

Antimicrobial hydrogel patches for deacidification and conservation of waterlogged archaeological wood

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ABSTRACT

The Nanhai No. 1 hull, a Chinese merchant ship sank during the Southern Song dynasty and excavated from the South China Sea, is an example of underwater cultural heritage waterlogged wood that has been preserved in situ for centuries. Although the overall structure of the wooden artifacts is still intact they are severely degraded and acidified. It is now urgent to explore effective approaches for its conservation, we explore the feasibility of antimicrobial hydrogel patches. Antimicrobial hydrogel patches dispersed with antibacterial and deacidification nanoparticles simultaneously deacidify, moisturize, and reinforce both antibacterial and mechanical aspects of waterlogged wood. In the construction of the antimicrobial hydrogel patches, the double network hydrogel was used to prepare the hydrogel substrate with stretch and mechanical strength. We have successfully applied the antimicrobial hydrogel patches to the waterlogged wood from Nanhai No. 1, with the support of the Maritime Silk Road Museum of Guangdong. We demonstrate here the advantages of hydrogel patches to protect waterlogged wood with testing in deacidification, compression and antimicrobial.

KEYWORDS: Underwater cultural heritage waterlogged wood; Antibacterial (preserve); Nanhai No. 1; Deacidification; Antimicrobial (preventative); Mechanical support (protect against the harsh external conditions)

INTRODUCTION

In 2007, the 800-year-old Nanhai No.1 shipwreck hull was raised from the seabed and moved to the Marine Silk Road Museum, where it was conserved (Z. Liu et al. 2018). Early studies of the wood at the museum showed that the structural damage of the underwater cultural heritage (henceforth UCH) waterlogged wood, composed of softwoods, was severe to not withstand long-term spray deacidification and moisture retention (Huang et al. 2021; R. Li et al. 2022; Z. Liu et al. 2018; Yin et al. 2019). As the archaeological excavation continues on the Nanhai No. 1, like other conservation efforts the severe acidification and salt deposition on the surface is an important challenge for the protection of the UCH (Amornkitbamrung et al. 2015; Babiński et al. 2017; Baglioni and Giorgi 2006; Cavallaro et al. 2017; Chelazzi, Giorgi, and Baglioni 2006; Dong et al. 2010; Durán et al. 2016; Eriksen, Gregory, and Matthiesen 2017; Giorgi, Chelazzi, and Baglioni 2005; Giorgi et al. 2002; L. Liu et al. 2019; Mahltig et al. 2008; Majka, Babiński, and Olek 2017; Piotrowska and Konieczny 2015; Poggi et al. 2016; Sandström, Fors, and Persson 2003; Sandström et al. 2002; Schofield et al. 2011; Walsh-Korb 2022; Walsh-Korbs and Avérus 2019; Y. Li et al. 2022; Zelinka 2014; Zhou, Wang, and Hu 2021). Temperature, salinity, fungi, and bacteria are the cause of the severe cell wall decay (Capretti et al. 2008; Colombini et al. 2009; Hoffmann and Jones 1989). To neutralize the sulfuric acid and add antimicrobial protection for UCH waterlogged wood we prepared and applied an antimicrobial hydrogel patch. Antimicrobial hydrogel patches dispersed with antibacterial and deacidification nanoparticles simultaneously deacidify, moisturize, and reinforce both antibacterial and mechanical aspects of waterlogged wood (Gong 2014; Gong et al. 2003). This antimicrobial hydrogel patch served as mechanical support, deacidification, and antibacterial functions, during post-excavation conservation and prior to the addition of consolidates (Bai et al. 2019). We conducted

a thorough literature review of shipwreck conservation of waterlogged woods; here we demonstrate in collaboration with the Maritime Silk Road Museum of Guangdong the advantages of antimicrobial hydrogel patches to protect waterlogged wood on the Nanhai No. 1 hull with testing in deacidification, compression, and antimicrobial.

EXPERIMENTS

Materials

The UCH waterlogged wood from the Nanhai No. 1 shipwreck was generously provided by the Maritime Silk Road Museum of Guangdong with a maximum moisture content of around 529%. The UCH waterlogged wood was stored in 0.5wt% isothiazolinone solution and washed with excess amount of water three times prior to conservation. The following chemicals were purchased: Acrylamide (AR, 99.0%) and sodium citrate (98%) from Aladdin; Potassium persulfate (GR, 99.9%), potassium bicarbonate (AR, 99.5%), and N,N,N',N'-Tetramethylethylenediamine (99%) from Macklin; N,N-methylenebisacrylamide (MBAA, 98%) from Maya Reagent; Silver nitrate (99%) from Alfa Aesar; Calcium Sulfate (97%) from Rhawn; and sodium alginate (AR, 98%) from RYON. All chemicals were used directly without additional purification.

Method

We prepared the antimicrobial hydrogel patches and performed three tests: deacidification, compression and antimicrobial.

Preparation of antimicrobial hydrogel patches

12.44grams (g) of acrylamide and 1.56g of sodium alginate were dissolved in deionized water to form an acrylamide solution with a water content of 60-80 per cent by weight (wt%). After degassing the solution for one day, we added 0.0018g and 0.0036g of silver nitrate and 0.2g sodium citrate. Then we added 0.5g potassium persulfate, 0.0074g MBAA, 0.031g tetramethylethylenediamine and potassium bicarbonate (KHCO_3) at 1.5g, 2.5g, and 3.5g. The solution was transferred to a transparent mold and exposed to UV light (254nanometers (nm), 8 watts (W) power output) for one hour. The resulting hydrogel was carefully removed from the molded and immersed in calcium sulfate solution for 20-40 minutes.

Deacidification test

The Nanhai No. 1 UCH waterlogged wood was wrapped for three hours with the antimicrobial hydrogel patch (see recipe above). The pH of the UCH waterlogged wood was measured by soaking 1g in 30g of deionized water for 30 minutes and measuring the pH of the soaking water (Mettler Toledo, FE28). The pH meter was calibrated with a standard solution before use.

Compression test

A compression test was conducted using a universal tensile tester (Haida Instrument, HD-A513). The displacement as a function of force was measured for the synthesized hydrogels with the KHCO_3 concentration at 1.5g, 2.5g, and 3.5g and compression speed of 116 millimeters per minute (mm/min).

Antimicrobial test

The antimicrobial performance of the hydrogels was measured via disk diffusion test based on Oxford cup method. Briefly, the prepared agar medium was sterilized at 121°C for 15 minutes, and cooled to about 55-50°C before pouring into a petri dish to form the bottom layer of agar gel. Then, E. coli culture grown in sterilized lysogeny broth (LB) media was applied on the surface of the agar media.

After one day when the *E. coli* culture completely covers the agar media, the prepared hydrogel was grinded into a flowable state and added dropwise into an Oxford cup. With 37°C and one day incubation, the antimicrobial performance was evaluated based on the zone of inhibition around the Oxford cup.

RESULTS AND DISCUSSION

In this paper, an antimicrobial hydrogel patch used in the early stages of UCH waterlogged wood conservation was prepared using weak alkaline compounds. Fig. 1a shows a sample of the waterlogged wood. Water was sprayed routinely to maintain the water content of the waterlogged wood. Waterlogged wood, on the hull of Nanhai No.1 shipwreck, in some areas show heavy precipitation and bacterial decomposition (Fig. 1b 1c and 1d).

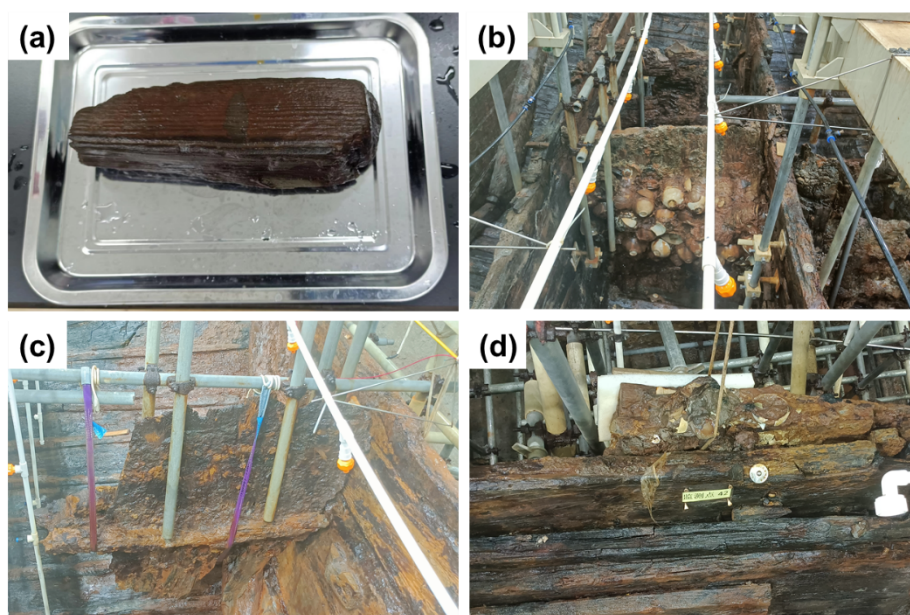


Figure 1 waterlogged wood (a) with precipitation cleaned; (b) on the hull of Nanhai No.1 shipwreck; (c) and (d) with severe bacterial decomposition.

Another advantage of the hydrogel deacidification material is that it is soft and easily stretches to change shape. The tensile and compression properties were measured. Fig. 2a and 2b are photographs of released and stretched hydrogel, respectively. More than 1000% elongation was achieved with the polyacrylamide/alginate hydrogel with silver nanoparticles dispersed.

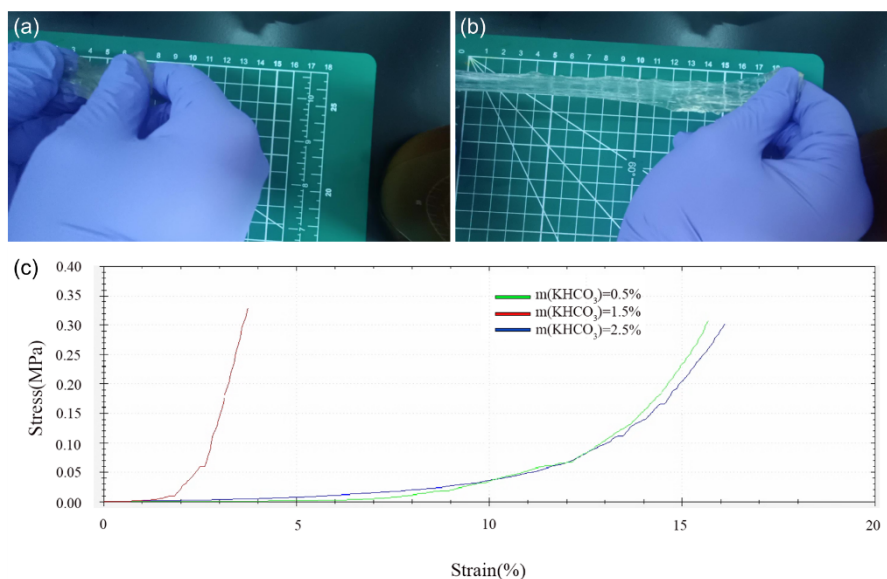


Figure 2 polyacrylamide/alginate hydrogel (a) at rest; (b) tensioned and elongated; (c) graph of compression with different KHCO_3 concentrations.

The hydrogels with 0.5% and 2.5% KHCO_3 are close in Young's modulus, while the hydrogel with 2.5% KHCO_3 has higher Young's modulus (Fig 2c), which might be caused by the difference in ionic crosslinking of silver and potassium ions. The hydrogel with potassium percarbonate was used to wrap the waterlogged wood (Fig. 3a-c). The weak alkaline KHCO_3 neutralized the sulfuric acid in the waterlogged wood, which resulted in a pH increase from 4.0 to 7.2 (Fig 3d). It was also confirmed that above 0.5% KHCO_3 concentration, the increase in KHCO_3 did not contribute to the pH increase remarkably. Gentle adhesion of the hydrogel to the wood neutralization occurs immediately, which lead to fast and significant pH increase. We suspect this is due to the large water content of the hydrogel, while also performing the adhesion underwater, is homogeneous.

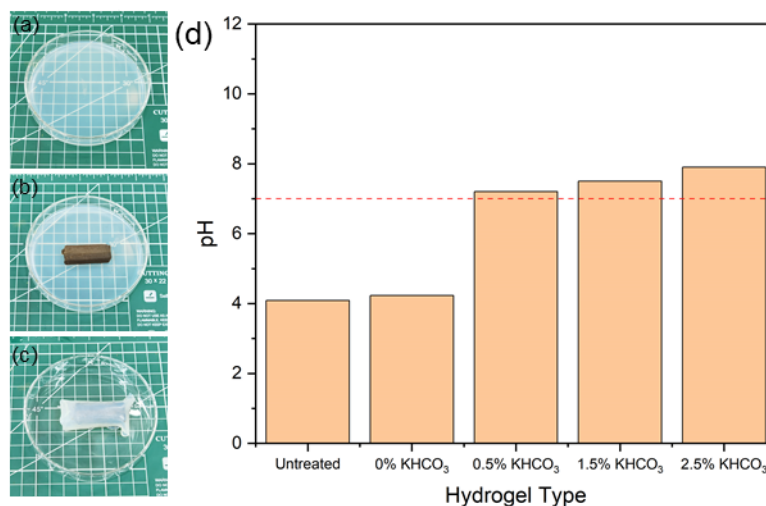


Figure 3 antimicrobial hydrogel (a) patch (b) patch and waterlogged wood (c) wrapped around waterlogged wood; (d) bar graph of pH test with different KHCO_3 concentrations.

The results of hydrogel antibacterial experiments proved it can protect waterlogged wood from bacterial degradation. When $30 \mu\text{g/mL}$ silver nitrate in the hydrogel was converted to silver nanoparticles, the antimicrobial properties of the hydrogels became sufficient to prevent bacterial degradation. Comparing Fig 4b and 4c, we see the increase of the silver nanoparticles from $30 \mu\text{g/mL}$

silver nitrate converted to silver nanoparticles to 60 $\mu\text{g/mL}$ silver nitrate converted to silver nanoparticles had less effect on the increase in antimicrobial properties.

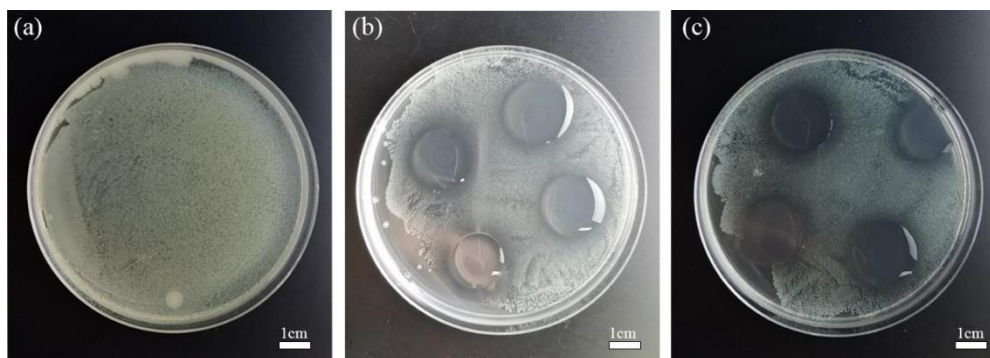


Figure 4 antimicrobial hydrogel with silver nitrate converted to silver nanoparticles (a) control sample without;(b) zones of inhibition caused by 30 $\mu\text{g/mL}$; (c) zones of inhibition caused by 60 $\mu\text{g/mL}$.

CONCLUSIONS

In this paper, we explore the feasibility of using antimicrobial hydrogel patches with excellent mechanical strength for conservation of waterlogged wood. We focused our testing on antimicrobial hydrogels deacidification and antibacterial properties. We noted the prepared hydrogel patches match well with weak alkaline and high water content properties to carry out ion exchange to reduce the acidity. Double network polymer structure was utilized to increase the stretch of the hydrogel, which provides mechanical support to the highly decayed softwood. These antimicrobial hydrogel patches can perform targeted restoration and preservation as indicated by our research and testing of UCH waterlogged wood from Nanhai No.1 with the help of the Maritime Silk Road Museum of Guangdong.

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ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (51972264).

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