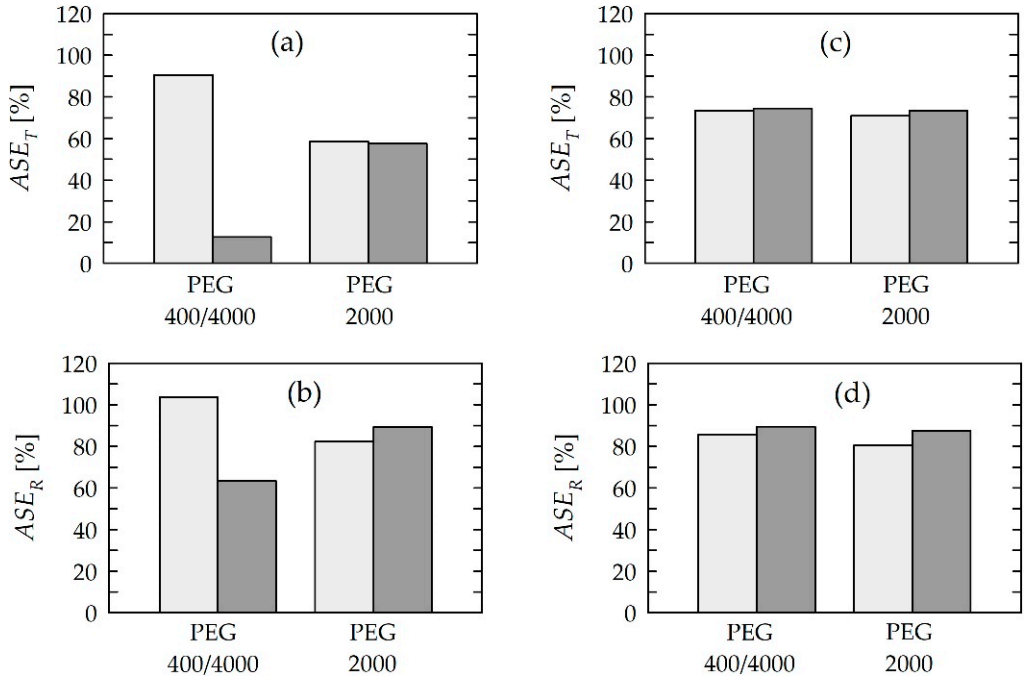


Figure 6. Anti-shrink efficiency (*ASE*) in tangential (T) and radial (R) direction of waterlogged Scots pine wood impregnated with PEG 400/4000 and PEG 2000 solution. (**a**,**b**) sapwood (SW) and (**c**,**d**) heartwood (HW). Light gray bar, air drying according to multi-stage schedule; dark gray bar, air-drying according to single-stage (alternative) schedule.

4. Discussion

Results of FTIR analysis confirmed the decomposition of hydrophilic chemical components of SW and HW in waterlogged Scots pine wood. In the case of slightly-degraded HW, the absorption of infrared radiation was higher for chemical groups related to hemicellulose and cellulose. The high content of hydrophobic diterpenoids could have a beneficial effect on reducing the hygroscopicity of slightly-degraded HW. On the other hand, in the case of highly-degraded SW, stronger signals associated with lignin, which has the lowest hygroscopicity among hydrophilic chemical components of wood [23], were observed in the FTIR spectrum. Meanwhile, comparison of *EMC* results indicated that highly-degraded SW tissue is more hygroscopic than slightly-degraded HW (see Table 3). High *EMC* values of highly-degraded waterlogged wood were also observed in earlier studies [32–34]. The results of X-ray diffraction measurements indicated that increased hygroscopicity is a result of the lowering the degree of crystallinity of cellulose and disorganization of cellulose crystallites. Similar conclusions were formulated based on the results of deuterium-exchange measurements on the availability of hydroxyl groups in excavated wood with different degrees of degradation [35]. This hypothesis is also confirmed by the calculated lateral order index and total crystallinity index, which for the tested samples were higher for HW than for SW.

Statistical analysis of the present results confirms that the method of drying immediately after waterlogged wood impregnation treatment may, under certain conditions, improve conservation, i.e., decrease hygroscopicity and increase dimensional stability. The conservation of highly-degraded sapwood of waterlogged Scots pine wood using two-stage impregnation with PEG 400/4000 mixture and then air-drying according to a multi-stage schedule (reference/standard approach), should provide acceptable results. The low value of equilibrium humidity and *ASE* values above 90 and 100% in tangential and radial anatomical directions, respectively, as confirmed in the case described above, indicate limited hygroscopicity and high dimensional stability of the conserved wood. On the other hand, a much poorer conservation effect of highly-degraded SW was observed when using impregnation with PEG 400/4000 mixture and air-drying according to the single-stage schedule (alternative drying approach). In this case, lower *ASE* values were found for both anatomical directions. While the radial *ASE* value (63.4%) was only slightly lower than the value considered acceptable for dimensional stability for archaeological wood conservation (75%) [36], the decrease of tangential *ASE* to 12.7% was dramatically high. For this reason, the use of PEG 400/4000 followed by single-stage drying should not be considered for the conservation of highly-degraded archaeological wood.

The dependence of conservation of highly-degraded archaeological wood on the method of drying may be the result of different concentrations of PEG mixtures in the cellular lumen and cell wall. According to [37], when wood is drying after impregnation, the PEG concentration in the cellular lumen increases as a result of water evaporation, which leads to the formation of a concentration gradient of PEG in the cellular lumen and cell wall. This phenomenon occurs at different speeds depending on the size of the PEG particle. The penetration of PEG with a molecular weight of more than 3000 is limited due to the anatomical characteristic of the cell wall [38]. Slower moisture loss during multi-stage air-drying results in prolonged diffusion time. Subsequently, most of the PEG used has the ability to diffuse into the cell wall during the conservation process. The impregnate introduced into the cell wall of waterlogged wood, replacing water, keeps the wood tissue swollen and reduces shrinkage. The drying schedules evaluated in this study differed significantly in their duration. The duration of air-drying in the single-stage schedule to equilibrate the sample to air RH of 44% took about 25% of the drying time of the multi-stage schedule. The use of PEG solutions of different molecular weights used in this study allowed additional conservation effects to be elucidated. For example, in the case of highly-degraded SW, the course of diffusion of PEG during the long-term (42 weeks) multi-stage drying process ensured the effective filling of free spaces in the cell walls by low molecular weight polyethylene glycol (PEG 400).

In the case of more intensive single-stage drying, the diffusion time from the cellular lumen to the cell wall of low molecular weight polyethylene glycol with PEG 400/4000 mixture was over four

times shorter (10 weeks). Moisture loss from the sample that was faster than the PEG diffusion rate may have caused rapid dehydration of the cell wall; greater shrinkage could result from limiting the opportunity for PEG diffusion. In a situation where PEG 4000 molecules are too large to penetrate the cell wall, the resulting osmotic pressure may lead to collapse within the wall, causing contraction during drainage of the sample [11].

The beneficial effect of the alternative drying approach used in this study on the dimensional stability of highly-degraded SW of waterlogged Scots pine wood was evident when the conservation schedule included impregnation with PEG 2000 solution followed by air-drying using the single-stage schedule. The lower *EMC* confirmed the results of previous findings on the advantages of using the less hygroscopic PEG 2000 solution for the conservation of irregularly-degraded waterlogged wood [16]. In addition, a significant increase in dimensional stability of highly degraded SW in both anatomical directions resulted from conservation using the schedule described. ASE_T values increased almost five times (from 12.7 to 57.5%), while the value of ASE_R indicated high dimensional stability (i.e., 89.2%).

In the case of impregnation with PEG 2000, the shorter drying time (faster moisture loss) did not limit the diffusion of the impregnate in the wood structure, because its concentration was four times higher than that of low molecular weight polyethylene glycol in the PEG 400/4000 mixture. In addition, when using PEG 2000 for wood impregnation, there is no impediment caused by the presence of larger molecules, as is the case of wood impregnation with a mixture of PEG 400/4000.

In the case of slightly-degraded HW, statistical analysis did not indicate differences in wood conservation with different drying approaches. This can be explained by the fact that due to the good state of conservation of HW, as well the presence of a large amount of extractable substances in the HW, there was seven times less uptake of PEG compared to highly-degraded SW. Taking into account the significantly-shorter time of single-stage drying compared to multi-stage drying and the possibility of achieving equally-satisfactory conservation effects, as measured by the reduction of hygroscopicity and high dimensional stability, it can be concluded that single-stage drying can be used with highly-degraded waterlogged wood as an alternative to long-term multi-stage drying. However, to obtain satisfactory wood conservation, it is important that the correct concentration and molecular weight of PEG be identified.

5. Conclusions

The effects of conservation of waterlogged Scots pine wood, i.e., decreasing hygroscopicity and increasing dimensional stability, is significantly dependent on the drying approach after PEG impregnation, but only in the case of highly-degraded sapwood.

The results indicate the possibility of shortening the time to conserve waterlogged wood. Air-drying highly-degraded Scots pine sapwood using a single-stage schedule results in a much shorter air-drying time than the multi-stage schedule. However, the use of PEG solution with a molecular weight permitting free diffusion through the cell wall is needed to obtain satisfactory conservation, by reducing hygroscopicity and increasing dimensional stability of the wood.

A conservation scenario that uses two-stage impregnation with a mixture of low and high molecular weight polyethylene glycol (PEG 400/4000), followed by single-stage drying to final moisture content, was unsuitable for conservation of highly-degraded sapwood from waterlogged Scots pine, due to the large shrinkage of samples perpendicular to the wood grain.

Because slightly-degraded heartwood of Scots pine achieves satisfactory dimensional stability regardless of drying method, the use of single-stage drying immediately after PEG impregnation may be beneficial for shortening the time and lowering the cost of wood conservation.

Author Contributions: Conceptualization. M.F., J.M., and M.Z.; methodology and investigation. M.F. and J.M.; writing—original draft preparation. M.F., J.M., and M.Z.; writing—review and editing. J.M.; preparing tables and figures, J.M.; performing statistical analysis, J.M.; All authors have read and agreed to the published version of the manuscript.

Funding: The article was financed within the Ministry of Science and Higher Education Program—"Regional Initiative Excellence" 2019–2022, project No. 005/RID/2018/19.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Schweingruber, F.H. *Tree Rings—Basics and Applications of Dendrochronology*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1988; ISBN 978-0-7923-0559-0. [CrossRef]
2. Ważny, J. The present classification of wood degradation factors. *Folia For. Pol. Ser. B* **1993**, *24*, 13–22.
3. Rowell, R.M.; Barbour, R.J. *Archaeological Wood: Properties, Chemistry, and Preservation*; American Chemical Society: Washington, DC, USA, 1989; Volume 225, ISBN 0-8412-1623-1.
4. Blanchette, R.A. A review of microbial deterioration found in archaeological wood from different environments. *Int. Biodeterior. Biodegrad.* **2000**, *46*, 189–204. [CrossRef]
5. Grattan, D.W.; McCawley, J.C.; Cook, C. The potential of the Canadian winter climate for the freeze-drying of degraded waterlogged wood: Part II. *Stud. Conserv.* **1980**, *25*, 118–136. [CrossRef]
6. Hoffmann, P. *Conservation of Archeological Ships and Boats*; Archetype Publications Ltd.: London, UK, 2013; ISBN 9781904982821.
7. Håfors, B. Conservation of the Wood of the Swedish Warship Vasa of A.D. 1628: Evaluation of Polyethylene Glycol Conservation Programmes. In *Göteborg Studies in Conservation*; University of Gothenburg, Acta Universitatis Gothoburgensis: Göteborg, Sweden, 2010; ISBN 978-91-7346-687-5.
8. Interactive HTML5 Flipping Book Publishing Platform; Your Universally Applicable Polymer, Clariant 2007. Available online: https://anyflip.com/rwuf/fuly (accessed on 25 November 2020).
9. Hoffmann, P. On the Stabilization of Waterlogged Oakwood with Polyethylene Glycol (PEG). *Holzforschung* **1988**, *42*, 289–294. [CrossRef]
10. Schnell, U.; Jensen, P. Determination of Maximum Freeze Drying Temperature for PEG-Impregnated Archaeological Wood. *Stud. Conserv.* **2014**, *52*, 50–58. [CrossRef]
11. Grattan, D.W.; Clarke, R.W. Conservation of waterlogged wood. In *Conservation of Marine Archaeological Objects*; Pearson, C., Ed.; Butterworth & Co. Ltd.: London, UK, 1987; pp. 164–206. ISBN 0-408-10668-9.
12. Jensen, P.; Gregory, D.J. Selected physical parameters to characterize the state of preservation of waterlogged archaeological wood: A practical guide for their determination. *J. Archaeol. Sci.* **2006**, *33*, 551–559. [CrossRef]
13. Giachi, G.; Capretti, C.; Donato, I.D.; Macchioni, N.; Pizzo, B. New trials in the consolidation of waterlogged archaeological wood with different acetone-carried products. *J. Archaeol. Sci.* **2011**, *38*, 2957–2967. [CrossRef]
14. De Jong, J.; Eenkhoorn, W.; Wevers, A.J.M. Controlled Drying as an Approach to the Conservation of Shipwrecks. In Proceedings of the 6th Triennial Meeting ICOM Committee for Conservation, Ottawa, ON, Canada, 21–25 September 1981; pp. 1–10.
15. Welling, J.; Schwarz, T.; Bauch, J. Biological, chemical and technological characteristics of waterlogged archaeological piles (Quercus petraea (Matt.) Liebl.) of a medieval bridge foundation in Bavaria. *Eur. J. Wood Wood Prod.* **2018**, *76*, 1173–1186. [CrossRef]
16. Majka, J.; Zborowska, M.; Fejfer, M.; Waliszewska, B.; Olek, W. Dimensional stability and hygroscopic properties of PEG treated irregularly degraded waterlogged Scots pine wood. *J. Cult. Herit.* **2018**, *31*, 133–140. [CrossRef]
17. Jensen, P.; Hjelm Petersen, A.; Strætkvern, K. From the Skuldelev to the Roskilde ships—50 years of shipwreck conservation at the national museum of Denmark. In *Shipwrecks 2011, Proceedings of the Chemistry and Preservation of Waterlogged Wooden Shipwrecks, Stokholm, Sweden, 18–21 October 2011*; Ek, M., Ed.; Vasa Museum: Stokholm, Sweden, 2011; pp. 14–20.
18. Schmidt-Reimann, P.; Reuter, T. Conservation and 3D-documentation of waterlogged wood from medieval mining. *Condition* **2015**, 125.
19. Majka, J.; Czajkowski, Ł.; Olek, W. Effects of Cyclic Changes in Relative Humidity on the Sorption Hysteresis of Thermally Modified Spruce Wood. *BioResources* **2016**, *11*. [CrossRef]
20. Nelson, M.L.; O'Connor, R.T. Relation of certain infrared bands to cellulose crystallinity and crystal lattice type. Part II. A new infrared ratio for estimation of crystallinity in celluloses I and II. *J. Appl. Polym. Sci.* **1964**, *8*, 1325–1341. [CrossRef]

21. Kollmann, F.F.; Côté, W.A. *Principles of Wood Science and Technology. I Solid Wood*; Springer: Berlin/Heidelberg, Germany, 1968; ISBN 978-3-642-87930-2.
22. Skaar, C. *Wood-Water Relations*; Springer: Berlin, Germany; New York, NY, USA, 1988; ISBN 0-387-19258-1.
23. Rowell, R.M. Moisture properties. In *Handbook of Wood Chemistry and Wood Composites*, 2nd ed.; Rowell, R.M., Ed.; CRC Press: Boca Raton, FL, USA, 2012; pp. 75–98. ISBN 9781439853818.
24. Faix, O. Classification of Lignins from Different Botanical Origins by FT-IR Spectroscopy. *Holzforschung* **1991**, *45*, 21–28. [CrossRef]
25. Gelbrich, J.; Mai, C.; Militz, H. Chemical changes in wood degraded by bacteria. *Int. Biodeterior. Biodegrad.* **2008**, *61*, 24–32. [CrossRef]
26. Huang, Y.; Wang, L.; Chao, Y.; Nawawi, D.S.; Akiyama, T.; Yokoyama, T.; Matsumoto, Y. Analysis of lignin aromatic structure in wood based on the IR spectrum. *J. Wood Chem. Technol.* **2012**, *32*, 294–303. [CrossRef]
27. Pandey, K.K. A Study of Chemical Structure of Soft and Hardwood and Wood Polymers by FTIR Spectroscopy. *J. Appl. Polym. Sci.* **1999**, *71*, 1969–1975. [CrossRef]
28. Pizzo, B.; Pecoraro, E.; Macchioni, N. A new method to quantitatively evaluate the chemical composition of waterlogged wood by means of attenuated total reflectance Fourier transform infrared (ATR FT-IR) measurements carried out on wet material. *Appl. Spectrosc.* **2013**, *67*, 553–562. [CrossRef]
29. Nuopponen, M.; Vuorinen, T.; Jämsä, S.; Viitaniemi, P. The effects of a heat treatment on the behaviour of extractives in softwood studied by FTIR spectroscopic methods. *Wood Sci. Technol.* **2003**, *37*, 109–115. [CrossRef]
30. Beltran, V.; Salvadó, N.; Butí, S.; Pradell, T. Ageing of resin from Pinus species assessed by infrared spectroscopy. *Anal. Bioanal. Chem.* **2016**, *408*, 4073–4082. [CrossRef]
31. Font, J.; Salvadó, N.; Butí, S.; Enrich, J. Fourier transform infrared spectroscopy as a suitable technique in the study of the materials used in waterproofing of archaeological amphorae. *Anal. Chim. Acta* **2007**, *598*, 119–127. [CrossRef]
32. Esteban, L.G.; De Palacios, P.; Fernández, F.G.; Guindeo, A.; Conde, M.; Baonza, V. Sorption and thermodynamic properties of juvenile *Pinus sylvestris* L. wood after 103 years of submersion. *Holzforschung* **2008**, *62*, 745–751. [CrossRef]
33. Esteban, L.G.; de Palacios, P.; García Fernández, F.; García-Amorena, I. Effects of burial of Quercus spp. wood aged 5910±250BP on sorption and thermodynamic properties. *Int. Biodeterior. Biodegrad.* **2010**, *64*, 371–377. [CrossRef]
34. García-Iruela, A.; García Esteban, L.; García Fernández, F.; de Palacios, P.; Rodriguez-Navarro, A.B.; Gil Sánchez, L.; Hosseinpourpia, R. Effect of Degradation on Wood Hygroscopicity: The Case of a 400-Year-Old Effect of Degradation on Wood Hygroscopicity: The Case of a 400-Year-Old Coffin. *Forests* **2020**, *11*, 712. [CrossRef]
35. Han, L.; Guo, J.; Wang, K.; Grönquist, P.; Li, R.; Tian, X.; Yin, Y. Hygroscopicity of Waterlogged Archaeological Wood from Xiaobaijiao No.1 Shipwreck Related to Its Deterioration State. *Polymers* **2020**, *12*, 834. [CrossRef] [PubMed]
36. Morgos, A.; Imazu, S. Comparing conservation methods for waterlogged wood using sucrose, mannitol and their mixture. In Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 August 1993; International Council of Museums, Hoffmann, P., Eds.; Dt. Schiffahrtsmuseum: Bremerhaven, Germany, 1994; pp. 287–299.
37. Tanaka, S.; Seki, M.; Miki, T.; Shigematsu, I.; Kanayama, K. Solute diffusion into cell walls in solution-impregnated wood under conditioning process I: Effect of relative humidity on solute diffusivity. *J. Wood Sci.* **2015**, *61*, 543–551. [CrossRef]
38. Tarkow, H.; Feist, W.; Southerland, C. Interaction of wood with polymeric materials. Penetration versus molecular size. *Prod. J.* **1966**, *16*, 61–65.

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).