Improvement of Bamboo Properties via *In Situ* Construction of Polyhydroxyethyl Methylacrylate and Polymethyl Methylacrylate Networks

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The chemical modification of bamboo culm was explored based on *in situ* construction of polyhydroxyethyl methylacrylate (PHEMA) and polymethyl methylacrylate (PMMA) networks into the cell walls. Scanning electron microscopy revealed that the synthesized polymers distributed in both the cell walls and the lumen with the pits blocked. The dimensional stability was tested under three water soaking-drying and moistening-drying cycles. The swelling efficiency of the treated bamboo was under 8% in three cycles of water soaking and drying cycles and was 4% in moistening-drying cycles. The anti-swelling efficiency was 60.5%, 52.7%, and 46.3%, respectively, in the moistening-drying cycles. Laboratory tests on mold resistance showed that no mycelium formed on the treated bamboo, while the untreated control was 100% covered by mold fungi.

Keywords: Polymer networks; Bamboo; Dimensional stability; Mold resistance

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INTRODUCTION

As an important renewable resource, bamboo has fast growth, large yields, high strength, and good toughness (Janssen 1991; Roach 1996). Bamboo products are widely used in household items, construction, furniture, packaging, and so forth (Lakkad and Patel 1981; McClure 1981; Lee and Liu 2003). Similar to wood, bamboo is mainly composed of cellulose, hemicellulose, and lignin, but it is rich in sugar and starch (Farrelly 1984), which provides more opportunities for mildew. In addition, bamboo contains a large number of hygroscopic groups and is anisotropic in the longitudinal, radial, and tangential directions, which causes splits, cracks, and deformation (Liese 1987).

There is great deal of research on preventing mold in bamboo. Chemical treatments are the most effective, using chemicals such as borate, 4,5-dichloro-N-octyl-3(2H)-isothiazolone (DCOIT), and 3-iodo-2-propynyl-butyl-carbamate (IPBC) (Wei and Qin 2011; Feng *et al.* 2016). Many efforts have been made to keep bamboo from splitting, cracking, and deforming. Heat treatment has been extensively researched and widely used to improve the dimensional stability of bamboo (Meng *et al.* 2016; Yang *et al.* 2016; Nishida *et al.* 2017). The pretreatment of bamboo with polyethylene glycol can lower the risk of cracks both under room temperature and higher drying temperatures (Kang *et al.* 2017). Modification of bamboo with chemicals, such as resins (Fadhlia *et al.* 2017), acetic anhydride, and silicon oil can also enhance its dimensional stability (Manalo and Acda 2009; Febrianto *et al.* 2012; Silviana 2014). During its outdoor usage, bamboo is susceptible to mold development, so it is necessary to improve its resistance to mold. The purpose of this paper was to find a way to simultaneously improve both the dimensional stability and fungi resistances of bamboo.

To enhance the bonding among transverse microstructures and impart hydrophobicity to bamboo, polymer networks based on hydroxyethyl methylacrylate (HEMA) and methyl methylacrylate (MMA), with physical and chemical crosslinking, were constructed *in situ*. Biocides were loaded in the network to offer protection from fungi.

EXPERIMENTAL

Materials

Five-year old moso bamboo (*Phyllostachys heterocycla var. pubescens*) was collected from Lin'an city, Zhejiang Province, China. After removing the outer and inner surfaces, bamboo strips were machined into specimens with dimensions of (i) 20 mm (longitudinal) × 20 mm (tangential) × 5 mm (radial) for dimensional stability tests, and (ii) 50 mm (longitudinal) × 20 mm (tangential) × 5 mm (radial) for mold resistance tests. All specimens were oven-dried at 60 °C for 2 h, 80 °C for 2 h, and 103 °C for 4 h to a constant weight. The volume of samples (V_1) was calculated from the length, width, and height, with an accuracy of 0.01 mm^3, and the weight (W_1) was accurate to 0.01 g.

Methyl methylacrylate and hydroxyethyl methylacrylate were purchased from Aladdin Industrial Corporation (Shanghai, China) and used without removing the inhibitor. Ammonium persulfate (APS), 2,2'-azobis(isbutyronitrile) (AIBN) and N,N'-methylene-bis(acrylamide) (N, N'-MBA) from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), were of analytical grade and used as received without further purification.

Three mold fungi including *Trichoderma viride* Pers. Ex Fr. (T.V), *Penicillium citrinum* Thom (P.V), and *Aspergillus niger* V. Tiegh (A. N) were separated from natural mildew bamboo and purified several times under a microscope at the Key Laboratory of Forestry Microorganism at Zhejiang Agriculture and Forestry University.

Methods

In situ construction of PHEMA and PMMA in bamboo

The modifying solutions were prepared as follows: 10 mL of MMA and 30 mL of HEMA were dissolved in 30 mL of ethanol and 90 mL of distilled water, respectively, under constant stirring at room temperature. The monomer solutions were mixed with APS and AIBN initiators at 1% (w/w) with respect to the weight of the monomers, and 2% N, N'-MBA was added as a crosslinker to the total monomers. To construct biocide-loaded polymer networks in bamboo, a combination of propiconazole and iodopropynyl butylcarbamate (PI, w/w = 4:3, PI) was added to the above solution.

Bamboo treatment was conducted under vacuum. The dried samples were placed in the impregnation apparatus and vacuumed at 0.1 MPa for 60 min before being impregnated with the modifying solutions. After treatment, the specimens were wrapped in foil and heated at 80 °C for 3 h to cure the monomers. The samples were unwrapped and dried at 103 °C for 4h to a consistent weight (W_2). The volume (V_2) was measured, and the polymer loading (PL) and bulking efficiency (B) were calculated by Eqs. 1 and 2,

$$PL = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

$$PL = \frac{V_2 - V_1}{V_1} \times 100\% \quad (2)$$

Scanning electron microscopy (SEM)

Hand-cut sections from the modified bamboo were processed for imaging using a SS-550 (Shimadzu, Kyoto, Japan) operating at 120 keV accelerating voltage and room temperature.

Dimensional stability test

Three cycles of water soaking-drying cycles were used to evaluate the influence of water on bamboo dimensions. According to GB/T 1934.2 (2009) and GB/T 1932 (2009), the specimens were first submersed into water at 25 °C for 72 h, and the increase in volume was calculated. The samples were oven-dried at 60 °C for 2 h, 80 °C for 2 h, and 103 °C for 4 h to a constant weight, and the decreases in volume were obtained. This procedure was carried out over three water-soaking and oven-drying cycles.

The use of water soaking-drying cycles for the determining dimensional stability of bamboo is a severe test, and it does not necessarily reflect the conditions that bamboo encounters in service. As a result, the dimensional stability was determined by subjecting the samples to three cycles of moistening-drying conditions. The moistening processes were performed at 25 °C with a relative humidity of 85%, and the oven-drying procedures were the same as mentioned above.

The dimensional stability was reported as the swelling efficiency (S_w), shrinking efficiency (S_k), and anti-swelling efficiency (*ASE*). These quantities were calculated according to Eqs. 3 to 5,

$$S_{\mathrm{w}} = \frac{V_{\mathrm{tn}} - V_{0\mathrm{n}}}{V_{0\mathrm{n}}} \times 100\% \quad (3)$$

$$S_{\mathrm{k}} = \frac{V_{0\mathrm{n}} - V_{\mathrm{tn}}}{V_{\mathrm{tn}}} \times 100\% \quad (4)$$

$$ASE = \frac{S_{\mathrm{wn}} - S\prime_{\mathrm{wn}}}{S\prime_{\mathrm{wn}}} \times 100\% \quad (5)$$

where the V_{tn} is the size of block after water soaking or moistening for n times and V_{0n} is the size of block after drying n times, where n = 1, 2, 3. S_{wn} is the swelling efficiency of the untreated bamboo, and S'_{wn} is that of modified bamboo.

Table 1. Standard Method for Rating the Infection Value

Infection Value	Mold Coverage on Specimens
0	The surfaces of specimens have no mycelium
1	The area of mold infection < 25%
2	The area of mold infection 25% to 50%
3	The area of mold infection 50%to75%
4	The area of mold infection > 75%

Mold resistance test

To determine the mold resistance of the bamboo after *in situ* construction of PHEMA and PMMA and PI loaded PHEMA and PMMA, anti-mold tests were performed on the treated and untreated bamboo according to GB/T 18261 (2013). After inoculating the target fungi, the growth of fungi was estimated visually under a score scale of 0 to 4, with 4 being the maximum intensity (Table 1).

RESULTS AND DISCUSSION

Dimensional Stability of Bamboo Treated with PHEMA and PMMA

An increasing gap between the filaments resulting from moisture permeability leads to the dimensional change of bamboo. By inserting a modifier into the gaps when they reach the maximum swelling and then limiting the return to their original state when the moisture is reduced, a stable dimension can be achieved (Liu and Meng 2003). The polymer loading and bulking of the treated bamboo were 8.7% and 3.6%, respectively, which suggested that the modifier entered and stayed inside the bamboo, even penetrating the cell wall. The volumetric swelling was determined after three cycles of water soaking-drying, as well as three cycles of moistening-drying (Figs. 1 and 2). The swelling efficiency of the treated bamboo in the three cycles of moistening-drying procedures were 6.8%, 7.1%, and 7.6%, respectively. These results were much lower compared with those of controls at 9.7%, 11.0%, and 10.6%, which indicated that the modified bamboo showed improved resistance against water swelling. The shrinking efficiency of the treated bamboo was also determined and averaged between 3.6% and 4.1% lower than the untreated controls. To better understand the swelling and shrinking of treated bamboo under fluctuating atmospheric humidity, bamboo specimens were tested in three cycles of moistening-drying. The swelling efficiency values of treated bamboo were 1.9%, 2.1%, and 2.5%, respectively, which was much lower than those of the controls at 4.7%, 4.5%, and 4.7%. Similar results were observed from the shrinking efficiency. The reduced swelling and shrinking efficiency of modified bamboo compared with the untreated controls indicated that a polymer network were probably formed in bamboo and played an important role in restraining water and moisture penetration and maintaining the volume of bamboo.

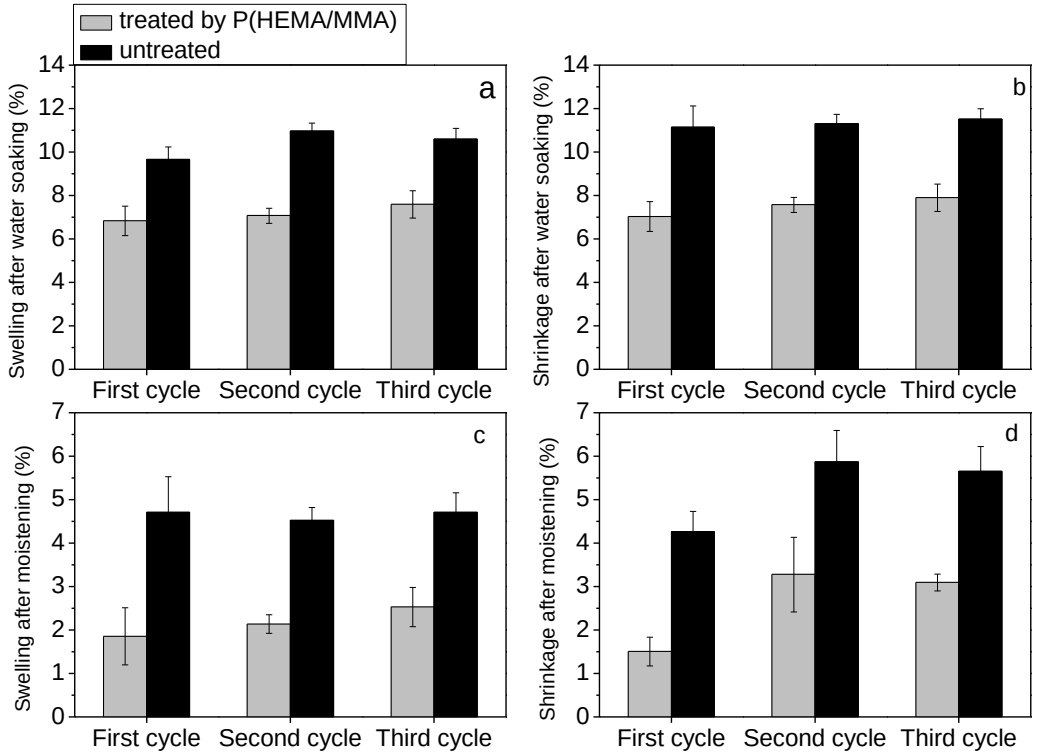

Fig. 1. Swelling and shrinkage of bamboo under water-drying cycles (a and b) and moistening-drying cycles(c and d)

Figure 2 represents the ASE of bamboo in the three cycles of water soaking-drying and moistening-drying procedures. Interestingly, when subjected to water soaking-drying cycles, the anti-swelling efficiency was above 28.3%, and anti-shrinking efficiency was above 31.4% during three cycles. These results suggested good resistance against shrinking. Under moistening-drying cycles, both the anti-swelling and anti-shrinking efficiencies were above 44.1%, even over 60% during the first cycle. The high ASE was attributed to the formation of a crosslinked PHEMA/MMA network in the bamboo cell wall and lumen, which could absorb limited water and had a lower swelling efficiency. In addition, when exposed to water, the polymer became swollen and blocked the pits, which reduced the penetration of water and moisture, thus improving the ASE of bamboo. However, the ASE tended to decrease with the increase of cycle times, which might be related to the swelling of the PHEMA/MMA polymer and the breakage of water sensitive weak bonds, such as physical entanglement and hydrogen bonds. Therefore, to obtain higher resistance against water and moisture, more chemical bonding and crosslinking are required.

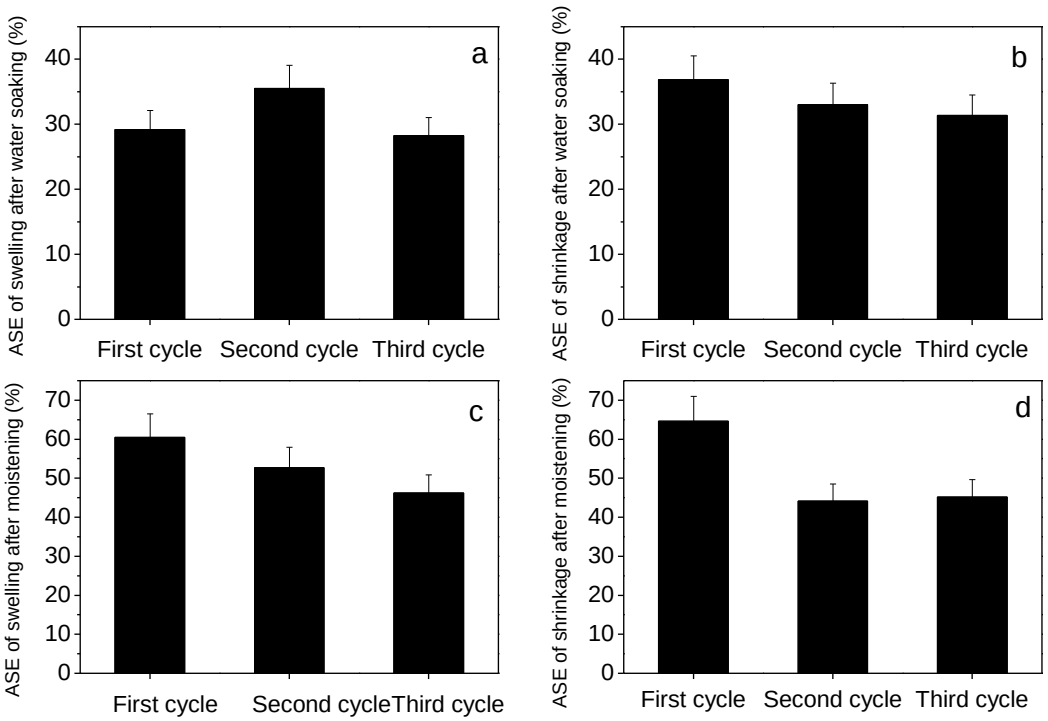

Fig. 2. ASE of treated bamboo (a) and (b) ASE of swelling and shrinkage after cyclic moisture treatment, (c) and (d) ASE of swelling and shrinkage cyclic water soaking treatment

Mold Resistance of Bamboo Treated with P(HEMA/MMA)

The polymer P(HEMA/MMA) partially blocked the pits and cell cavities of bamboo, which changed the composition and structure of bamboo. The mold resistance was improved, which might be attributed to the removal of necessary conditions for fungi (Sun and Duan 2004). Table 2 and Fig. 3 show the resistance of bamboo against *Trichoderma viride* Pers. Ex Fr. (TV), *Penicillium citrinum* Thom (PV) and *Aspergillus niger* V. Tiegh (AN). The untreated controls began to mold after 3 days, and the mycelium coverage developed over 50% (Infection value 3) after 15 days for all three test fungi. However, the modified bamboo resisted mold fungi, and no mycelium was found on bamboo specimens during the one-month laboratory test.

Table 2. Development of Mold on the Treated and Untreated Control Bamboo

Duration (Days)	*Aspergillus niger*		*Trichoderma viride*		*Penicillium citrinum*	
	Control	Treated	Control	Treated	Control	Treated
5	0.9±0.5	0.0±0.0	1.5±0.5	0.0±0.0	0.5±0.4	0.0±0.0
10	1.7±0.6	0.0±0.0	3.1±0.6	0.0±0.0	1.5±0.4	0.0±0.0
15	1.9±0.6	0.0±0.0	3.1±0.5	0.0±0.0	2.5±0.5	0.0±0.0
20	3.3±0.6	0.0±0.0	3.7±0.5	0.0±0.0	3.3±0.5	0.0±0.0
25	3.3±0.5	0.0±0.0	3.7±0.0	0.0±0.0	3.7±0.5	0.0±0.0
30	3.6±0.4	0.0±0.0	4.0±0.0	0.0±0.0	3.8±0.3	0.0±0.0

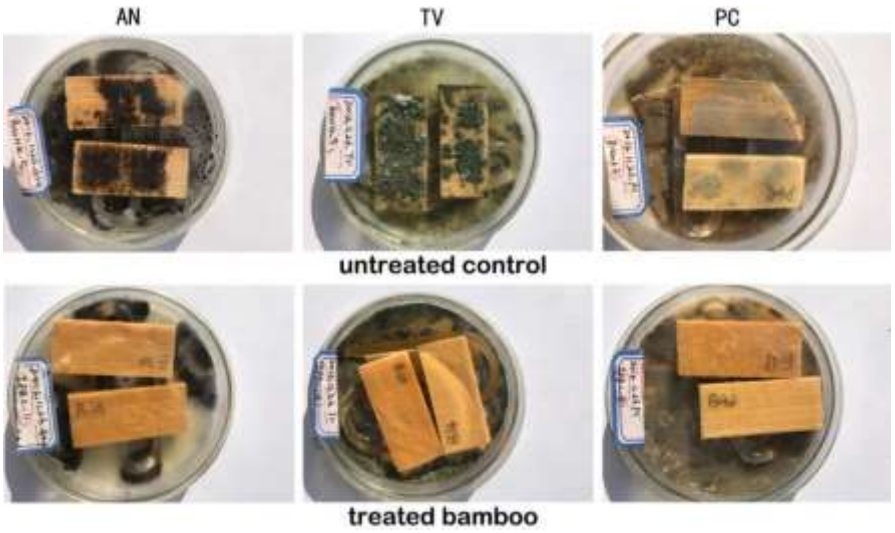

Fig. 3. Mold resistance against *Aspergillus niger* (AN), Trichoderma viride (TV), and *Penicillium citrinum* (PC) after 30 days cultivation

SEM of Bamboo

The microstructure of the treated bamboo was observed under SEM, and images of unmodified controls were also provided as references in Fig. 4. The starch granules in parenchyma cells were obvious in the controls but they disappeared after modification, as shown below. Starch can graft onto monomers or crosslink with polymers during initiating and crosslinking procedures (Haroon 2016). Starch is an important nutrient for mold fungi. Therefore, with the reduction of starch in the modified bamboo, the growth of mold fungi is expected to be retarded (Liese 2003; Sun *et al*. 2011). The cell wall and the inner layer of parenchyma cells were covered with polymers, as can be seen in the cross section. The pits were visible from the longitudinal section, and they were also covered and even blocked with the polymer (Fig. 4d), which reduced the absorption and conduction of water and moisture, and accordingly increased the dimensional stability of the bamboo. The modifying reagents formulated with monomer, initiators, and crosslinker were of strong permeability in the bamboo and formed a crosslinking polymer structure in the lumen, cell wall, and pits, which helps bamboo to resist water and fungi.

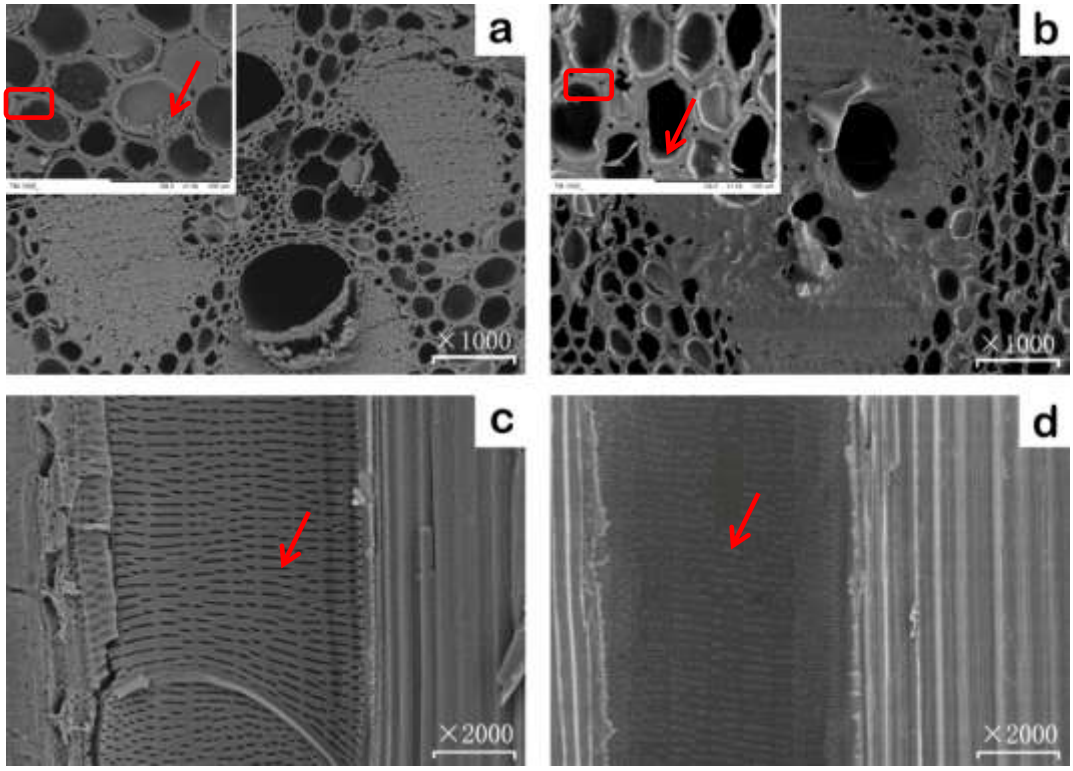

Fig. 4. SEM of untreated control (a and c) and treated bamboo (b and d)

CONCLUSIONS

1. The formulation of monomer, initiator, and crosslinker had good permeability in the bamboo, and SEM morphology showed that starch granules disappeared after modification. The formed polymer partially blocked the pit, cell cavity, and cell wall, endowing the treated bamboo with strong dimensional stability and mold resistance.
2. Under the water soaking-drying procedures, the anti-swelling efficiency was above 28.3% and the anti-shrinking efficiency was above 31.4% during the three cycles. Under moistening-drying cycles, both the anti-swelling and anti-shrinking efficiencies were above 44.1%, even over 60% during the first cycle.
3. No mold mycelium covered the treated bamboo during the 30 day laboratory mold test.

ACKNOWLEDEGEMENTS

The work was financially supported by the National Natural Science Foundation of China (31470587) and Key Natural Science Foundation of Zhejiang Province (Z14C160009).

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Article submitted: September 11, 2017; Peer review completed: October 22, 2107; Revised version received and accepted: October 26, 2017; Published: November 2, 2017.
DOI: 10.15376/biores.13.1.6-14