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Rosin reinforcement and protection of the unearthed outer coffin from the tomb of Marquis Yi of Zeng in Hubei, China

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Abstract

The tomb of Marquis Yi of Zeng was unearthed in 1978 at Leiguudun in Suizhou City, Hubei Province, China. This is the largest wooden coffin in rock pit and vertical cave in the Warring States period in China. The large wooden coffin components provide reliable material data for the study of the feudal burial system in the pre-Qin period and have high value. In this paper, the wooden coffin excavated from the tomb of Marquis Yi of Zeng was studied. By understanding the composition of wood, studying the weight gain rate, shrinkage rate, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and compression resistance, the wood reinforced by rosin and epoxy resin was compared, and the reinforcement effect and principle of the two reinforcement methods were discussed. The study found that the wood properties of rosin reinforced group were better than those of epoxy reinforced group in the aspects of compressive strength, weight gain rate and volume shrinkage rate, and the mechanical properties of wood were significantly improved. In addition, methanol or ethanol can be used to dissolve the rosin shellac in this strengthening process, which can achieve reversible strengthening treatment. The results provide valuable examples and research ideas for the selection of different conservation techniques of large wooden cultural relics unearthed in the middle and lower reaches of the Yangtze River during the Warring States Period.

Keywords The tomb of Marquis Yi of Zeng, The unearthed outer coffin, Rosin, Reinforcement and Protection

Research background and introduction

In September 1977, a unit of the Chinese People's Liberation Army discovered the tomb of Marquis Yi of Zeng while building a camp and leveling a hill. In March 1978, the relevant departments of Hubei Province formed a joint exploration team to conduct a comprehensive survey and drilling. The chambers (as shown in Fig. 1) are divided into four chambers: north, east, middle and west. Each chamber is separated by a wall, and each chamber is connected by a doorway at the bottom. The wall panels and floor boards are reserved in the chamber. There are 72 wall panels and 50 floor boards, both of which are rectangular timbers. Each of them is 3.35 ~ 10.1 m long, 0.43 ~ 0.6 m wide and 0.43 ~ 0.6 m thick. The bottom plate is tiled according to the bottom of the pit, the east chamber is vertically north–south, and the other chamber is horizontally tiled east–west. The wall panels are spliced with shallow grooves and tenons to make the structure of the chamber more firm. The tomb of Marquis Yi of Zeng is the largest rock pit and outer coffin tomb in the Warring States period of our country, which provides reliable material materials for the study of the tomb system of the pre-Qin period, and has very high value of scientific

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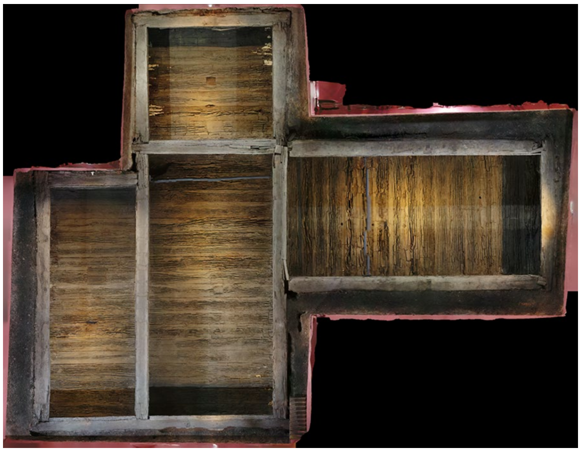


Fig. 1 Panoramic view of the coffin chamber of Marquis Yi of Zeng's tomb

research, history and culture, and display and education [1–5].

In 1978, the tomb of Marquis Yi of Zeng was excavated, the cover of the coffin was removed, the artifacts were extracted, and the grave pit and chambers were preserved on site for in-situ protection and display. From the excavation to 2008, the wood of the coffin chamber was protected by on-site water immersion, the "dewatering project" of the grave pit was naturally dried, dehydrated and reinforced, and the cracks in the wall of the coffin chamber were reinforced and repaired. In order to better understand the structural composition of the wooden coffin tombs in the rock pit, the structural composition and material preservation status of the wooden wall panels of the excavated coffin chambers were sampled, and the related preservation status were tested.

As in Fig. 2, from the physical and chemical properties of the coffin, that it can be roughly divided into the outer layer, the transition layer and the inner layer, and the approximate position from the outside to the inside is 0 ~ 2.0 cm, 2.0 ~ 4.0 cm and above 4.0 cm. Macro-outer wooden coffin has a wide range of cracking and warping, micro-layer wood cells are seriously damaged, the cell wall is thin, and the rot is very serious, which is directly related to the high water content of the wooden coffin caused by water seepage in the tomb, and the lack of environmental control such as temperature and humidity in the exhibition hall. The phenomenon of side delamination cracking is very serious, which may be due to the

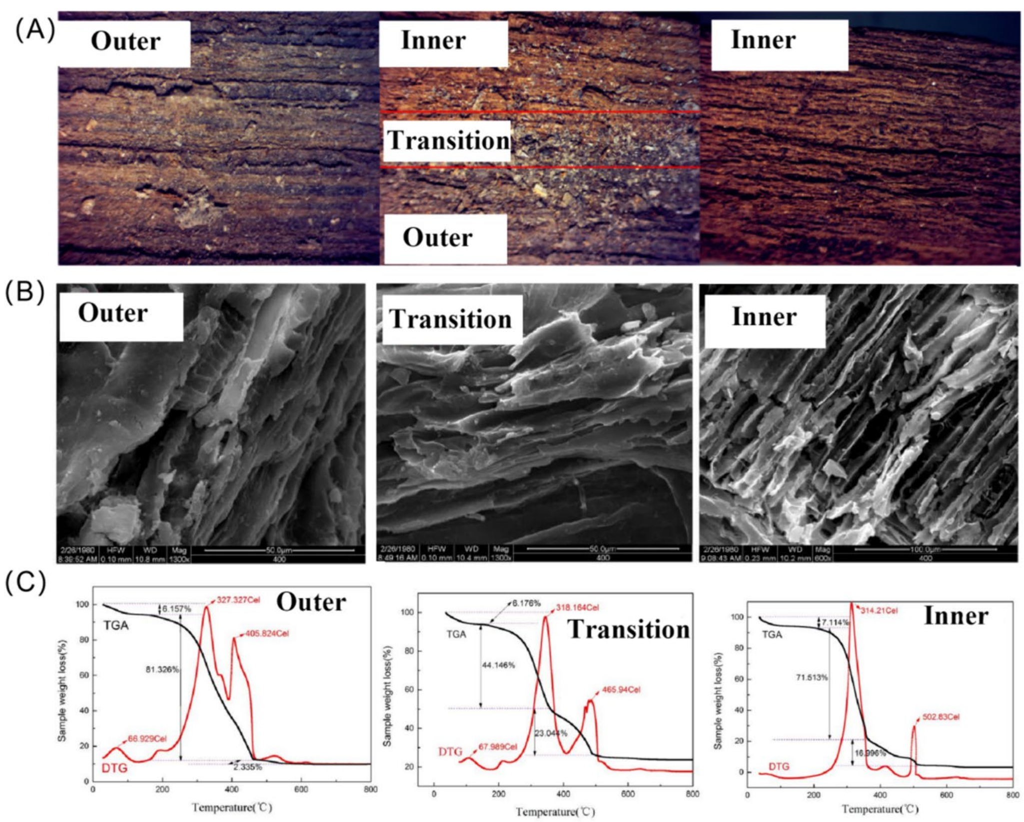


Fig. 2 Conservation status and performance of the unearthed outer coffin of Marquis Yi of Zeng's tomb

mismatch between the surface structure formed by the early reinforcement liquid applied to the upper layer of wood and the wood body structure, and the difference in physical and chemical properties leads to the cracking delamination. The composition and physical properties of the composite formed by the early reinforcement material and the wood body (thermal expansion coefficient, dry and wet expansion and contraction degree) were seriously mismatched, and severe cracking and falling occurred in a large range under the periodic temperature and humidity alternating for a long time. A large amount of silicon was detected in the outer wooden coffin, but the transition layer was less, and the inner layer was not detected. It reflects that the treatment effect of the early protection material is not deep enough, resulting in the degradation of the outer layer and the transition layer, and the deterioration degree of the inner layer is also very serious. To sum up, rescue reinforcement and protection measures should be taken as soon as possible to improve the overall structural stability and ensure that the precious wooden coffins unearthed can be preserved for a longer time [6, 7].

A large number of wooden cultural relics were unearthed in a land saturated environment rich in groundwater. Because the groundwater environment formed a relatively closed preservation space in a long-term burial environment, these water-saturated wooden cultural relics usually maintained a good appearance. However, the acids, alkalis, salts and some biological factors contained in groundwater may still cause tissue degradation of wooden cultural relics. In this process, with the degradation and destruction of cellulose and hemicellulose, the density of the wood becomes smaller and the porosity increases, resulting in continuous infiltration of water into the wood tissue. Because the water content in the wood in this state is much higher than normal, the wooden relics are often in a water-filled state. Therefore, the higher the degree of water saturation, the more serious its degradation. During the protection process of water-filled wooden cultural relics unearthed, irreversible shrinkage occurs after natural dehydration, which may lead to secondary destruction of cultural relics and decrease the dimensional stability of wood. Therefore, it is necessary to strengthen and protect the unearthed wet coffin timely and appropriately, to maintain its original form and appearance and realize the long-term preservation and display of wooden cultural relics [8–11].

Rosin is a natural wood preservative produced by pine trees. It exists at room temperature as a viscous liquid that can be separated into rosin and turpentine. In nature, when plants such as pine trees are attacked by the outside world, a large amount of rosin will be secreted at the wound, thus playing a role in preventing and promoting healing of the wound [12] The chemical composition of rosin is mainly composed of resinous acid ($C_{19}H_{29}COOH$), in addition to a small amount of fatty acids and neutral substances, with special chemical properties, which can occur a variety of chemical reactions [13, 14]. As the main composition of wood is cellulose and hemicellulose, containing a large number of free hydroxyl, wood has hygroscopic and desorption characteristics, there are defects of dry shrinkage and wet expansion, through rosin reinforcement treatment, can close the free hydroxyl in wood, to make up for the defects of wood. Rosin can also penetrate the interior of the wood, with anti-corrosion, anti-moth, and anti-cracking effects, so that the wood has better wettability and tightness. Compared with epoxy resin, the wood formed after epoxy resin reinforcement has higher hardness and strength; the wood formed after rosin reinforcement has strong viscosity and elasticity [15–17].

In this paper, the wooden coffin excavated from the tomb of Marquis Yi of Zeng was studied. By comparing the weight gain rate, shrinkage rate, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and compression resistance of wood before and after reinforcement with rosin and epoxy resin, the reinforcement effect and principle of the two reinforcement methods were discussed. It provides important research ideas for the restoration and protection of the tomb of Marquis Yi of Zeng.

Material and method

Sample preparation

The samples are from the tomb of Marquis Yi of Zeng in Suizhou. Cut into small pieces of about 8 cm (chord), 9 cm (radial), 10 cm (axial/longitudinal). The wood is naturally dried in the shade and dried to constant weight.

Reinforcement reagents and materials

Anhydrous ethanol, rosin, shellac, xylene, n-butanol, epoxy resin, polyamide resin. Among them, the method of rosin reinforcement was adopted for sample 1. Rosin, shellac and anhydrous ethanol were used to strengthen the sample, and their mass ratio was 12:12:76. Sample 2 was reinforced with epoxy resin, and the reinforcing reagent consisted of reinforcing resin, curing agent and diluent. The reinforcing resin was epoxy resin. The curing agent is 650 low molecular polyamide resin; The diluent was xylene and n-butanol with a mass ratio of 7:3; The mass ratio of reinforcement resin to curing agent is 3:1. Sample 3 was treated with glyoxal and rosin reinforcement, and 40% glyoxal was added to sample 1. Sample 4 was treated with glyoxal and epoxy resin, and 40% glyoxal was added to sample 2. Sample 5 is a blank sample. Sample 1 is reinforced with rosin, sample 2 is reinforced with epoxy, sample 3 is reinforced with glyoxal and rosin, sample 4 is reinforced with glyoxal and epoxy, sample 5 is blank.

Identification of wood species

A cubic wood block with a side length of about 1 cm was obtained from 6 archaeological wood samples. For samples that cannot meet the above requirements, the size of the wood block taken should not be less than 0.5 (radial) × 0.5 (chord) × 0.5 (longitudinal) cm^3. After the wood blocks were treated, three sections (transverse section, radial section and cross section) with a thickness of about 15–20 μm were prepared by a sliding slicing mechanism, and then permanent sections were prepared by dyeing, dewatering, transparency and sealing.

Determination of compressive strength parallel to grain

Mechanical strength is an important factor in ensuring that cultural relics are not damaged during long-term storage, display and transportation. Due to long-term groundwater erosion, cellulose molecular depolymerization, lignin molecular decay, and weak hydrogen bonds between cell wall polymers, the mechanical strength of water-saturated wooden relics is almost lost. In this experiment, an AGS-X series electronic universal testing machine (5KN) was used to measure the compressive strength along grain to characterize the change of mechanical properties before and after reinforcement.

According to the wood sample size, the size of the processed into 30 mm × 20 mm × 20 mm, the length of the grain direction; Place the sample at the center of the spherical movable support of the electronic universal mechanics testing machine, load at a uniform speed, destroy the sample within 1.5 min ~ 2.0 min, and record the maximum load Pmax at the time of failure; Calculate the longitudinal compressive strength σ.

σ = Pmax/bt

Formula: σ—The compressive strength parallel to grain of the sample is measured in Mpa (MPa);

Pmax—The maximum load on the specimen at failure, expressed in N (N);

B—Specimen width, in mm (mm);

T—Specimen thickness, in mm (mm);

Chemical structure analysis of wood

The wood sample was ground by air dry and the powder was mixed with KBr at room temperature and then pressed. Infrared spectrometers (Perkin Elmer Inc., Shelton, CT, USA) were used to acquire 4000–400 cm^{-1} spectra with a resolution of 1 cm^{-1}, and each spectrum was scanned 64 times to improve the signal-to-noise ratio. The FTIR data of 6 samples were clustered by principal component analysis (PCA).

Measurement of weight gain and shrinkage

The volume and mass of samples before and after reinforcement are recorded using electronic vernier calipers and precision electronic scales and then calculated: electronic balance was used to weigh the mass (R_A) of the saturated wood block, accurate to 0.001 g. The stringed, radial and axial dimensions of the saturated wood blocks were measured according to GB/ T1933-2009 "Wood Density Determination Method", and the volume was measured by drainage method. After that, the saturated wood blocks were placed into centrifugal tubes according to the numbering sequence, 3 sets of parallel samples were set for each concentration, and the prepared cork fat reinforcement agent was added respectively. The water-saturated sample was placed in a vacuum drying oven (DZF type, Shanghai Lichen Bangxi Instrument Technology Co., LTD.) for vacuum impregnation for 1 h, then removed, covered with a sealing cover and impregnated for 7 days. During this period, the mass, chord size, radial size, axial size and volume of the ancient wood were measured every 48 h. When the mass change of the sample was less than 0.1%, the penetration was completed. Vacuum freeze dryer (FD-1G-50, Shanghai Hefan Instrument Co., LTD.) was used to freeze dry the reinforced ancient wood and untreated water-filled ancient wood for 24 h to complete the dewatering and shaping of ancient wood.

The mass increase rate of wood is calculated according to the quality change of ancient wood before and after reinforcement:

$$\text{Mass increase rate} = \frac{R_B - R_A}{R_A} \times 100\% \quad (1)$$

Formula: R_A is sample weight before reinforcement (g), R_B is sample weight after reinforcement (g).

According to the volume change of the dry sample before and after reinforcement, that is, the swelling rate, the degree of swelling of the cell wall can be judged by the calculation formula as follows:

$$\text{Swelling rate} = \frac{V_2 - V_c}{V_c} \times 100\% \quad (2)$$

Formula: $\boldsymbol{V}_2$ is to strengthen treated the volume of ancient wood after freeze-drying (mm3);$\boldsymbol{V_c}$ is the volume of untreated ancient wood after freeze-drying (mm^3).

As a standard to measure the dimensional stability of wood, the formula for calculating the shrinkage resistance of wood is as follows:

$$\text{shrinkage resistance} = \frac{\beta_c - \beta_2}{\beta_c} \times 100\% \quad (3)$$

Formula: β_c and β_2 are respectively the dimensional shrinkage rates of untreated and reinforced ancient wood after freeze-drying, referring to GB\ T1932-2009 "Wood drying shrinkage determination Method", which can be calculated by formula (4) and (5)

$$\beta_c = \frac{L_0 - L_c}{L_0} \times 100\% \quad (4)$$

$$\beta_2 = \frac{L_0 - L_2}{L_0} \times 100\% \quad (5)$$

Formula: L_0 is the axial dimension of the saturated wood block; L_c is the axial size of untreated ancient wood after freeze-drying (mm); L_2 is the axial dimension of the reinforced old wood after freeze-drying (mm).

Surface contact angle

Hydrophobicity is one of the important indexes to measure the effect of ancient wood reinforcement. In this study, surface contact Angle was used to characterize the hydrophobicity of ancient wood reinforcement. The samples were placed in the oven with constant weight and dried at 103 ℃ ± 2 ℃ for 8 h. Then 2–3 samples were selected and weighed every 2 h. When the difference between the last two weights did not exceed 0.5% of the sample mass, the samples were considered to be 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 10 μL manual injection needle and 2 μL of water was dropped each time. The three sections of the sample were measured respectively, and take 10 photos of each section and take the average of the 10 measured values.

Color difference measurement

The Konica MinoltaCM-2600d spectrophotometer was used for color measurement and comparison. According to the CIE standard chromaticity system issued by the International Lighting Commission, the brightness (L*) and chromaticity index (a, b*) of untreated and reinforced ancient wood were measured by color chromaticity meter. 3 points were selected on the sample surface, and each point was measured 3 times, and the average value was taken. Where: L* is brightness, 0 is all black, and 100 is all white. ΔE* represents the overall integrated color difference.

In situ needle measuring instrument (impedance measuring instrument) detection analysis

The working principle of impedance meter detection is: using a small drilling needle with a diameter of 1.5 mm, the RESISTOGRAPH tree needle measuring instrument (impedance measuring instrument) produced by RINNTECH Company of Germany (R650-EA model) is used to detect the wooden bridge pile. After electricity is applied, it is inserted into the wood and the drilling resistance of the probe is measured in real time. Determine the stress of various parts of the wood and the internal decay of the tree, the cavity and the moth, etc., and evaluate and detect the problems existing in the wood.

Results and discussion

Identification of wood species, anatomical and structural characteristics of wood and assessment of wood preservation status

According to the microscopic characteristics of IAWA broad-leaved trees (IAWA Committee, 1989), The archaeological wood species were determined by comparing with the specimens and sections of the Wood Herbarium of the Chinese Academy of Forestry and referring to the Wood Annals of China. As shown in Table 1, by combining the analysis results of the anatomical structure and chemical structure of wood and comparing them with the sample data of the archaeological wood specimen library of the Wood Herbarium of the Chinese Academy of Forestry, the preservation status of the archaeological wood extracted from the site was assessed as low degradation, moderate degradation or severe degradation respectively [18–20].

Compressive strength along grain

Due to the different degrees of decay in different parts of wood, samples with cracks and large differences were removed during sampling in this experiment, and samples made on the same wood were grouped into one group for the reinforcement experiment.

The compressive strength obtained by different reinforcement methods is shown in Table 2. Compared with unreinforced samples, the strength of rosin reinforced samples increased by 110.35%, that of epoxy reinforced samples increased by 185.58%, that of glyoxal reinforced samples decreased by 23.58% compared with the treated group, and that of glyoxal reinforced samples with epoxy resin reinforced samples decreased by 54.71%. The results show that the sample strength strengthened by rosin is the best.

Rosin has a good reinforcement effect. Due to its natural nature, we chose different concentrations of rosin for reinforcement experiments in the follow-up experiments. As shown in Fig. 3, the strength of the whole sample was improved after the natural resin reinforced the sample's compressive strength along grain. When the rosin concentration exceeds 12%, the compressive strength of the rosin concentration increases greatly. The compressive

Table 1 Archaeological wood sample information and preservation status evaluation

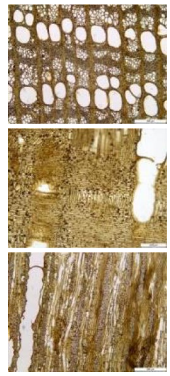
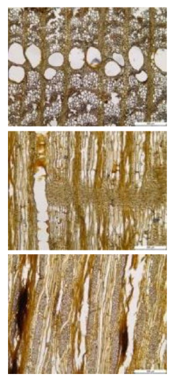
Sample information	Preservation status	Microscopic structure photos (transverse section, radial section and section)	Tree species
East chamber, bottom floor, coffin No. 2, pit wall side of the chamber.	Moderate degradation		Zelkova sp. Ulmaceae
East chamber, bottom floor, coffin No. 120, top.	Severe degradation		Zelkova sp. Ulmaceae
East chamber, bottom floor, coffin No. 119, top.	Severe degradation		Zelkova sp. Ulmaceae

Table 1 (continued)

Sample information	Preservation status	Microscopic structure photos (transverse section, radial section and section)	Tree species
East chamber, bottom floor, coffin No. 119, sole.	Moderate degradation		Zelkova sp. Ulmaceae
East chamber, bottom floor, coffin No. 120, sole.	Moderate degradation		Zelkova sp. Ulmaceae

Table 2 Compressive strength after different reinforcement methods

No	Thickness/mm	Width/mm	Height/mm	Contact area/ mm^2	Pressure/N	Compressive strength/kPa	Strength increase percentage%
1	9.10	12.87	23.62	117.12	483.15	4125.40	110.35%
2	10.65	13.19	24.30	140.47	786.74	5600.62	185.58%
3	10.88	13.73	25.57	149.38	223.89	1498.80	−23.58%
4	11.46	14.05	23.82	161.01	143.03	888.29	−54.71%
5	8.28	13.39	23.44	110.87	217.43	1961.17	Control

strength of the highest group is 10.9962 MPa, which is about 10 times that of the unreinforced sample. It was speculated that the natural resin formed a chemical bond with the hydroxyl group in the wood cell wall, which significantly improved the mechanical strength of the reinforced specimens, and met the requirements of cultural relics protection.

As shown in Fig. 4, the highest compressive strength of the epoxy five reagents reinforced was 8.29 MPa of 3:1 group, which was about 4 times that of the unreinforced sample.

Results of FTIR spectral cluster analysis of wood

The FTIR spectral analysis results of 6 archaeological wood samples from Zeng Hou Yi tomb are shown in Fig. 5. The main signals come from wood components, and it is impossible to determine whether reinforcement agents are present according to the existing data.

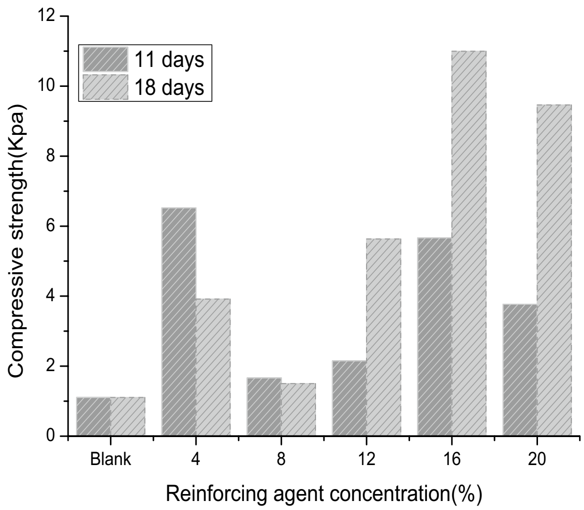


Fig. 3 Comparison of four times compressive strength after rosin reinforcement

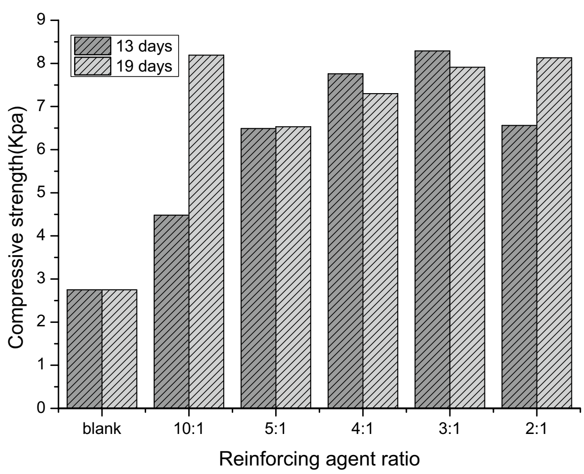


Fig. 4 Comparison of two compressive strengths after epoxy reinforcement

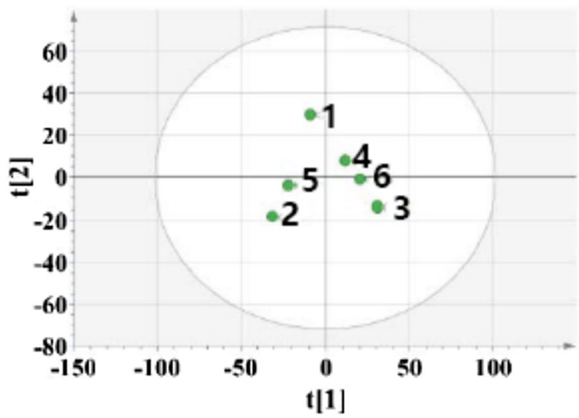


Fig. 5 FTIR spectral PCA clustering results of archaeological wood samples

On the whole, the hemicellulose degradation was serious in the cell wall of the samples, while the lignin was well preserved and the relative proportion increased, especially in the wood samples No. 2 and No. 3. The PCA clustering results are shown in Fig. 5. The larger the eigenvalue, the larger the variance of the matrix on the corresponding eigenvector, and the more discrete the sample points. Through cluster analysis, the high-dimensional data was converted into two-dimensional scatter display, and it was found that the 6 wood samples showed a discrete state, and the preservation status of different parts of the wood samples was significantly different. Among them, the degradation of No. 2 wood samples is the most serious, No. 3 and No. 1 wood samples also have relatively serious degradation, No. 4, No. 5, and No. 6 wood samples have less deviation, indicating that the lignin content is high, the degradation degree is low, and the material preservation condition is good.

Weight gain rate and shrinkage rate

Through the volume shrinkage rate, it can be seen whether the state of the cultural relic is stable during the reinforcement process. If the volume shrinkage rate is too high or too low, it indicates that internal deformation such as cracking or shrinkage may occur. It can be seen from Fig. 6 that with the increase in weight gain rate, volume shrinkage rate gradually increases. The weight gain rate of rosin reinforced at 20% ratio is the highest, reaching 173.8%, and the penetration and absorption effect is ideal. The volume shrinkage rate is 16.65% ~ 59.94%. In Fig. 6, the weight gain rate of epoxy reinforcement is the highest at 3:1 ratio, reaching 126.2%, and the volume shrinkage rate ranges from 26.61% to 62.86%. Compared with the results of the two groups, the penetration effect of rosin is better than that of epoxy, and it is speculated that a large number of pores inside the sample are filled by rosin and shellac. The volume shrinkage of rosin was more stable than that of epoxy group after reinforcement with different proportions of reagents. The experimental results show that the rosin reinforcement method is better than the epoxy reinforcement method in the compressive strength, weight gain rate and volume shrinkage rate, and the hydrophobicity is not as good as the epoxy reinforcement method Fig. 7.

Surface contact angle

If the hydrophobicity of the ancient wood is obviously enhanced after reinforcement, the water content inside

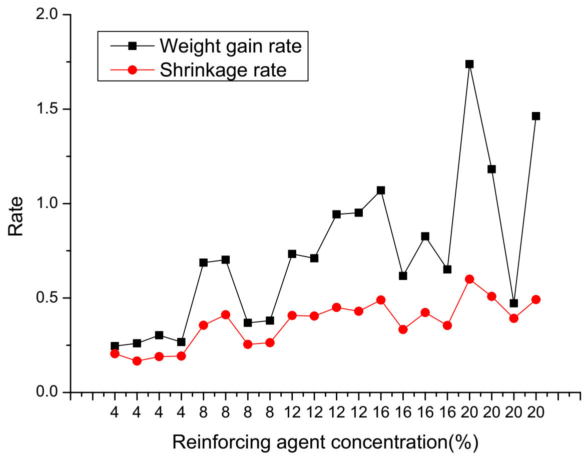


Fig. 6 Weight gain rate and shrinkage rate after rosin reinforcement in relation to the ratio of five reagents

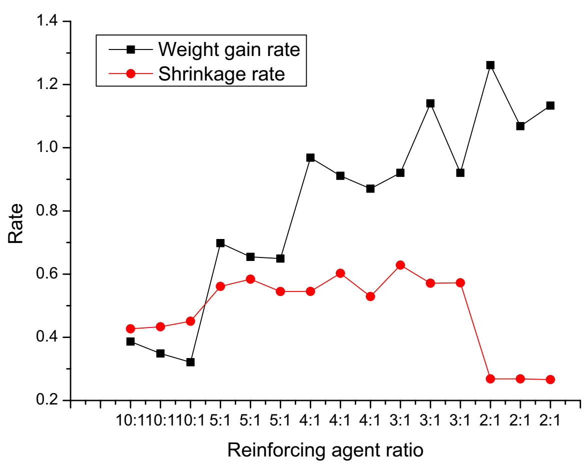


Fig. 7 Relationship between weight gain rate and shrinkage rate after epoxy reinforcement and the ratio of five reagents

the ancient wood can not meet the survival and reproduction of microorganisms such as fungi, which can improve the durability of the wood. Due to the dry and loose texture of the blank sample, water droplets quickly infiltrated the sample, and the surface contact Angle changed from 90.892° to 0°. However, the change of the contact Angle of the sample surface after rosin and epoxy reinforcement is obviously slow, which indicates that the hydrophobicity of the ancient wood is obviously improved by reinforcement. Both rosin and epoxy have strong hydrophobicity, which gives ancient wood better hydrophobicity, which is conducive to the long-term drying and stability of cultural relics [21–23]. Fig. 8

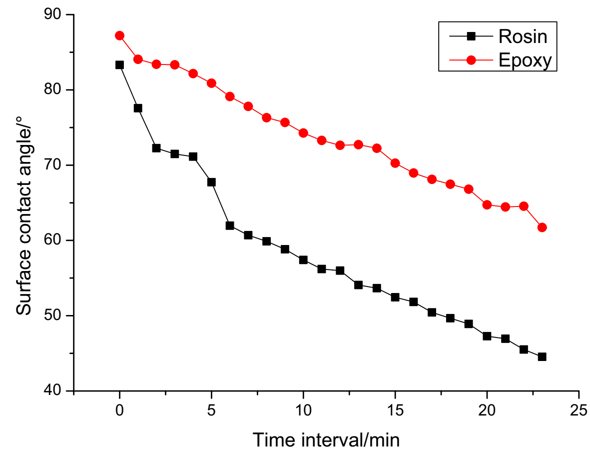


Fig. 8 Trend of surface contact angle

Chromatic aberration

As can be seen from Table 3 and Table 4, after different reinforcement methods, the average color difference ΔE value ranges from 0 to 30.9. Among them, the color difference after rosin reinforcement is larger, which has exceeded 30, and the color difference can be observed by the naked eye. The color difference of the sample after epoxy reinforcement is slightly smaller than that of rosin, which is basically less than 26.3. After the hardening, the overall appearance of the sample did not change greatly after natural drying, but the overall color of the 20% rosin group (20% rosin + 20% shellac + 60% anhydrous ethanol) after the hardening was darker than that of the epoxy group. Although the hydrophobicity of rosin reinforcement method is poor, it is significantly higher than that before reinforcement. Rosin and shellac make cultural relics hydrophobic, which can better maintain the internal drying of cultural relics, control humidity to prevent microbial diseases and avoid deformation such as expansion and contraction caused by humidity changes. The weight gain rate of rosin reinforcement is higher than that of epoxy reinforcement, and the volume shrinkage rate is more stable with the increase of concentration, indicating that rosin reinforcement has better absorption and penetration effect and less influence on the interior of cultural relics. Fig. 9

Impedance meter detection

From the impedance test data, the 18 charts in Fig. 10 can be divided into 6 groups, the first three groups are: ① point 1, point 7, point 13, ② point 2, point 8, point 14, ③ point 3, point 9, point 15, they are the same distance from the east, the last three groups are: ④ point 4, point 10, point 16, ⑤ point 5, point 11, point 17, ⑥ point 6,

Table 3 Color difference before and after rosin reinforcement

Sample	Concentration	Before reinforcement (ΔE)	After reinforcement (ΔE)	δ(ΔE)
Blank	Blank	65.00	65.00	0
1	4%	60.60	66.80	6.2
2	4%	55.90	65.50	9.6
3	4%	46.70	66.70	20
4	4%	45.10	68.50	23.4
5	8%	49.80	71.90	22.1
6	8%	51.40	74.90	23.5
7	8%	45.70	56.80	11.1
8	8%	57.30	75.70	18.4
9	12%	50.30	75.70	25.4
10	12%	55.10	75.10	20
11	12%	45.70	76.60	30.9
12	12%	53.80	77.70	23.9
13	16%	52.50	77.60	25.1
14	16%	56.10	78.40	22.3
15	16%	58.80	78.40	19.6
16	16%	50.30	71.90	21.6
17	20%	57.30	75.00	17.7
18	20%	61.10	76.70	15.6
19	20%	51.30	70.00	18.7
20	20%	56.20	75.00	18.8

Table 4 Color difference values before and after epoxy reinforcement

Sample	Proportion	Before reinforcement (ΔE)	After reinforcement (ΔE)	δ(ΔE)
Blank	Blank	66.30	66.30	0
1	5:1	62.70	70.30	7.6
2	5:1	66.70	64.60	2.1
3	5:1	60.90	58.3	2.6
4	4:1	64.00	74.40	10.4
5	4:1	60.50	76.50	16
6	4:1	61.40	72.1	10.7
7	3:1	56.90	80.20	23.3
8	3:1	54.70	79.00	24.3
9	3:1	55.70	54.4	1.3
10	2:1	53.70	80.00	26.3
11	2:1	63.50	79.90	16.4
12	2:1	58.80	71.1	12.3
13	10:1	54.30	75.9	21.6
14	10:1	53.70	74.3	20.6
15	10:1	62.20	69.9	7.7

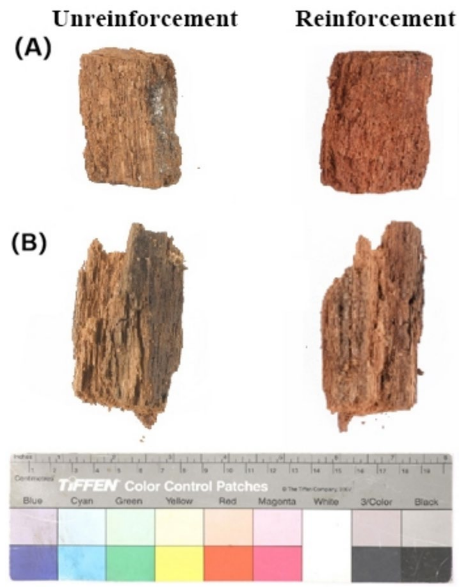


Fig. 9 Color change of wood before and after rosin (**A**) and epoxy resin (**B**) reinforcement

point 12, point 18, they are the same height. Through the overall analysis of the 6 groups of different data and the calculation of the average value, it can be seen that the overall impedance strength of the coffin from the tomb of Marquis Yi of Zeng is low, less than 10% of the impedance strength of modern wood.

Through a comparative study of 6 data groups, the research found that: the three charts in each set of data are relatively similar, because each set of data is distributed in the same wood along the grain direction, so their mechanical properties are also very similar. Among them, the analysis of the part of the six groups of data with a depth of 200–300 mm can find that the internal rotten distribution of the wood is uneven, the overall strength of the pulp is poor, and there are wood defects. The first four groups of data are particularly obvious, with an average amplitude of about 10% and low bit resistance, while the data of the fifth and sixth groups are relatively good, with an average amplitude of about 30% and normal bit resistance. It can be concluded that the defects of the wood pulp core are mainly distributed in the higher part of the wood pulp core, and the upper part of the wood pulp core has been damaged. Through the analysis of the parts with depths of 50–200 mm and 300–400 mm in the 6 groups of data, it can be found that the main parts of the wood are relatively complete, the overall strength of the xylem is similar to that of the pulp, and there are fewer cracks and rotten. Because the bit resistance of the third and fourth data is low, the amplitude is about 5% on average, the amplitude of the other group data is

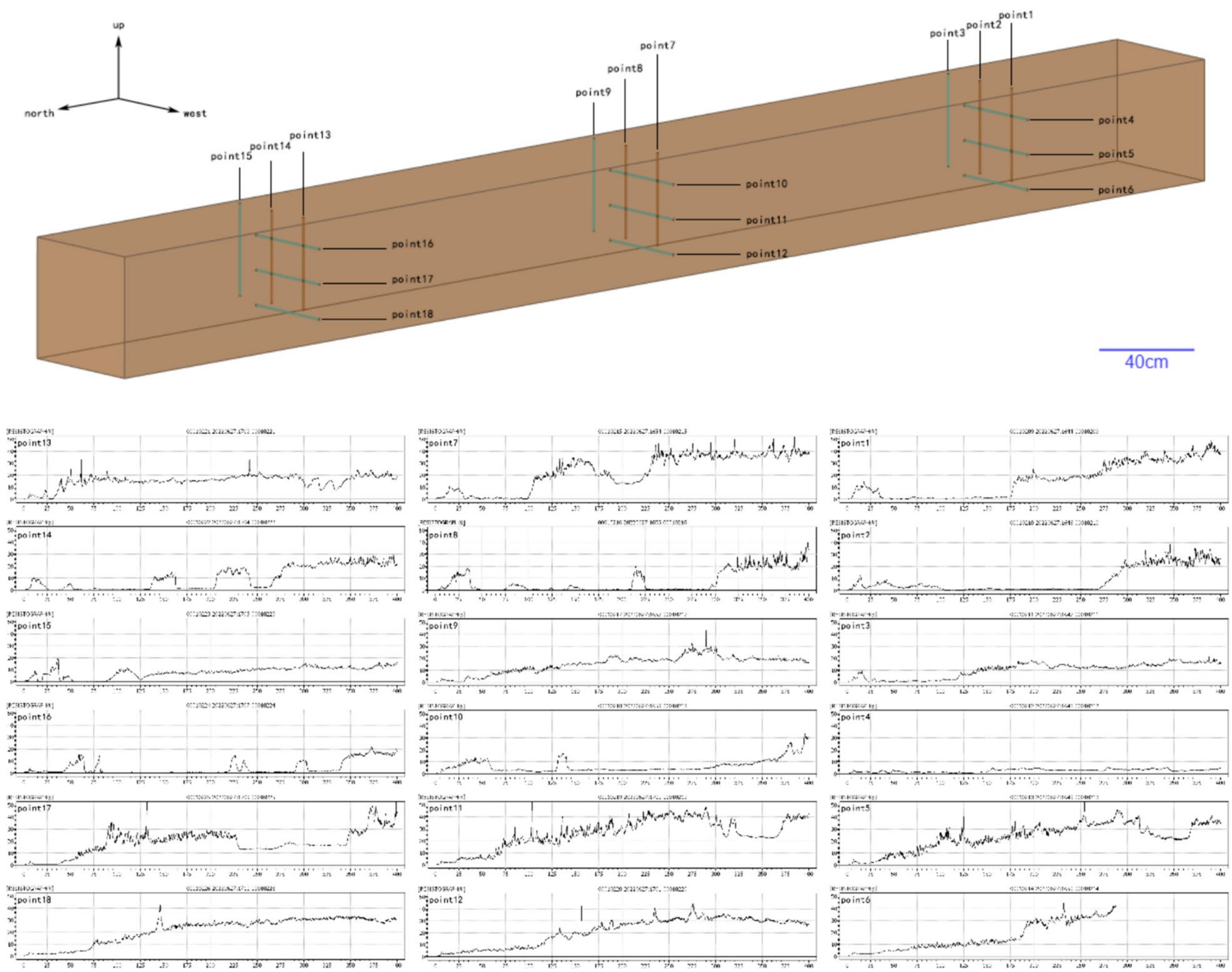


Fig. 10 Impedance test results of the sample after rosin reinforcement

about 20% on average, and the amplitude of the part with a depth of 300–400 mm is higher than that of the part with a depth of 50–200 mm in the first three data groups, all of which indicate that the wood defects in the xylem are mainly distributed in the upper and eastern parts of the wood.

Finally, by analyzing the parts with depth of 0–50 mm in 6 groups of data, it can be found that there are great differences in the strength of different positions of the wood surface, and the overall strength of the wood surface part is the worst. The bit resistance of the first three groups of data is significantly higher than that of the last three groups of data. The amplitude of the first three groups of data is about 5% on average, and the amplitude of the last three groups of data is about 2% on average. It can be seen that the defects of the wood surface are mainly distributed around the horizontal surface [24–26].

There is also a certain correlation between the bad rot of wood and the tree species. Most of the voids in the wood are invisible to the naked eye, and the voids are randomly distributed, which is related to the anisotropy of wood rot and dry shrinkage cracking, and the voids are relatively more distributed in the upper and eastern parts.

Conclusion

The study found that this batch of wooden coffins excavated from the tomb of Marquis Yi of Zeng had very different levels of structural decay in the outer layer, the transition layer and the inner layer. Macroscopically, the outer wooden coffins were cracked and warping in a wide range, and microscopically, the wood cells of each layer were seriously damaged, with thin cell walls and serious rot. The side layer cracking phenomenon is very serious, and the inner layer rot degree is also very serious. The tree species identification results of archaeological wood samples were all ulmus family.

Through the comparative study of the performance of rosin and traditional epoxy reinforcement, it is found that: rosin reinforcement performed better than the traditional epoxy reinforcement in the aspects of compressive strength along grain, weight gain rate and volume shrinkage rate. The hydrophobicity of the wood after reinforcement was poor, but it was significantly improved than that before reinforcement. In addition, the rosin reinforced wooden cultural relics and shellac make cultural relics hydrophobic, which can better maintain the internal drying of cultural relics, control humidity to prevent microbial diseases and avoid deformation such as expansion and contraction caused by humidity changes.

From the appearance point of view, the reinforced ancient wood can truly reflect its appearance before being buried, and the natural traces on the ancient wood (such as the sores and annual rings of the wood itself) and artificial traces (artificial knife and axe) are still preserved clearly and well. However, the natural resin reinforced ancient wood is closer to the color of modern wood, and from the perspective of dimensional stability, the dry shrinkage rate and wet expansion rate of natural resin reinforced ancient wood are the smallest. From the point of view of reinforcement shrinkage, the reinforcement shrinkage rate of natural resin reinforced ancient wood is the smallest, therefore, natural resin reinforcement method is suitable for large size, or serious water loss and easy shrinkage deformation of water-filled ancient wood. This method is also suitable for reinforced ancient wood whose ambient air humidity varies greatly with the seasons.

In summary, considering that the protection object is the large wooden coffin of Marquis Yi of Zeng, the overall reinforcement effect should be given priority compared with the color difference. In the case of large color difference between the rosin reinforcement group and the one before reinforcement, the rosin reinforcement group performs better than the epoxy reinforcement method in the aspects of compressive strength along the grain, weight gain rate and volume shrinkage rate, and improves its mechanical properties. In addition, methanol or ethanol can be used to dissolve the rosin shellac to achieve the reversibility of reinforcement. This project breaks through laboratory exploration and directly strengthens and protects large-sized water-saturated ancient wood, which can provide valuable experience for direct reference for the reinforcement and protection application of large-sized water-saturated ancient wood in the future.

Supplementary Information

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Supplementary Material 1.

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Author contributions
The manuscript was prepared through contributions of all authors. Hua Chen planned the study together with Jing Cao, conducted all data analysis, and wrote most of the manuscript. Shaohui Chen, Changxiong Wu, Bingjie Mai and Zhuofeng Chen contributed to the collection of samples in the article. All authors have given approval to the final version of the manuscript.

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Availability of data and materials
The datasets used and/or analysis results obtained in the current study are available from the corresponding author upon request.

Declarations

Ethics approval and consent to participate
Ethics approval was not required for this research.

Competing interests
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.

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