

Monitoring Technology during the Consolidation of Waterlogged wood Cultural Relics

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ABSTRACT

Waterlogged wood cultural relics often need consolidation before drying to prevent shrinkage and cracking of the object. Polyethylene glycol (PEG), as one of the commonly used consolidating agents, is widely used in archaeological wood consolidation. The moderately degraded archaeological wood samples from the Nanhai No.1 shipwreck, were treated with PEG solution in equipment with the simultaneous incorporation of consolidant spray and immersion. In order to monitor the effect of consolidation, this study analysed the morphological structure, chemical structure, water states, and water content of untreated and PEG-treated archaeological wood. Herein, non-destructive methods involved an ultra-depth-of-field three-dimensional video microscope, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), and low-field nuclear magnetic resonance (LF-NMR). Results showed that the band at 3400 cm^{-1} reduced notably after PEG spray and immersion and the content of free water utilizing LF-NMR analysis was related to the amount of PEG impregnation. These values had the potential to monitor and assess the consolidation of waterlogged wood cultural relics, which suggested the PEG 2000 solution is better than either immersion or spray treatment, while the PEG 4000 solution is more suitable for immersion treatment. During the conservation process, the consolidation condition can be preliminarily assessed by using non-destructive testing methods, which helps to adjust the protection method in time.

Keywords: waterlogged archaeological wood, spray, immersion, PEG

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INTRODUCTION

In recent years, ancient shipwrecks such as the Nanhai No.1 shipwreck and Changjiangkou No.2 shipwreck have been salvaged one after another. Waterlogged archaeological wood will degrade to different degrees in a burial environment, resulting in increased pores in the wood tissue and decreased mechanical strength (Broda and Hill 2021; Huang et al. 2019). After excavation, dehydration is necessary for the preservation of waterlogged archaeological wood because the presence of water will accelerate the deterioration of the wood and affect its dimensional stability. In this process, waterlogged archaeological wood from different preservation conditions is prone to shrinkage deformation, warping and cracking, and even collapse and damage. Thus, consolidants have been developed to avoid shrinkage deformation of wood relics, such as polyethylene glycol (PEG), polyethylene glycols, grease, polymeric reagents, halloysite nanotubes, natural compounds, and sugars (Han et al. 2022; Lisuzzo et al. 2020; Broda 2020; Walsh-Korb and Avérous 2019). PEG, due to being cheap, nontoxic, easy-to-use, and with relatively better dimensional stability enhancement than some other options, has been widely used in the cases of the *Vasa*, *Mary Rose*, *Batavia* and *Bremen Cog* and as consolidant for countless other waterlogged wood relics (Sandström et al. 2005; Hocker, Almkvist, and Sahlstedt 2012; Hoffmann et al. 2004).

There are two main ways to conserve waterlogged shipwrecks, one is to disassemble and soak wood items individually, and the other is to protect the shipwreck as a whole. Disassembly immersion is the

most widely used protection method at present. However, the conservation of a complete shipwreck without disassembly can avoid damaging the hull structure and reduce the damage to individual artefacts during protection or reassembly. In China, ancient wood shipwrecks usually are excavated archaeologically with artefacts recovered item by item. In 2007, the Nanhai No.1 shipwreck was recovered as a whole (Yongjie 2008), it is the preferred choice to undertake conservation without disassembly for display. While smaller shipwrecks can potentially be protected by immersion, for larger shipwrecks it is difficult to adopt the same method. For larger shipwrecks such as *Vasa* and *Mary Rose*, spray protection was chosen. To adjust the conservation treatment for optimal outcomes, methods need to be used to monitor the effects of consolidation during the conservation of archaeological wood.

Wood is a kind of natural hygroscopic material, and its environmental regulation ability, dimensional stability, and physical and mechanical properties are closely related to the water in wood cells. During the consolidation and dehydration processes, the research of chemical structure and water states is of great significance to elucidate the physical and mechanical properties of archaeological wood and guide the processing and utilization of wood products. Fourier transform infrared spectroscopy (FTIR) with attenuated total reflection mode (ATR) is frequently used to assess the condition of wood decay and evaluate PEG amount in consolidated waterlogged archaeological wood due to its speediness and sensitivity, it is also non-destructive. The lateral relaxation characteristics of water in the wood drying process were investigated based on the low-field nuclear magnetic resonance (LF-NMR) technique, for the purpose of explaining the change mechanism of the water states in archaeological wood dehydration and to provide a theoretical basis and data support for wood drying and water treatment. The study of the transverse relaxation of water in wood by LF-NMR provides a new idea for studying the interaction between wood and water. There were three water states in wood, namely free water, adsorbed water, and capillary water (Ma et al. 2017). As the water in waterlogged archaeological wood is replaced by consolidating agents, the water states in archaeological wood vary.

In summary, it is necessary to monitor the structure and performance of archaeological wood in the consolidation process, to evaluate the efficacy of consolidation. In this study, samples from Nanhai No.1 shipwreck were sprayed and immersed using an aqueous PEG 2000 and PEG 4000 solution, and then the morphological structure, chemical structure, water states, and water content were tested and analysed, to propose a pathway for the evaluation of consolidation effect of wood cultural relics.

CASE STUDIES

The case studies under consideration are determining the indicators to monitor and evaluate the effect of consolidation by data analysis, including the morphological structure, chemical structure, water states, and water content.

RESOURCES

PEG treatment

The resources available to conduct the work include the data on structure and properties collected from waterlogged wood cultural relics of the Nanhai No.1 Shipwreck. In this study, the moderately degraded waterlogged archaeological wood of the same species was selected. Equipment with the simultaneous incorporation of consolidant spray and immersion was designed, as shown in Figure 1. The device guarantees that the archaeological wood was treated with the consolidation solution which had the same viscosity and density. The consecutive dilutions method prepared a series of PEG 2000 and PEG 4000 solutions with increasing concentrations from 30 wt% to 35 wt%. The wood relics were sprayed and immersed using an aqueous PEG 2000 and PEG 4000 solution, respectively.

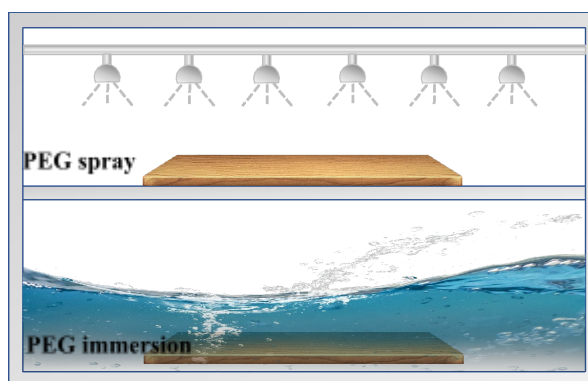


Figure 1 Diagrammatic drawing of PEG 2000 and PEG 4000 spray and immersion on archaeological wood samples.

Ultra-depth-of-field three-dimensional video microscope

The surfaces of untreated and PEG-treated archaeological wood samples were cut by a rotary microtome assisted with a tungsten steel blade. The cross-section pictures of samples were obtained by the ultra-depth-of-field three-dimensional video microscope, VHX-2000 (Keyence Co., Ltd., Japan).

ATR-FTIR spectroscopy analysis

To illustrate the changes in the chemical structure of untreated and PEG-treated archaeological wood, samples were collected by direct transmittance using ATR-FTIR (Perkin Elmer Inc., USA) through 32 scans at a resolution of 4 cm^{-1} ranging from 700 to 4000 cm^{-1} . Each sample was tested with at least 3 replicates. The ATR-FTIR spectra of the samples were baseline corrected.

Water content calculation

All samples' water content was measured using a drying oven under 103°C . An electronic-analytical balance (A&D Co., Ltd., Guangzhou, China) with a precision of 0.001 g was used for the measurement. The mass of samples was recorded before and after drying, and then the water content of untreated and PEG-treated archaeological wood samples was calculated via the following equation.

$$\text{Water content} = \frac{W - W_0}{W_0} \times 100\%$$

where W (g) is the specimen weight before drying, and W_0 (g) is the specimen weight after drying.

LF-NMR analysis

LF-NMR parameters were tested using an NMI20 spectrometer (Niumag Co., Ltd., Suzhou, China). By measuring the archaeological wood of the LF-NMR signal and deconvoluting it, the distribution of transverse relaxation time (T_2) is determined using the Carr-Purcell-Meiboom-Gill decays.

RESULTS

The results reveal that the morphological structure, chemical structure, water content, and water states had the potential for evaluating the consolidation effect of waterlogged archaeological wood.

Morphological structure

The softwood, *Pinus* spp. was predominant in the Nanhai No.1 shipwreck (Li et al. 2022). Tracheids in cross-sections were mostly long-sided, square, and polygonal. Some cell walls had been deformed,

indicating that there was a slight shrinkage of the waterlogged archaeological wood selected in this study, with deterioration likely caused by humidity change. PEG was physically filled into the cell lumens of archeological wood. The morphological structure of archeological wood samples was characterized by an ultra-depth-of-field three-dimensional video microscope. Figure 2 shows the cross-sections of untreated and PEG-treated archeological wood samples in the same magnification. There was a great difference in penetration between spray (PEG 4000s) and immersion treatment (PEG 4000i) using the same concentration of the consolidant solution. For waterlogged wood samples treated with consolidant solution spray, PEG 4000 had only filled in some tracheids. When the archeological wood was soaking in PEG 4000, it was evident that thick PEG 4000 had attached to the tracheid walls of the specimens. Compared with spray treatment, PEG4000 consolidant is penetrated into the wood more easily by immersion treatment. In order to improve the spray filling and reinforcement effect of large-size wood relics, the treatment time should be extended and the number of sprinklers should be increased to ensure the uniformity of spray. Further experiments are needed for the spray-filling reinforcement technology of waterlogged wood relics which have different sizes and shapes, especially for large shipwrecks.

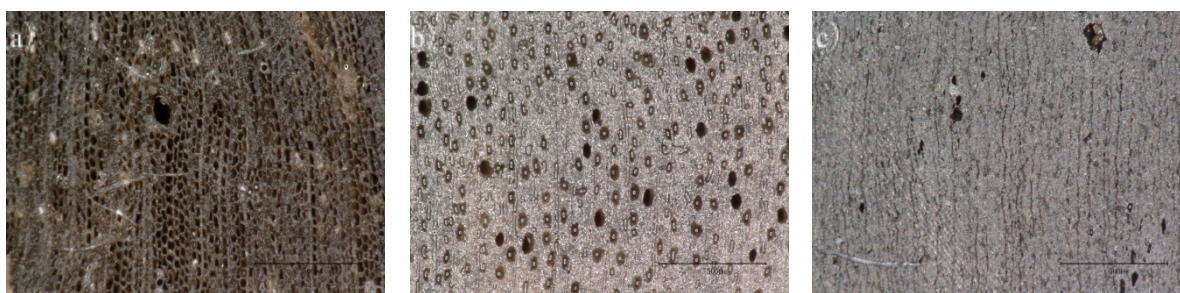


Figure 2 Morphological structure of untreated and PEG-treated archaeological wood samples under an ultra-depth-of-field three-dimensional video microscope. (a) untreated, (b) PEG 4000s, (c) PEG 4000i.

Chemical structure

Figure 3 shows the FTIR spectra of untreated, PEG2000-treated archaeological wood samples through spray (PEG 2000s and PEG 4000s) and immersion (PEG 2000i and PEG 4000i), to assess changes in the chemical structure. In all archaeological wood samples, the ratios between lignin and holocellulose (1374 cm^{-1} and 1158 cm^{-1}) were often selected to determine its preservation status, while this study mainly analysed the influence of PEG treatment (Fejfer et al. 2022). The spectrum of PEG-treated wood samples was different from that of untreated wood samples. The region of $3800\text{ cm}^{-1}\sim 3200\text{ cm}^{-1}$ belongs to the O–H stretching vibration peak, and the free hydroxyl group affects the dimensional stability. After PEG spray and immersion, the band at 3400 cm^{-1} related to the stretching vibration of hydroxyl reduced notably in archaeological wood, contributing to improving the dimensional stability of archaeological wood, which was consistent with previous research results (Liu et al. 2022).

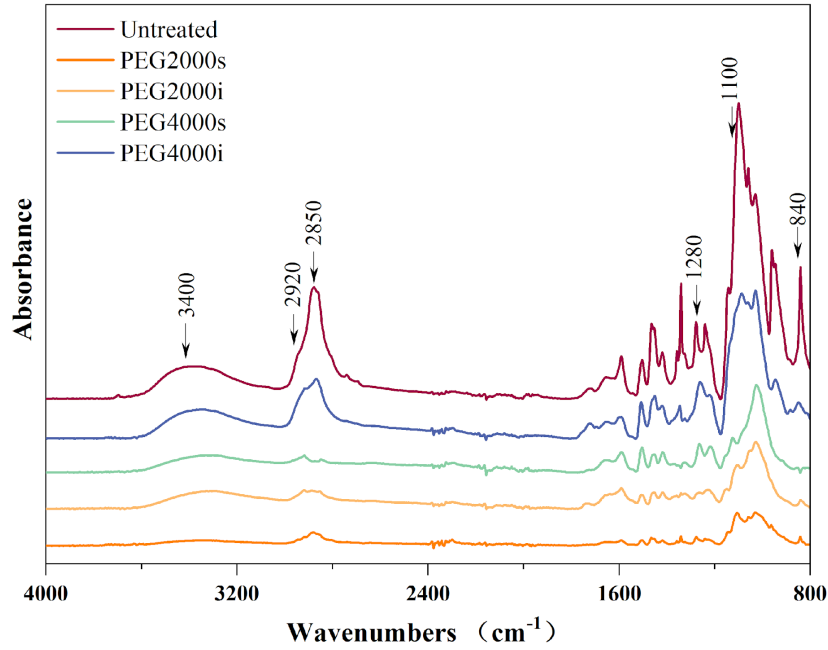


Figure 3 The ATR-FTIR spectra of untreated and PEG-treated archaeological wood samples.

Water states

LF-NMR was performed on the samples to further analyse the water states in the untreated and PEG-treated archaeological wood. Multiple components of water molecules and PEGs in PEG/water mixtures can be quantified, and also the mobility of each component can be characterized through a multiexponential inversion algorithm of the T_2 of PEG/water mixtures (Wu et al. 2012). As shown in Figure 4a, four proton components are found in untreated archaeological wood, assigned to T_{21} , T_{22} , T_{23} , and T_{24} , respectively, which are considered to be the water in and on the cell wall, and the water in the vessel lumens. In addition, the area of the first peak at about 0.1 ms, which accounted for about 0.02%, represents the total amount of adsorbed water. The second and third fractions are capillary water in the wood cell cavity. Free water T_{24} with a relaxation time higher than 100 ms is attributed to flowing water, accounting for about 27.98% of the total signal. The waterlogged wood is similar to modern wood. The closer the binding of water to wood, the shorter the transverse relaxation time. Conversely, the less adsorbed water is, the longer the transverse relaxation time will be (Li and Ma 2021). Thus, the existence and variation of water in wood can be revealed by measuring its lateral relaxation peak.

As to archaeological wood treated by PEG spray or immersion, five transverse relaxation peaks can be seen in Figure 4b to Figure 4e. After PEG treatment, a new fraction at around 1 ms occurs in PEG 2000s, PEG 2000i, PEG 4000s, and PEG 4000i. This is due to PEG filling in the wood tracheids. By calculating the respective relaxation peak area in the decay curves of the relaxation signal, the content of water in different states of archaeological wood can be qualitatively analysed. The adsorbed water content of PEG-treated samples was slightly higher than that of waterlogged archaeological wood because PEG displaced some of the water in the archaeological wood. However, the content of capillary water in the samples is the most dominant, and the second is free water. Compared with the samples treated by spray and immersion, more PEG was filled in the archaeological wood treated by immersion (PEG 2000i and PEG 4000i). To increase the molecular weight of PEG from 2000 to 4000, the capillary water content was decreased while the free water content was increased when using the same treatment, as shown in Figure 4b to Figure 4e. A likely reason for the result lies in the viscosity of the PEG solution. PEG 2000 diffuses into wood voids more easily than PEG 4000. Therefore, it is necessary to improve the impregnation rate of PEG 4000 by increasing the ambient temperature or processing time. The content of bulk content in PEG 4000i achieved the highest value, accounting for

about 70% (Figure 4d). Water content can also confirm the amount of PEG filling (Figure 4f), showing that more water in the wood is replaced by PEG by immersion.

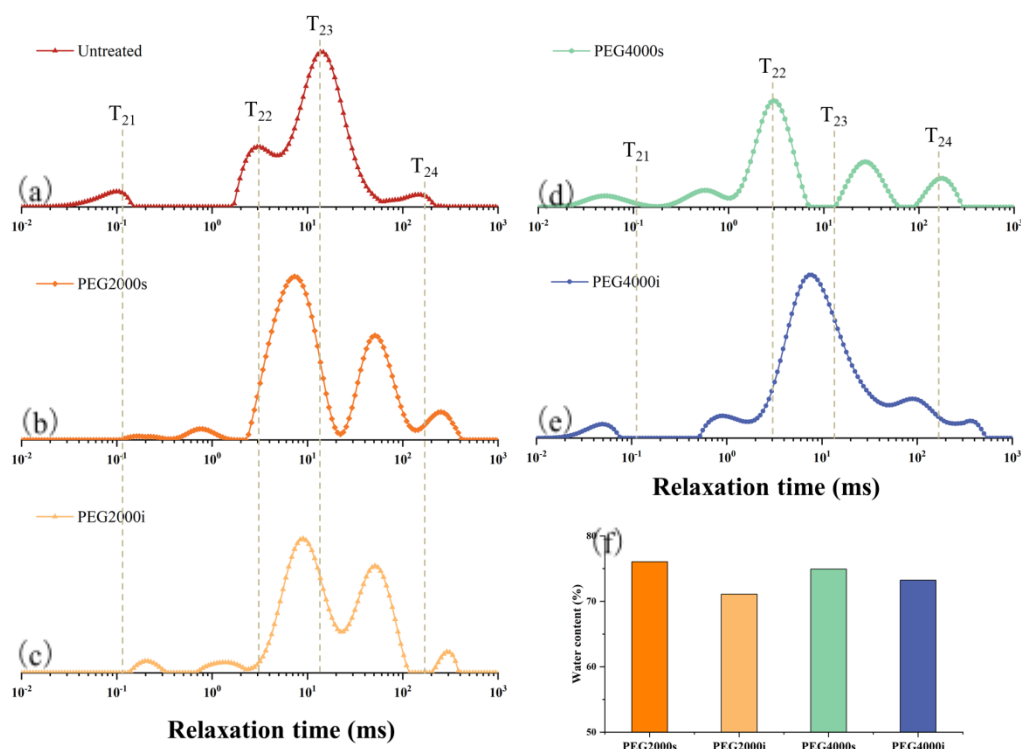


Figure 4 Transverse relaxation time of untreated and PEG-treated archaeological wood samples. (a) untreated, (b) PEG 2000s, (c) PEG 2000i, (d) PEG 4000s, (e) PEG 4000i, (f) Water content.

As filling proceeded, the positions of the relaxation peak for free water shifted right continuously, indicating the average transverse relaxation time for free water was gradually shorter. The PEG 2000 solution is better as either an immersion or spray treatment because of its lower molecular weight and solution viscosity. However, the PEG 4000 solution is more suitable for immersion treatment. This suggests that the filling reinforcement method needs to be selected according to the type of impregnation solution. In addition, LF-NMR, as a nondestructive testing analysis technique, can be used to qualitatively monitor the water state in saturated archaeological wood, especially the transverse relaxation time, T_{24} , which represents the free water in archaeological wood. In addition, the consolidation condition can be assessed by using the above non-destructive testing methods during the conservation process.

CONCLUSION

In this study, sample preparation methods of PEG 2000 and PEG 4000 solution spray and immersion for moderately degraded archaeological wood were explored. According to the results, the relative intensity of the band at 3400 cm^{-1} obtained from ATR-FTIR spectra and the content of free water utilizing LF-NMR analysis had the potential to monitor and assess the consolidation of waterlogged wood cultural relics. The results themselves, suggested PEG 2000 solution is a better consolidant for using either immersion or spray treatment, while the PEG 4000 solution is more suitable for immersion treatment. During the conservation process, the consolidation condition can be assessed by using non-destructive testing methods, i.e., ATR-FTIR and LF-NMR, which helps to adjust the protection method in time.

Acknowledgments

We gratefully acknowledge the assistance of Juan Guo, Xin Gao, and Yang Lu from Chinese Academy of Forestry.

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