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Super-hydrophobic Wood Composite with Plexiglass Coating

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Abstract

As a typical anisotropic material, wood exhibits significant volume expansion/contraction during the adsorption/desorption of water, increasing the risk of mold infection and cracking. Herein, we have designed a plexiglass coating on the surface of the wood to overcome this shortcoming. Based on the high light transmittance of the acrylic glass, the as-prepared composite material retains the original texture and color of the wood. Ethanol solvent enhances the wettability of methyl methacrylate (MMA) with wood, so that acrylic glass can grow in situ in shallow pores on the surface of the wood. The design enhances the interface contact between the plexiglass coating and wood. Further relying on the super-hydrophobic properties of stearic acid (SA), the composite wood exhibits long-lasting mildew and cracking resistance. The excellent comprehensive performance of composite wood has great application potential in the field of structure and decoration.

Keywords: Wood building material; Plexiglass coating; Superhydrophobicity; Crack resistance; Mildew resistance.
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1. Introduction

Wood, composed of cellulose, hemicellulose, and lignin, plays a very important role in the field of ecological architecture. The unique composition and microstructure endow wood materials with many advantages, such as a high strength-to-weight ratio, renewability, natural degradation, and dynamic adjustment of environmental humidity.[1-5] Most of the world-famous ancient buildings use wooden structures[6,7] such as the imperial palace (Beijing, China; AD 1406), yuntai temple (Mianyang, China; AD 1210), and foguang temple (Zhengzhou, China; AD 857). Unfortunately, hygroscopicity not only increases the risk of fungal and insect attack but also causeswood to crack under hygroscopic expansion and/or dehydration shrinkage.[8-11] As a consequence, long-lived wooden buildings are mostly distributed in arid high latitudes. To reduce hygroscopicity and improve the dimensional stability of wood materials, various protective techniques have been reported, such as high-temperature carbonization,[12,13] chemical modification,[14,15] inert medium filling,[16,17] and waterproof coating.[18,19] Fu *et al.* reported that irradiated pine wood subjected to heat treatment at 185–230 °C for 4 h. Water absorption ratio of the heat-treated wood decreased from 175% of the natural wood to 134%.[20] Carbonized wood loses its inherent color and elasticity.[21-23] The carbonization process is complex, making it unsuitable for the entire wood. Wood chemical modification technology refers to the chemical reaction between monomer/oligomer with functional groups and wood cell wall components, thereby reducing the moisture adsorption ability of wood material.[24,25] Chemical modification involves expensive, toxic, and difficult-to-recover reagents, leading to the fact that the modification technology has not yet been industrialized. Liu *et al*. prepared a composite wood loaded with 11% furfuryl alcohol resin by the vapor physical deposition method.[26] Shen *et al*. used TiO_2 sol and paraffin emulsion to treat wood to improve the weather resistance of the material.[27] Lacking a bonding mechanism, inert media such as vegetable oil are not easily filled in wood efficiently and reliably.[28,29] The non-transparent nature of the coating such as paraffin wax, and paint causes wood to lose its intrinsic color and texture, and there is a risk of peeling off.[30] In this work, we employed a simple solution polymerization reaction to in-situ grow a hydrophobic plexiglass coating on the surface of wood materials in Fig. 1. Based on the high transmittance of plexiglass, composite wood exhibits the

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natural texture and color of the wood. Under the action of ethanol solvent, methyl methacrylate polymerizes in the shallow pores of the wood, thereby strengthening the interfacial interaction between the coating and wood. Benefiting from the hydrophobic coating, the equilibrium adsorption capacity of the composite wood to water vapor only accounts for 1/3 of that of natural wood. As a result, composite wood exhibits long-lasting mildew and cracking resistance.

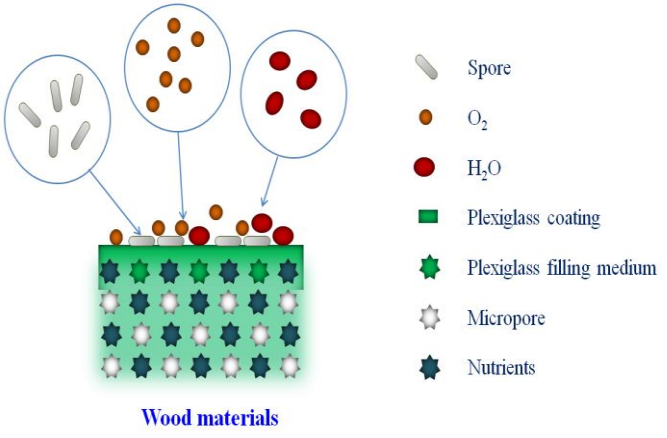

Fig. 1 Schematic diagram of mold and crack resistance of the composite wood.

2. Experimental section

2.1. Material

All the experimental chemicals were of analytical grade and used without further purification. Methyl methacrylate (99%), benzoyl peroxide (BPO, 99%), stearic acid, and absolute ethanol (99.5%) were supplied by Aladdin (Shanghai, China). Porous balsa and red willow wood materials were purchased from Cao County Huahui Wood Industry Co., Ltd.

2.2. Preparation of composite wood

Plexiglass coating was prepared by free radical polymerization of MMA.[31,32] 6 g MMA and x g SA were dissolved in 6 mlethanol at 50 °C, and then wood materialsare soaked in a mixture for 24 hours. 0.04 g BPO as an initiator was added and stirred continuously at 85 °C for one hour. The wood was transferred to an incubator at 90 °C for 24 hours to obtain WPS-xg (x = 1, 2, 3, and 4) composite wood. Finally, the composite was placed in a vacuum environment at 60 °C for 24 hours to fully remove ethanol and unpolymerized methyl methacrylate. Similarly, composite wood without the addition of super-hydrophobic SA is named WP.

2.3 Characterizations

FT-IR spectra were recorded on a Fourier transform infrared spectrometry (FT-IR, Nicolet 5700, USA) using PCM composite (4,000–500 cm^{-1}). The surface morphology investigation was carried out on a field emission scanning electron microscope (FE-SEM, Hitachi S4800). Before the FE-SEM investigation, the samples were sputtered with gold. Powder X-ray diffraction (XRD) measurements were performed using Cu Kα (λ = 0.154056 nm) radiation with a step size of 0.03° in the 2θ range of 10° to 60°. The transmittance of the plexiglass composite was measured with a commercial tester (LS116, China) at a wavelength of 550 nm. Compression tests were performed on the wood materials using a commercial tensile tester (MTS E44) at room temperature. The test sample was cut into a cubic shape with a length of 30 mm, width of 30 mm, and thickness of 60 mm.

3. Results and discussion

The WPS-2g composite wood loaded with 5.9% plexiglass was prepared by in-situ polymerization in ethanol solution, based on the fact that both SA and MMA were easily soluble in hot ethanol. As shown in Fig. 2a and Fig. S1, the composite wood with a PMMA/SA coating still retains the natural texture and color of the wood. Fig. 2b is the FE-SEM images of the WPS-2g composite wood. A plexiglass coating with a thickness of 100–500 μm was observed on the wood surface. Through the solubilization of ethanol, PMMA and SA were filled in the pores of wood material with a filling depth of less than 300 μm. The smart design increases the interface force between wood and hydrophobic coating. On the other hand, wood composites possess the porous properties inherent in balsa wood, with thermal insulation and sound absorption properties. According to Fig. 2c, the PMMA glass obtained by solution polymerization is still amorphous, with a light transmittance of 88.5%. After ethanol evaporation, polymethyl methacrylate (PMMA) is cross-linked to form a dense glass (Fig. S2). For WPS-2g composite wood, characteristic diffraction peaks of stearic acid were detected at 6.7, 11.2, 21.7, and 24.2°, indicating that SA was physically dispersed in PMMA. FT-IR spectrum further proves that there is no chemical reaction between wood, PMMA, and SA (Fig. 2d). Fig. 2e is compressive stress–strain curves of the natural wood, WP, and WPS-2g. Yield stress of the WPS-2g with an m_{PMMA}/m_{SA} mass ratio of 3:1 increases from 6.9 kPa of natural balsa wood to 11.6 kPa. The cross-grain compression test also shows that the plexiglass coating increased the yield stress of wood material in Fig. S3.

Figure 3a is digital photos of the natural wood, WP, and WPS-2g. Natural wood is a hydrophilic material. Spherical water droplets were observed on the surface of WPS-2g composite wood, indicating that the PMMA/SA coating with an m_{PMMA}/m_{SA} mass ratio of 3:1 further increased the hydrophobicity of the wood. The balsa wood shows a contact

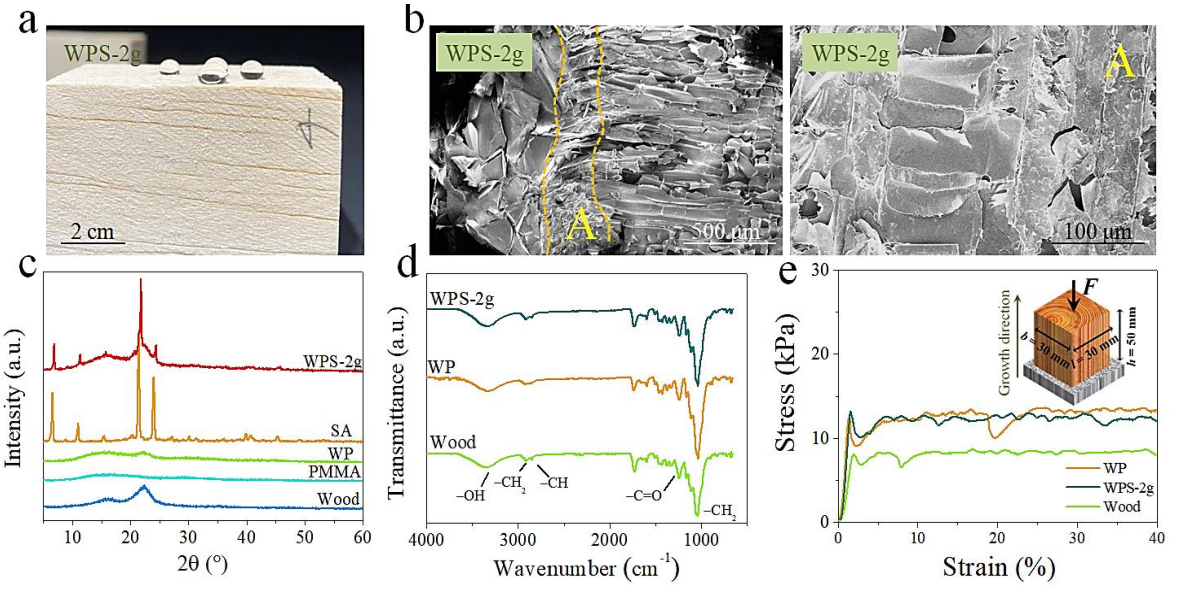

Fig. 2 Characterization of the WPS-2g composite wood. (a) Digital photo of the WPS-2g composite wood; (b) FE-SEM of the WPS sample; (c) XRD spectra of the natural wood, PMMA, SA, WP and WPS samples; (d) FT-IR spectra of the natural wood, WP and WPS composite; (e) Compressive stress–strain curve of the wood materials.

angle of 20.1° in Fig. 3b. For the WP, WPS-1g, and WPS-2g composite wood materials, the contact angles are equal to 60.5, 107.2, and 121.5°, respectively. After 30 days of exposure to a relative humidity of 90%, there is no significant change in the contact angle of the wood materials.When the wood materials are soaked in water at 25 °C for 30 days, the contact angles of the WP, WPS-1g and WPS-2g composites are equal to 51.7, 47.3, and 114.5° in Fig. 3c, respectively. Therefore, the super-hydrophobicity of the composite wood with an m_{PMMA}/m_{SA} mass ratio of 3:1 withstands the test of simulated fog and rain. Fig. S4 is the hygroscopic curve of the balsa, WP, and WPS-2g wood materials at 25 °C during a humidity of 90%. The natural wood achieves adsorption equilibrium after 276 hours, with a maximum adsorption capacity of up to 76.2 g per 100 g of wood. For the WPS-2g composite wood, the equilibrium adsorption capacity is 27.2 g per 100 g of wood, accounting for about 1/3 of natural wood. Excellent waterproof performance means that the plexiglass coating with an m_{PMMA}/m_{SA} mass ratio of 3:1 is beneficial to the mildew and cracking resistance of wood material.

Mold resistance of the composite wood was carried out at 25 °C during a humidity of 90%, as shown in Figs. 4(a, b).

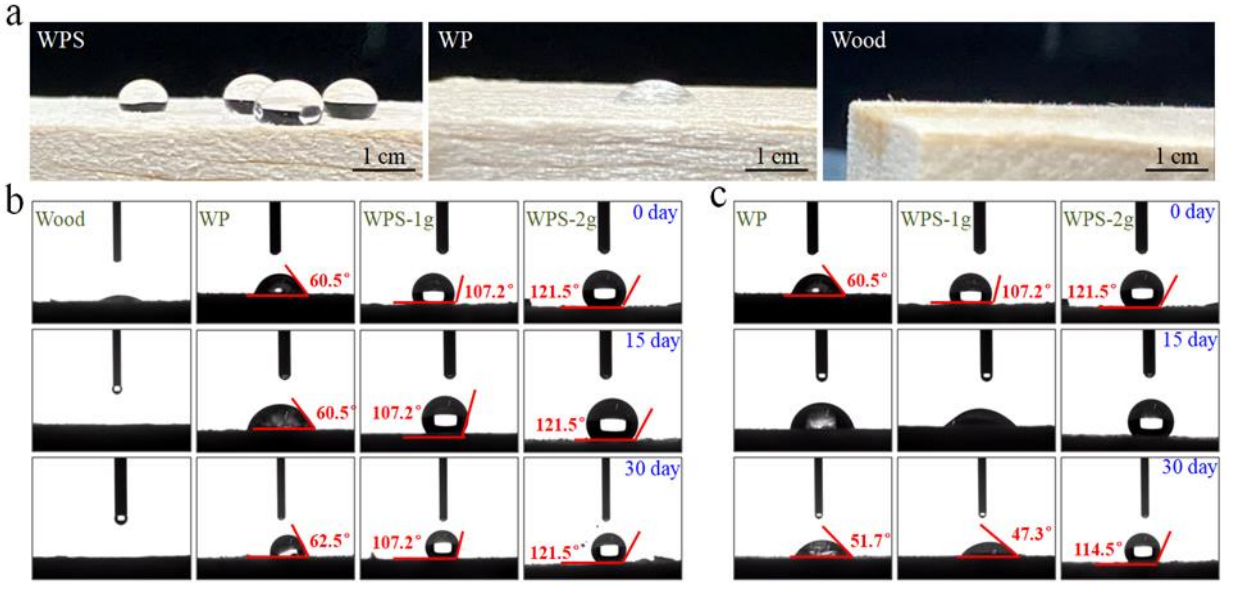

Fig. 3 Characterization of hydrophobicity of the composite wood. (a) Digital photo of the natural wood, WP, and WPS-2g; (b) Contact angle of the composite wood after 30 days of exposure to 90% relative humidity; (c) Contact angle of the composite wood after immersion in deionized water at 25 °C for 30 days.

After 7 days, obvious mold spots were observed on the surface of natural balsa and red willow materials. In contrast, the composite wood with a PMMA/SA coating always maintains its initial morphology. It is reasonable to speculate that the plexiglass coating blocks the contact of wood nutrients with spores, water, and oxygen in the air, resulting in improved mildew resistance. In addition, we observed mold on the surface of the WP sample. This indicates that the mildew resistance of the WPS-2g composite wood is also related to the hydrophobicity of the plexiglass coating with an m_{PMMA}/m_{SA} mass ratio of 3:1.

Fig. 4 Characterization of anti-mold and anti-cracking properties of composite wood materials. (a) Digital photos of the balsa-based composite wood after being placed at 25 °C for 15 days; (b) Digital photos of the willow-based composite wood after being placed at 25 °C for 7 days; (c) Cracking resistance of willow-basedcomposites during high-low temperature cycling. Note: Composite wood was placed at 25 °C for 12 hours during a relative humidity of 90%, and then transferred to an environment of 80 °C for 12 hours.

Figure 4c displays the crack resistance of the composite wood. After 5 cycles of high-low temperatures, dense cracks appeared in the radial section of the natural red willow wood, belonging to large cracks. For the WP wood with a plexiglass coating, small cracks appear on the cross-section. The hydrophobic coating with an m_{PMMA}/m_{SA} mass ratio of 3:1 protects the wood from cracking after 1000 temperature-humidity cycles in Fig. S5.

3. Conclusions

Mildew and cracking are problems that cannot be ignored in the practical application of wood materials due to the phenomenon of adsorption expansion and dehydration shrinkage. We have designed a synergistic anti-mold and crack technology by growing plexiglass composite film in situ on the surface of wood material. Composite wood maintains the original texture and color of the wood. With the help of the coating with an m_{PMMA}/m_{SA} mass ratio of 3:1, the mechanics, mold, and crack resistance of wood have been significantly improved. Experiments have revealed that excellent comprehensive performances benefit from the hydrophobicity and low moisture adsorption of the composite coating. The straightforward modification method may promote the application of wood materials.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Applicable.

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