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Strengthening and Protecting the Unearthed Wet Outer Coffin Wooden Cultural Relics: A Case of the Tomb of Marquis Yi of Zeng in Hubei, China

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ABSTRACT

Significant variations in climate exist between the northern and southern regions of China, resulting in varying degrees of decay observed in wooden relics unearthed from different areas. The preservation of wooden cultural artifacts in humid environments is influenced by numerous factors including regional environmental conditions (such as temperature, humidity, and biological mold), and site structural characteristics, among others, making the conservation efforts more specialized and intricate. This study utilizes the example of the unearthed wet outer coffin wooden cultural relics from the Tomb of Marquis Yi of Zeng to demonstrate a method involving the use of polyvinyl acetate (PVAc) composite material for the reinforcement and protection of such artifacts. Through a comprehensive analysis of various analytical techniques including scanning electron microscopy, Fourier transform infrared spectroscopy (FT-IR), density increase rate, wood compression strength along the grain, hydrophobic property, and other micro and macro properties, it was determined that: The combination of PVAc and shellac as a reinforcement agent has been shown to enhance the mechanical properties of wooden cultural relics while also maintaining minimal color variation, increased biocompatibility, and durability. This method is particularly well-suited for fortifying and preserving damp wooden cultural relics that exhibit varying degrees of decay. The findings offer significant insights and potential avenues for further research on the preservation methods for large wooden cultural artifacts discovered in the middle and lower regions of the Yangtze River dating back to the Warring States Period.

Keywords: Tomb of Marquis Yi of Zeng, Unearthed, Wet Outer Coffin, Strengthening.

INTRODUCTION

Due to the great difference in climate between the north and the south of China, the main chemical components of wooden cultural relics excavated in different regions, such as cellulose, hemicellulose and lignin, have degraded to varying degrees in the long-term burial process, affected by the regional environment (temperature and humidity, biological molds, etc.) and site structural characteristics, etc (Q. Li et al., 2018; L. Li, 2011) Archaeological timber unearthed in the dry environment is prone to deformation, dry cracking, twisting and serious collapse deformation in the degradation process, and few cultural relics are preserved; The water-saturated or moist archaeological wood with high moisture content is mainly attacked by bacteria and other microorganisms in the long-term groundwater environment (Elkhial & El Hadidi, 2022; Song et al., 2023). Although the cell wall degrades, the appearance of the water-saturated archaeological wood remains mostly intact. However, the unearthed water-saturated archaeological wood may be damaged twice due to improper protection, and irreversible shrinkage occurs after natural dehydration, and the dimensional stability of the ancient wood

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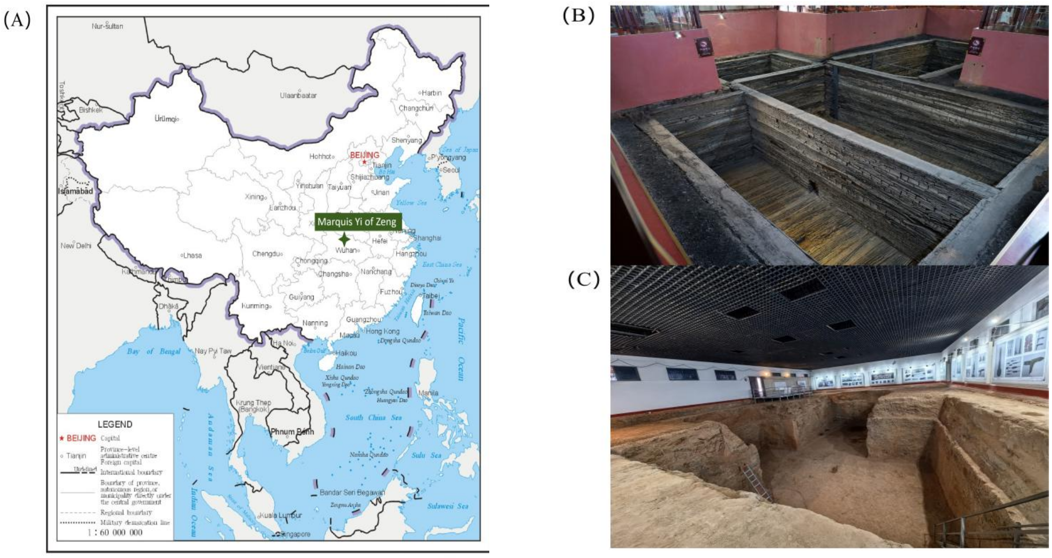
material is greatly reduced. Therefore, it is necessary to carry out timely and appropriate reinforcement and protection treatment for unearthed water-filled ancient wood to maintain its original form and appearance, realize long-term preservation and collection display of water-filled or moist archaeological wood relics with high moisture content (Macchioni, Pecoraro, & Pizzo, 2018; Abdelmoniem, Mahmoud, Mohamed, Ewais, & Abdrabou, 2020; Guo et al., 2022; Capretti et al., 2008).

The commonly used preservation methods of traditional wet archaeological wood with saturated water or high moisture content are saturated water preservation and dehydration protection. The reasonable and long-term preservation of wooden cultural relics can be achieved through dehydration and replacement reinforcement of water-saturated wooden cultural relics (Guo et al., 2022; Capretti et al., 2008; Spirydowicz et al., 2001; De Figueiredo Junior, Marques, & Silva, 2022; Chen, Ma, Zhang, & Hu, 2024; Cao et al., 2022; Omar, Abdelmoniem, El Wekeel, & Taha, 2022). Since the 19th century, experts in the field of conservation science have reported that various materials such as polyethylene glycol (PEG), sugars, natural resins, paraffin, and volatile solvent replacement have been used for the reinforcement and protection of water-saturated wood cultural relics. The treatment methods are simple and effective, but the surface color of the wood after reinforcement is deepened, the texture is blurred, and the performance is unstable. Among them, the PVAc solution has been reported to strengthen bamboo slips and other cultural relics, mostly by cross-linking method, from thermoplasticity to thermosetting, mainly through copolymerization modification, protective colloid modification, blending modification and other methods to modify wood properties. Although the performance of modified PVAc has been improved to some extent, compared with the market demand, the strengthening strength has not been increased much, and the desired effect cannot be reached. In situ polymerization is reinforced by small molecule monomer polymerization and has good permeability, but it is a free radical polymerization reaction, which will release heat strongly and damage wood, and it is difficult to find a suitable normal temperature initiator. At the same time, the composition of wet wood is complex, containing more water and impurities, which may lead to some side reactions, the induction period of the polymerization reaction increases, and there are more interference factors in the reinforcement process. At present, there is much research on the protection of wooden cultural relics in arid areas at home and abroad, but the protection of wooden cultural relics in humid environments is a more targeted and more complicated work. Beisong Fang innovated the filling dewatering method of hexadecyl alcohol for such water-filled wooden tablets, gradually replacing the water in the water-filled tablets with ethanol. After the water was fully replaced, the ethanol in the tablets was gradually replaced with hexadecyl alcohol, and after the ethanol was repeatedly replaced, the tablets were removed from the hexadecyl alcohol solution. A certain concentration of glyoxal was used to soak the water-saturated wood lacquerware directly, and the water was allowed to evaporate naturally after full penetration. After the small glyoxal molecules completely penetrated into the interior of the wooden lacquerware relics, triethanolamine solution with a concentration of 1-5% was added to it, which triggered the in-situ polymerization of the small glyoxal molecules, and the reaction was 4h, making the molecular chain structure grow. Then soluble starch with a concentration of 1-10% was added for 24h, and the molecular chain structure was crosslinked in situ to form a spatial network structure. The structure can play a good supporting role in the interior of the wooden lacquerware relics. When the artifacts are removed from the glyoxal solution and dried naturally, there will be no shrinkage, cracking, deformation and other diseases. At the same time, due to the in-situ polymerization crosslinking reaction of small glyoxal molecules, the molecular quantity becomes larger, and it is not easy to precipitation from the interior of the wooden lacquerware relics. In summary, humid wood cultural relics are generally located in the area of high relative humidity of the air, and the unearthed wood cultural relics have a large internal water content. The internal fiber structure of wood is seriously damaged by microbial corrosion, and the body is fragile. The existing reinforcement materials still have poor permeability and poor controllability of curing speed in the reinforcement process, and the wood material body becomes white and black after curing. And a series of problems such as the poor compatibility between the reinforcement material and the body (Klaassen, van't Oor, Kloppenburg, & Huisman, 2023; El-Gamal, Abdel-Maksoud, Darwish, Topakas, & Christakopoulos, 2018; Liu et al., 2022; Sidoti et al., 2023; Pu & Wang, 2023; Walsh-Korb & Avérous, 2019; Plavcová, Jansen, Klepsch, & Hacke, 2013; Albersheim, Darvill, Roberts, Sederoff, & Staehelin, 2010).

In the actual study on the protection of wet wooden cultural relics unearthed in archaeology, there are very strict requirements on strengthening protection materials, preservation environment, construction technology and so on. Therefore, it is urgent to find a reinforcement and protection method that can maintain good biocompatibility with wood and achieve certain strength, toughness, stability and color change after wood reinforcement. Taking the reinforcement and protection of the damp wooden burial timber unearthed from the tomb of Zenghouyi in Hubei Province, China as an example, this paper introduces a method of reinforcement and protection for damp wooden cultural relics using PVAc composite materials (Figure 1).



(A) The Distribution Area of the Tomb of Marquis Yi of Zeng on the Map of China

(B) The Unearthed Tomb and (C) Current Preservation Status of Marquis Yi of Zeng

Figure 1. The Tomb of Marquis Yi of Zeng

SAMPLE COLLECTION AND REINFORCEMENT TREATMENT METHODS

Sample

The Tomb of Marquis Yi of Zeng is a significant archaeological discovery located in the Zengdu District, Suizhou City, Hubei Province, China. Dating back to the Spring and Autumn period, this tomb belongs to Marquis Yi of Zeng, a nobleman of the Chu state. Unearthed in 1978, the discovery of this tomb is regarded as a major milestone in Chinese archaeology due to its vast scale, the abundance and well-preserved state of the artifacts found within. The tomb's complex structure comprises the main burial chamber and accompanying burial pits, covering a total area of approximately 220 square meters. The interior of the tomb is elaborately decorated and divided into a front chamber, rear chamber, and a lateral room. A wide array of valuable artifacts was discovered inside, including bronzeware, jade objects, lacquerware, and silk textiles.

A large amount of charcoal was filled between the pit wall and the coffin wood of Marquis Yi of Zeng's tomb. Due to local water seepage from the pit wall, the moisture content of charcoal in different parts varied greatly. The burial wood next to the charcoal was mostly in a humid environment, and the fluctuation of environmental humidity led to the great difference in the rot degree of the burial wood. There are 122 pieces of burial wood displayed at the original site of Marquis Yi of Zeng's tomb, including 72 wall panels and 50 bottom panels. The experimental samples were selected from the burial wood at the partial seepage of Marquis Yi of Zeng's tomb. The loose sample was the south end of the east wall panel Q30 of the middle chamber, and the dense sample was the north end of the east wall panel Q65 of the east wall panel of the east chamber.

Preparation of Reinforcement Agent

The wood cultural relics reinforcement agent introduced in this paper is realized through the combination of various materials. In terms of mass parts, the reinforcement agent contains 5 parts PVAc, 40 ~ 60 parts methanol, 1 ~ 10 parts shellac, and 1 ~ 7 parts 30% H_2O_2 PVAc, the main reinforcement agent used, is a small amorphous polymer particle formed by polymerization of vinyl acetate. Dissolved in methanol, PVAC is a transparent water-soluble colloid with good adhesion, colorless, tasteless, toughness, plasticity, good acid and alkali resistance, and good permeability to wet wooden cultural relics. The reinforcement auxiliary shellac used is Yunnan shellac purchased in the market. It is a kind of natural resin secreted by shellac insects, with similar color to ancient woods, good hydrophobicity and is non-toxic. Shellac resin is a mixture of lipid and polyester composed of hydroxyl fatty acids and hydroxyl sesquiterpene acid. It has the advantages of elastic spatial network structure, strong adhesion, good toughness, good luster, UV stability, acid resistance, oil resistance, etc., which is very suitable for the reinforcement of damp ancient wood.

Preparation method: A certain amount of methanol solution was mixed with 30% H_2O_2 at room temperature 25℃, according to PVAc: methanol: shellac: H_2O_2=5:45:5:7 ratio, add shellac, stand for 10 minutes, slowly stir to completely dissolve shellac, add PVAc particles, stir to completely dissolve, and timely add the volatile amount of methanol.

Reinforcement Treatment Process

The wooden cultural relics reinforcement method described in this paper is the polymer permeation filling method, as shown in Figure 2. PVAc is directly filled in the cell cavity and pore structure of wood. The process is simpler and more convenient than the in-situ polymerization method, with lower requirements for construction conditions, less interference and strong process adaptability.

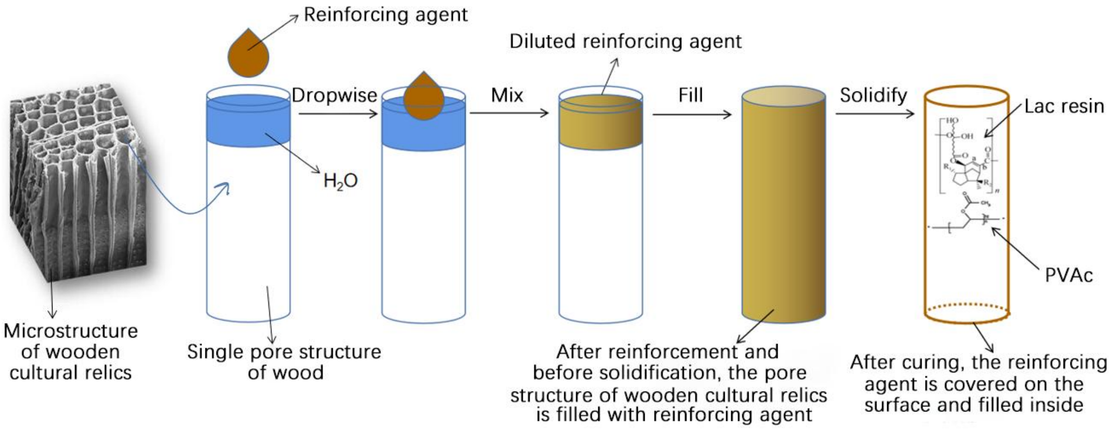


Figure 2. Schematic Diagram of the Reinforcement Mechanism of Wet Wooden Cultural Relics

METHODS AND INSTRUMENTATION

Scanning Electron Microscope Test

Experimental method: Field emission scanning electron microscopy (HITACHI, SU 8010, Japan) was used to observe the microstructure of the surface and cross-section of the wooden relics before and after reinforcement.

(1) Sampling: The wood from the tomb of Marquis Yi of Zeng in Hubei Province was sampled from about 2/3 of the outer core of the ancient wood pith. The sample size is about 10mm*10mm*10mm. The three sections (transverse section, diameter section, chord section) should be cut accurately.

(2) Drying: try to simulate the drying conditions of large specimens, and take measures to slow down the drying speed. The above specimens were placed in a glass dish, covered with filter paper and then fixed with tape, and placed in a cool and ventilated place for 1 week. Then remove the filter paper and continue to dry in a cool place for 1 week.

(3) Flatten the sample: After the sample is air-dried, use the above blade to flatten the wood block, and the revised sample size is about 5mm*5mm*2mm, 2mm is the thickness.

The dried sample was fixed on the sample tray in three sections, the sample was sprayed with gold on the surface, and the sample was observed by scanning electron microscopy. The acceleration voltage is 15Kv.

Density Increase Rate

Experimental methods: Firstly, the mass m1 of wooden cultural relics before reinforcement was weighed and recorded, and then the mass m2 of wooden cultural relics after reinforcement was weighed and recorded.

Because the wooden cultural relics have a certain water absorption, the volume measured directly by the drainage method has a large error, and the volume (v) before and after reinforcement is unchanged, density (ρ)=mass (m)÷volume (v), so the mass increase rate of wooden cultural relics is also the density increase rate.

$\rho 1 = m1 \div v$, $\rho 2 = m2 \div v$,

Density increase rate=$(\rho 2-\rho 1)/\rho 1 \times 100\% = (m2-m1)/m1 \times 100\%$.

Compressive Strength Test of Wood Along Grain

According to the People's Republic of China national standard GB 1935-1991 wood along grain compressive strength test method, the wood was tested.

Sample size: 20mm×20mm×30mm, 30mm is the direction of the grain.

Experimental equipment: AGS-X series electronic universal testing machine (5KN).

Experimental procedure:

(1) Adjust the moisture content of the sample to the range of 9%-15%: Put the sawn sample into the constant temperature and humidity box, temperature (20±2) °C, humidity (65±3) °C. Three of the samples were weighed every other day. When the difference between the last two weights did not exceed 0.5% of the sample mass, the sample was considered to have reached the equilibrium moisture content.

(2) Measure the specimen size: At the center of each side of the specimen, measure the width b and thickness t. Accurate to 0.1mm.

(3) The sample is placed in the center of the testing machine's movable support, the sample is uniformly loaded at the speed of 0.017mm/s, and the sample is damaged within 1.5-2min. When the display number of the testing machine is significantly reduced, the sample is damaged. The load P_{max} and the stroke of the indenter were recorded.

(4) The moisture content of the sample was measured immediately after the sample was damaged.

(5) The compressive strength along the grain was calculated when the moisture content of the sample was W% and converted to the compressive strength along the grain when the moisture content was 12%.

When the moisture content of the sample is W%, the compression strength along the grain is calculated as shown in Formula (3-1) :

$$\sigma_W = \frac{P_{max}}{bt}$$

Formula:σ_W: Compressive strength along the grain when the moisture content of the sample is W% (Mpa);

P_{max}: Failure load (N);

b: Sample width (mm);

t: Sample thickness (mm).

When the moisture content of the sample is 12%, the compression strength along the grain is calculated as shown in Formula (3-2) :

$$\sigma_{12} = \sigma_W[1 + 5(W - 0.12)]$$

Formula:

W: Air-dry moisture content of the sample (%);

σ_{12}: Compressive strength along the grain when the moisture content of the sample is 12% (Mpa).

Contact Angle test

The samples were placed in the oven with constant weight and dried at (103±2) °C for 8h. Then 2-3 samples were selected and weighed every 2h. When the difference between the last two weights did not exceed 0.5% of the sample mass, the samples were completely dry. After solvent drying, the interfacial tension was measured using a SZ10-JC2000A intravenous drop contact Angle measuring instrument. Distilled water was used as the test liquid with a 10uL manual injection needle and 2uL of water was dropped each time. The three sections of the sample were measured respectively, and the chord section was divided into early evening wood. Take 10 photos of each section and take the average of the 10 measured values.

Fourier Transform Infrared Spectrum (FT-IR)

Experimental method: The molecular structural characteristics of the surface tissue of dense and loose specimens before and after reinforcement were tested using a Nicolet 50 FT-IR in a dry environment at 25°C. It is necessary to preheat the instrument and grind the wood sample in advance, then prepare the solid sample using the tablet method, and finally perform the infrared spectrum test and the result analysis (Table 1 & Table 2).

Calculation of retention rate C: Retention is the percentage of a certain functional group or chemical composition i in the old wood relative to the fresh wood. Its calculation is shown in Formula (3-3) :

$$C = \left(\frac{A_{Wi}}{A_{W1505}}\right) \Big/ \left(\frac{A_{ni}}{A_{n1505}}\right) \times 100\%$$

Formula:

wi: Absorbance of ancient wood materials;

W1505: Absorbance of benzene ring carbon skeleton vibration near 1505 cm^{-1} of ancient wood material;

ni: Absorbance of modern health materials;

n1505: Absorbance of benzene ring carbon skeleton vibration near 1505 cm^{-1} of modern healthy materials.

Table 1. Typical Infrared Spectral Characteristics of Rosin

Wave Number/cm^{-1}	Functional Group	Absorbance	Description of Functional Group Attribution
2930	$-CH_2-$, $-CH_3$	0.8357	C-H stretching vibration
2869	$-CH_2-$, $-CH_3$	0.6431	C-H stretching vibration
1695	C=O	1.0759	The absorption peak of carbonyl groups (C=O) on carboxyl groups (-COOH)
1463	C=O	0.2515	Aldehyde (-CHO) stretching vibration
1384	$-CH_3$	0.1918	Methyl ($-CH_3$) stretching vibration
1278	O=C-OH	0.4219	Stretching vibration of carbon oxygen bonds (=C-OH) on carboxylic acids

Table 2. Typical Infrared Spectral Characteristics After Natural Resin Reinforcement

Wave Number/cm^{-1}	Functional Group	Absorbance	Description of Functional Group Attribution
3419	O-H	0.1827	O-H stretching vibration
2931	$-CH_2-$, $-CH_3$	0.1922	C-H stretching vibration
2866	$-CH_2-$, $-CH_3$	0.1384	C-H stretching vibration
1695	C=O	0.1618	The absorption peak of carbonyl groups (C=O) on carboxyl groups (-COOH)
1510	C=C	0.1054	Carbon skeleton vibration of benzene ring (lignin)
1461	C-H, C=C, C=O	0.1028	C-H bending vibration (CH_2 in cellulose, hemicellulose, and lignin), carbon skeleton vibration of benzene ring, stretching vibration of carbonyl groups (C=O) on aldehyde groups (-CHO)
1422	C-H	0.0767	Plane deformation and stretching vibration of C-H on the benzene ring
1381	$-CH_3$	0.0720	Methyl ($-CH_3$) stretching vibration
1270	C-O-C	0.1479	Stretching vibration of lignin phenol ether bond (C-O-C)
1032	C-O	0.1345	C-O stretching vibration (cellulose, hemicellulose, and lignin)

RESULTS AND DISCUSSION

As shown in Figure 3, this paper mainly introduces the application of a combination of polyvinyl acetate (PVAc) and shellac in the reinforcement and protection of wet wooden cultural relics by taking the reinforcement and protection of wood from the tomb of Marquis Yi of Zeng in Hubei Province, China as an example. It is found that this method can effectively improve the mechanical properties of wooden cultural relics on the basis of keeping the color difference small, and is suitable for wet wooden cultural relics with different rot degrees.

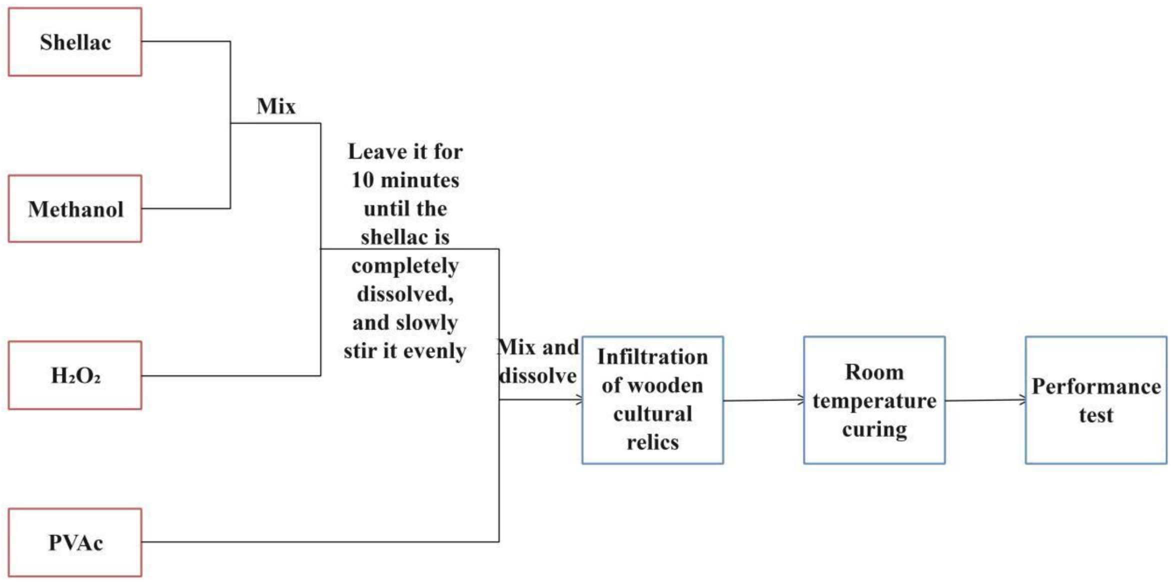


Figure 3. Preparation Process of PVAc Compound Reinforcement Agent

The diameter and number of wall-pitted cells in the diametral section of ancient wood are large, and the pitted membrane has been destroyed. Because the permeability of wood is closely related to the pore, quantity and radius of the wood pitted membrane, the damaged pitted membrane provides a good condition for the reinforcement agent to enter the interior of ancient wood cell wall (Manoudis, Gemenetzis, & Karapanagiotis, 2017; Shmulsky & Jones, 2019; Lou et al., 2021).

It can be seen from Figure 4 that the surface of the wood of the dense sample is powdered before reinforcement, and there are many pits of different depths and powdered wood particles and impurities. After reinforcement, the pore structure is basically filled by the reinforcement agent. At the same time, the concentration of hydrogen peroxide is high and the amount of hydrogen peroxide added is relatively large, the colloid does not sink, and there is no residue or production of insoluble substances after the solidification of the reinforcement agent. The surface roughness of wood decreased significantly. Pulverized wood particles and thinner wood chips are wrapped with reinforcing agents and bonded to the wood, so that it is not easy to fall off, and the wooden cultural relics are well protected and reinforced. Before strengthening the loose sample, it is particularly worm-eaten, and due to the influence of wet burial environments, it has many pores and contains many impurities, and its texture is softened and brittle.

Figure 4. Comparative Effect of Dense and Loose Wooden Relics Before and After Reinforcement

As shown in Figure 5, the reinforcement agent effectively penetrates into the interior of the wood through small holes and forms a transparent PVAc film on the surface tissue of the wood. This process isolates the wood from adverse factors such as oxygen and water in the external environment. The density and viscosity of the added reinforcement agent are not high, and due to gravity factors, the relatively large trench pore structure in the wood is not completely filled. As a result, the surface of the wood remains completely smooth.

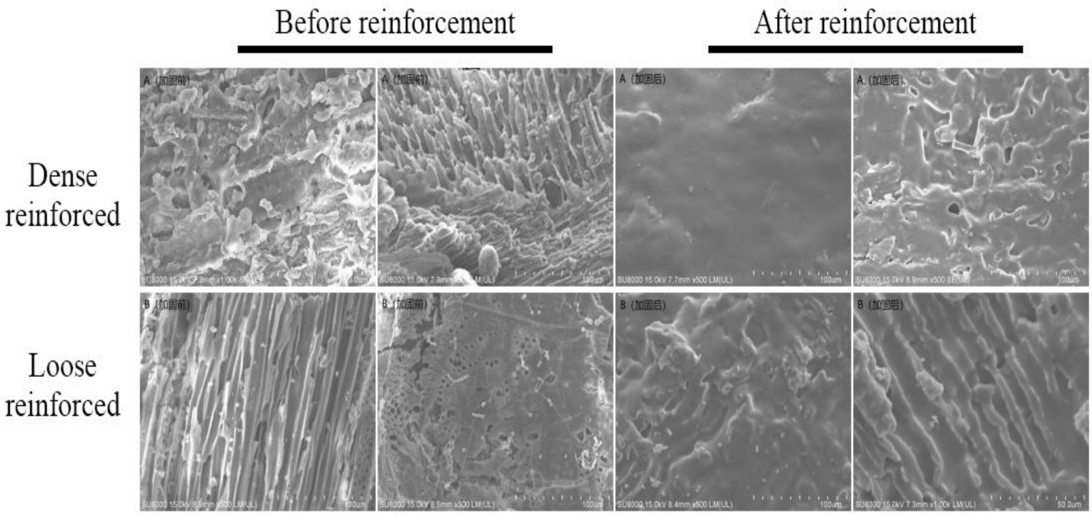


Figure 5. SEM of Dense and Loose Samples Before and After Reinforcement

Macro density is a scientific and relatively convenient index to reflect the degradation degree of water-saturated ancient wood (Kristian, 2009; Qaseem, Shaheen, & Wu, 2021). Decay and degradation of ancient wood led to the enlargement of cell wall pore size, the increase of pore number and the decrease of crystallinity. Cellulose, hemicellulose and lignin are the three main chemical components of wood cell walls. The degradation and fracture of the cellulose molecular chain weaken its original rigidity (Machinet, Bertrand, Barrière, Chabbert, & Recous, 2011; X. Li, 2021). The degradation of hemicellulose and lignin reduces the tightness of the cell wall matrix. The different rot degree of wooden relics leads to the significant difference in their penetration and absorption capacity to reinforcement reagents. After calculation, as shown in Table 3, the density increase rate of wooden relics with different rot degrees before and after reinforcement is different. Dense samples have small specific surface areas and small porosity, and the density increase rate before and after reinforcement is 2.3%. The bulk sample has a large specific surface area and large porosity, and the density increase rate is 33.3% before and after reinforcement. In general, the density of the reinforcement agent is relatively small, and the proportion of the quality change of wooden cultural relics after reinforcement is not large.

Table 3. Quality and Density Increase Rate of Dense and Loose Sample Before and After Reinforcement (Quality Increase Rate)

Sample	Quality Before Reinforcement(g)	Quality After Reinforcement(g)	Density Increase Rate
Dense blank sample	0.766	-	-
Dense reinforced sample	0.562	0.575	2.3%
Loose blank sample	0.151	-	-
Loose reinforced sample	1.096	1.461	33.3%

As shown in Table 4, it is found through testing that: The compressive strength of dense samples before and after reinforcement was increased by 47.0%; The compressive strength of the loose sample increased by 115.4% before and after reinforcement. The average compressive strength was increased by 81.2%. The results indicated that the dense sample had a hard texture and better compressive strength, the reinforcement agent was difficult to penetrate, and the compressive strength was not significantly improved before and after reinforcement. The loose sample is honeycomb with a soft texture, poor compressive strength, serious decay, large pores, large specific surface area, reinforcement covering the surface, easier to penetrate, and compressive strength improvement is obvious.

Table 4. Testing of Compressive Strength Along Grain for Dense and Loose Samples

Sample	Sample Cross-sectional Area (cm^2)	Destructive Load (kN)	Pressure ($\times 10^7$Pa)	Improvement Rate of Reinforcement Strength
Dense blank sample	0.84	1.68	2.00	
Dense reinforced sample	0.90	2.65	2.94	47.0%
Loose blank sample	2.70	0.14	0.052	
Loose reinforced sample	4.80	0.54	0.112	115.4%

The surface contact Angle is used to measure the hydrophobicity of the wood surface. The larger the surface contact Angle, the better the hydrophobicity. As shown in Figure 6, The hydrophobic Angle of the dense sample changed from 87° to 101° after reinforcement, and the hydrophobic Angle of the loose sample changed from 104°to 114° after reinforcement. The hydrophobicity of dense samples increased by 16.5% before and after reinforcement. The hydrophobicity of the loose sample increased by 9.64% before and after reinforcement. The average hydrophobicity increased by 11.9%. The results showed that PVAc combined shellac material had certain hydrophobicity, and the proportion of hydrophobicity improvement was slightly different according to the different rot conditions of the wood surface.

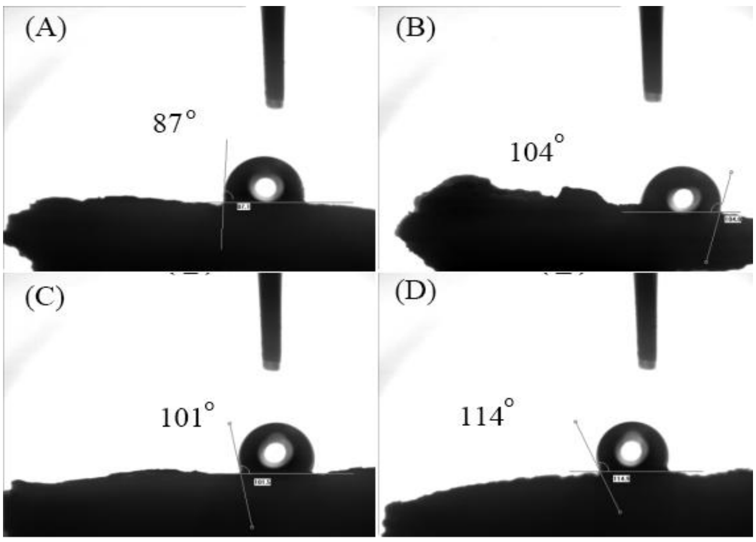


Figure 6. Contact Angle test before and after reinforcement

Note: A is a dense blank sample, B is the loose blank sample, C is the dense reinforced sample after reinforcement, and D is the loosened reinforced sample after reinforcement.

Figure 7 is the infrared spectrum of the dense blank sample before reinforcement. 3422.78cm-1 corresponds to hydroxy-OH, and 2938.24cm-1 corresponds to C-H of methyl, methylene and ethyl. 1600.81cm-1 and 1507.64cm-1 correspond to the C-H bond on the benzene ring, 1459.07cm-1 is the methoxy-group absorption peak, and the stretching vibration peak between 1331cm-1 and 1122cm-1 corresponds to the methoxy-group absorption peak of guaiac ring and lilac ring, which are the basic substances constituting lignin. 1224.83cm-1 corresponds to the specific absorption peaks of C-C, C-O, and C=O, and 1122.78cm-1, 1032.22cm-1, and 872.33cm-1 correspond to C-H on the benzene ring.

In Figure 7, Curve (3) has a characteristic peak of 1736cm-1 more than Curve (1), and Curve (4) has a characteristic peak of 1736cm-1 more than Curve (2). The absorption peak of C=O structure, which is analyzed to form a conjugated structure with the aromatic ring, is the characteristic peak of shellac, indicating that shellac successfully adhered to wooden cultural relics. Curve (2) has 1421.04cm-1 more peaks than Curve (1), which is analyzed as the characteristic peak of C=O, indicating that the difference between the two kinds of wooden relics with different rot degrees is that honeycomb has more carbonyl peaks on the benzene ring than block, which should be formed by the oxidation of the hydroxyl group on the benzene ring. Therefore, the loose sample has a higher oxidation degree and worse rot than the dense sample. The infrared spectra of the dense reinforced sample and the loose reinforced sample are basically the same, indicating that the functional groups of the two kinds of wooden cultural relics after reinforcement are basically the same. C=O on the aromatic ring in shellac and C=O on the fat chain in PVAc make up for the C=O functional groups generated by wood oxidation, indicating that the reinforcement agent is fully and evenly mixed and filled on the surface of the wooden cultural relics or inside the wooden cultural relics. It has played a role in strengthening and protecting the wooden cultural relics.

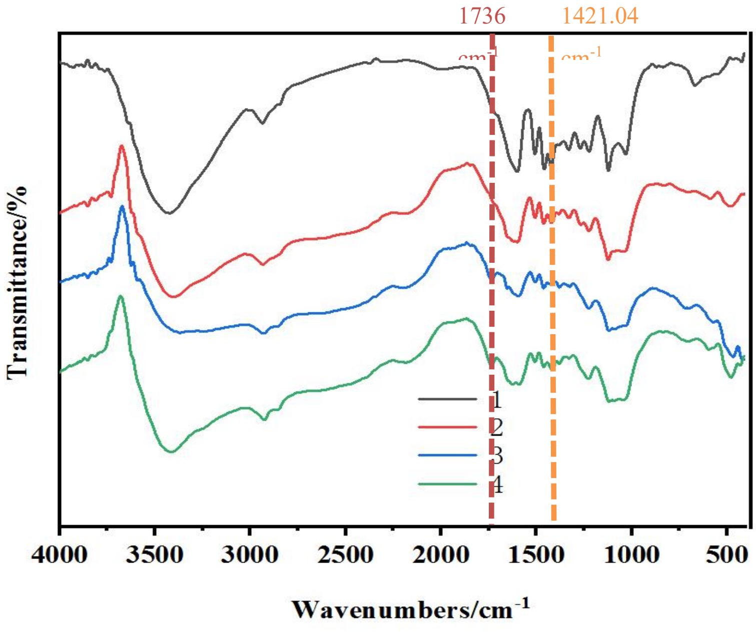


Figure 7. Infrared Spectra Before and After Reinforcement

Note: 1 is the dense blank sample, 2 is the loose blank sample, 3 is the compact reinforced sample after reinforcement, and 4 is the loose reinforced sample after reinforcement.

CONCLUSION

Taking the reinforcement and protection of the wet burial wood unearthed from the tomb of Marquis Yi of Zeng in Hubei Province, China as an example, this study found that the compound reinforcement of PVAc and shellac can effectively improve the mechanical properties of wooden cultural relics on the basis of ensuring the color difference is small. It is suitable for wet wooden cultural relics with different degrees of decay and has the following advantages: (1) The prepared compound reinforcement agent is water-soluble, good permeability, room temperature curing, simple preparation process, and good biocompatibility; (2) The reinforced wooden cultural relics have good toughness, high strength, small color difference, low surface reflectance, good durability, and can be reinforced and repaired twice, and the overall performance of the product is excellent; (3) The methanol solution of PVAc is a water-soluble adhesive. The direct permeation filling method can form a concentration gradient in the original environment inside the wet wooden cultural relics, curing faster, and the water will not have much impact on the reinforcement process and reinforcement time.

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CONFLICTS OF INTEREST

The authors declare that they have no conflicts of interest related to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

REFERENCES

Abdelmoniem, A. M., Mahmoud, N., Mohamed, W. S., Ewais, A. Y., & Abdrabou, A. (2020). Archaeometric study of a polychrome wooden coffin from 26th dynasty-Egypt. *Mediterranean Archaeology and Archaeometry*, *20*(1), 7-17.

Albersheim, P., Darvill, A., Roberts, K., Sederoff, R., & Staehelin, A. (2010). *Plant cell walls*. New York, NY: Garland Science.

Cao, H., Gao, X., Chen, J., Xi, G., Yin, Y., & Guo, J. (2022). Changes in moisture characteristics of waterlogged archaeological wood owing to microbial degradation. *Forests*, *14*(1), 9.

Capretti, C., Macchioni, N., Pizzo, B., Galotta, G., Giachi, G., & Giampaola, D. (2008). The characterization of waterlogged archaeological wood: the three Roman ships found in Naples (Italy). *Archaeometry*, *50*(5), 855-876.

Chen, M., Ma, Y., Zhang, B., & Hu, Y. (2024). Feasibility study on conservation of water-saturated archaeological wood in earthen sites by hot air with different humidity. *The European Physical Journal Plus*, *139*(1), 55.

De Figueiredo Junior, J. C. D. A., Marques, H. D. P., & Silva, G. G. (2022). Expanded vermiculite and polyvinyl acetate composite as gap filler for wooden objects conservation. *Journal of Cultural Heritage*, *55*, 88-94.

El-Gamal, R., Abdel-Maksoud, G., Darwish, S., Topakas, E., & Christakopoulos, P. (2018). FTIR analysis for the evaluation of some triazole fungicides for the treatment of wooden artifacts. *Mediterranean Archaeology and Archaeometry*, *18*(2), 141-151.

Elkhial, M. M., & El Hadidi, N. M. N. (2022) Multi-instrumental investigation and analysis of a unique ancient Egyptian wooden obelisk (new kingdom) at the Grand Egyptian Museum. *Scientific Culture*, *8*(1), 1-14.

Guo, J., Chen, J., Li, R., Luo, R., Jiao, L., & Yin, Y. (2022). Thermoporometry of waterlogged archaeological wood: Insights into the change of pore traits after the water-removal by supercritical drying. *Thermochimica Acta*, *715*, 179297.

Klaassen, R., van't Oor, M., Kloppenburg, A., & Huisman, H. (2023). Rate of occurrence of wood degradation in foundations and archaeological sites when groundwater levels are too low. *Journal of Cultural Heritage*, *63*, 23-31.

Kristian, B. D. (2009). *Mechanical properties of clear wood from Norway spruce* (Doctoral thesis, Norwegian University of Science and Technology, Trondheim, Norway). Retrieved from https://ntnuopen.ntnu.no/ntnu-xmlui/handle/11250/236422

Li, L. (2011). *China's cultural relics*. Cambridge, England: Cambridge University Press.

Li, Q., Cao, L., Wang, W., Tan, H., Jin, T., Wang, G., . . . Xu , R. (2018). Analysis of the bacterial communities in the waterlogged wooden cultural relics of the Xiaobaijiao No. 1 shipwreck via high-throughput sequencing technology. *Holzforschung*, *72*(7), 609-619.

Li, X. (2021). Plant cell wall chemistry: Implications for ruminant utilisation. *Journal of Applied Animal Nutrition*, *9*(1), 31-56.

Liu, X., Tu, X., Ma, W., Zhang, C., Huang, H., Varodi, A. M. (2022). Consolidation and dehydration of waterlogged archaeological wood from Site Huaguangjiao No. 1. *Forests*, *13*(11), 1919.

Lou, Z., Yuan, T., Wang, Q., Wu, X., Hu, S., Hao, X., . . . Li, Y. (2021). Fabrication of crack-free flattened bamboo and its macro-/micromorphological and mechanical properties. *Journal of Renewable Materials*, *9*(5), 959-977.

Macchioni, N., Pecoraro, E., & Pizzo, B. (2018). The measurement of maximum water content (MWC) on waterlogged archaeological wood: A comparison between three different methodologies. *Journal of Cultural Heritage*, *30*, 51-56.

Machinet, G. E., Bertrand, I., Barrière, Y., Chabbert, B., & Recous, S. (2011). Impact of plant cell wall network on biodegradation in soil: Role of lignin composition and phenolic acids in roots from 16 maize genotypes. *Soil biology and biochemistry*, *43*(7), 1544-1552.

Manoudis, P. N., Gemenetzis, D., & Karapanagiotis, I (2017) A comparative study of the wetting properties of a superhydrophobic siloxane material and rose petal. *Scientific Culture*, *3*(2), 7-12.

Omar, A. M., Abdelmoniem, A. M., El Wekeel, F., & Taha, A. S. (2022) Spectroscopic and molecular investigation of Cheops wooden boat for microbial degradation applying proper microbicides and methods. Scientific Culture, *8*(1), 115-127

Plavcová, L., Jansen, S., Klepsch, M., & Hacke, U. G. (2013). Nobody's perfect: can irregularities in pit structure influence vulnerability to cavitation?. *Frontiers in Plant Science*, *4*, 66923.

Pu, H., & Wang, X. (2023) The impact of environment on cultural relics. *Scientific Culture*, *9*(2), 49-62.

Qaseem, M. F., Shaheen, H., & Wu, A. M. (2021). Cell wall hemicellulose for sustainable industrial utilization. *Renewable and Sustainable Energy Reviews*, *144*, 110996.

Shmulsky, R., & Jones, P. D. (2019). Forest products and wood science: An introduction. Hoboken, NJ: Wiley-Blackwell.

Sidoti, G., Antonelli, F., Galotta, G., Moscatelli, M. C., Kržišnik, D., Vinciguerra, V., . . . Romagnoli, M. (2023). Inorganic component in oak waterlogged archaeological wood and volcanic lake compartments. *Biogeosciences*, *20*(15), 3137-3149.

Song, J., Deng, J., Zhao, J., Lu, S., Ming, H., & Shu, C. (2023). Influence mechanism of dry and wet alternate aging on thermal property characteristics of wood. *Journal of Thermal Analysis and Calorimetry*, *148*(11), 5111-5129.

Spirydowicz, K. E., Simpson, E., Blanchette, R. A., Schniewind, A. P., Toutloff, M. K., & Murray, A. (2001). Alvar and Butvar: The use of polyvinyl acetal resins for the treatment of the wooden artifacts from Gordion, Turkey. *Journal of the American Institute for Conservation*, *40*(1), 43-57.

Walsh-Korb, Z., & Avérous, L. (2019). Recent developments in the conservation of materials properties of historical wood. *Progress in Materials Science*, *102*, 167-221.