Study on Dimensional Stability of Bamboo Chemically Modified by Am/PVA Semi-IPN

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Abstract. This research discussed a new way to prepare a construction of polyacrylamid (Am) / polyvinyl alcohol (PVA) semi-interpenetrating polymer network (semi-IPN), using Am, PVA with ammonium persulfate (APS) and N, N’-methylenbis acrylamide (N, N’-MBA) as initiator and crosslinker, respectively, to improve the dimensional stability of bamboo. The PAM/PVA semi-IPN was characterized by FTIR, SEM and TEM. Bamboo samples were impregnated in vacuum with prepared solution, and then tested with the dimensional stability. The results showed that the physical cross-linking occurred between polymers of PAm and PVA. The pores and parenchyma of bamboo cells were filled up with polymers by SEM. The results of anti-swelling efficiency (ASE) of treated bamboo were 47.1%, 52.9% and 34.2%, respectively. The property of dimensional stability of treated bamboo was improved to some degree.

1. Introduction
Bamboo (Bambusoideae), a subfamily of the Gramineae[1-2], was perennial grasses with woody stems of culms, which was an abundant and inexpensive natural resource in China reliably used to replace woods in alleviating the contradiction between the supply and the demand of timber in many fields[3]. However, as a lignocellulosic material, the porous structure and abundant hydrophilic groups of bamboo lead to water absorption and hygroscopicity, which affects the dimensional stability of bamboo[4]. In addition, there were no radial organizations or formation of transfer layers in bamboo. Besides, the internal structure of bamboo cells was hollow, and the axial arrangement was tight, which led to poor shear strength of bamboo. So solving the problem of cracking was urgent to improve dimensional stability of bamboo to realize the efficient utilization of bamboo.

Dimensional stability was the degree of a material size or shape change under the action of temperature, humidity or external forces. Now the common treatment methods of dimensional stability were mainly heat treatment[3-4], phenolic resin treatment[5], polyethylene glycol treatment[4-5], treatment of hot melting paraffin[4,6], acetylation treatment[6] and isopropenyl acetate[3,6], etc. Bamboo tubes impregnated in the solution of PEG-1000 has been conducted to develop a new drying technology in order to quickly and massively dry without crack and check, and increase the dimensional stability of the products made of bamboo tubes[6]. Also, bamboo treated by
impregnation and soaking with medium molecular weight phenol formaldehyde (MMwPF) resin has been applied.

PAm was a nontoxic chemical with typical three-dimensional networks and stable performance[7]. However, the mechanical strength of PAm was low. To overcome the low mechanical strength of PAm, PVA was mixed to modify using the method of IPN. PVA was a widely used hydrophilic polymer with characteristics of processing ability, strength, pH, as well as temperature stability[6,8]. With the brilliant properties of materials, IPN has already been widely applied in various fields such as molding, tissue engineering and controlled drug-delivery[8].

2. Experimental

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2.1. Materials

Bamboo samples were taken from the three-year Moso bamboo(Phyllostachys heterocycla var. pubescens) without the yellow and green sides. The dimension test specimens were cut into 10 mm (longitudinal) ×10 mm (tangential) ×2.5 mm (radial). All the specimens were oven dried at a temperature of 65 ℃ for 2 h, then up to 82 ℃ for 2 h, and last up to 103 ℃ for 4 h to a constant weight. All the reagents in the experiment were purchased from Aladdin Reagent.

2.2. Method

2.2.1. Synthesis of PAm/PVA semi-IPN

PAm/PVA semi-IPN was prepared by free radical polymerization at temperature 82℃. 3.4 g of PVA were dissolved in 30 mL of distilled water at temperature of 82 ℃ up and to the total solution, 10 g of Am were added with 0.03 g of APS as initiator dissolved in 30 mL of distilled water. 0.01 g of N,N’-MBA was added as cross-linking agent. Then, the polymerization took place at temperature of 82 ℃ for 1h and at last, the final polymers obtained were soaked into distilled water for 5 days which was changed on a daily basis.

2.2.2. Preparation of PAm/PVA semi-IPN in situ of bamboo

Bamboo specimens for dimensional stability tests were performed on the controls and in situ polymerized PAm/PVA semi-IPN in bamboo and the specimens were treated with a given concentration of chemicals (Table 1). The samples were placed in the impregnation apparatus and the apparatus attached to the vacuum, reducing the pressure in the treating chamber to 0.1 MPa for 60 min before sucking in the prepared solutions. Then, the bamboo specimens were removed from the solution and wrapped inside tinfoil for polymerization to take place at temperature of 80 ℃ for 3 h. The samples were dried as in 2.1, and weighed (W2) and measured to get the volume (V2). The bulking efficiency (B) and polymer loading (PL) were calculated as follows:

\[ PL = \frac{W_2 - W_1}{W_1} \times 100\% \]

\[ B = \frac{V_2 - V_1}{V_1} \times 100\% \]

Where V2 is the volume of absolutely drying treated bamboo, V1 is the volume of absolutely drying untreated bamboo; W2 is the weight of absolutely drying treated bamboo, W1 is the weight of absolutely drying untreated bamboo.

The effectiveness of in situ constructed PAm/PVA semi-IPN in bamboo against mold was compared to that of two commercially used mold resistant chemicals, 0.2% of 3-Iodopropynyl butylcarbamate and 0.5% of a mixture of propiconazole and tebuconazole 0.5% PT, saw table1.
Table 1. Treatment bamboo specimens

| Samples | Treatment |
|---------|-----------|
| 1       | control   |
| 2       | PAm/PVA SIPN |
| 3       | 0.2% IPBC |
| 4       | 0.5% PT |

2.3. Characterization

SEM(SS-550), TEM and FTIR(IR Prestige – 21) were purchased from Shimadzu (Japan). Constant temperature magnetic stirrer was purchased from Yuhua instrument company, limited (China).

2.3.1. FTIR spectroscopy of PAm/PVA semi-IPN

The samples were placed in an oven up to a constant weight. Ground PAm/PVA semi-IPN powder samples with 200 mesh (0.15mm) were mixed with KBr crystals in a mass ratio of 1%, and pressed in a special mold to form a sample pellet which was used to take the spectra with FTIR over the range of 500-4000 cm⁻¹, 32 scans /min.

2.3.2. SEM of treated bamboo

The samples were placed in an oven until a constant weight. The morphology of PAm/PVA semi-IPN and the treated bamboo were observed using a Scanning electron microscope (SEM, SS-550) at 120 keV accelerating voltage and room temperature.

2.3.3. Dimensional stability test

Water-soaking and oven-drying series of cycles were used to evaluate the influences of liquid water on bamboo dimensions. The specimens were submersed into water at 25°C for 72 h, and the volume increase was calculated. They were oven dried as mentioned in Step 2.1 and the volume decrease calculated. This procedure was carried out over three oven-dry water soak cycles. Dimensional stability was then reported as the swelling coefficient (SW), shrinking coefficient (SK) and anti swelling efficiency (ASE), calculated as follows:

\[
SW = \frac{V_{tn} - V_{0n}}{V_{0n}} \times 100\%
\]

\[
SK = \frac{V_{0n} - V_{tn}}{V_{tn}} \times 100\%
\]

\[
ASE = \frac{S_{wn} - S'_{wn}}{S_{wn}} \times 100\%
\]

Where the \(V_{tn}\) is the size of block after immersing in water for \(n\) times; \(V_{0n}\)is the size of block after drying \(n\) times, \(n = 1, 2, 3\). The \(S_{wn}\) is of bamboo treated by PAm/PVA, and \(S'_{wn}\) is of the untreated bamboo.

3. Results and Discussion

3.1. FTIR of PAm/PVA semi-IPN

Fig.1 showed the FTIR of PAm, PVA and PAm/PVA semi-IPN. The peaks at 2275 cm⁻¹ and 2836cm⁻¹ of PAm were due to -N-C≡O and –CH2 respectively, and the characteristic bands in the range of 3000-3600cm⁻¹ attributed to the stretching vibration of the PVA hydroxyl groups(-OH). The peak of PAm/PVA IPN at 2275cm⁻¹ of -N-C≡O and 2836cm⁻¹ of –CH2 weakened resulted from the -H bond combination of –NH2 of PAm and the –OH of PVA in the presence of N,N-MBA. And the characteristic bands in the range of 3000-3600cm⁻¹ appeared of PAm/PVA semi-IPN, which indicated the existing of PVA.
3.2. SEM and TEM of PAm/PVA semi-IPN

The morphology of PAm/PVA film was observed by SEM, as shown in Fig.2. The homogeneous surface was presented by the SEM micrograph (a). While the phenomenon that some PVA polymers separated from the system was found from the TEM image (b). Uniformly distributed PVA-rich domains were observed particles with very vague interface and small diameter. Such vague interface and small size of the phase separated domains combined with the good physical and chemical interactions between PVA and PAM polymers described in Fig.1 could clearly indicate that a large amount of PVA polymer chains still could be miscible and entangled with the PAM polymers leading to the formation of the interpenetrating network, which played a vital role in the improvement of dimensional stability and mold resistance of bamboo timber.

3.3. SEM of treated bamboo

The SEM of untreated and treated bamboo specimens were shown in Fig.3. From the cross section of untreated (a) and treated bamboo (b), the starch existing in the parenchyma disappeared after treatment, and the possible reasons were that starch grains are covered by modifying agent, or starch grains react in the presence monomer. And a layer of PAm/PVA semi-IPN covered the cell lumen. The cell walls of treated bamboo were expanded, and cells extruded into deformation after the treatment. Also, the pores and parenchyma were also filled up with polymer. The radial section of untreated (c) and treated bamboo (d) showed that the addition of PAm/PVA semi-IPN entered into pits.
3.4. Dimensional stability of bamboo

The average weight gain ratio of treated bamboo was 2.28% after in situ construction of PAm/PVA semi-IPN, and the volume increment ratio was 3.87%. During that first cycle of moisturizing, the swelling rate of treated bamboo was 1.65% and the following cycles were even better for the second and the third cycles 0.87% and 1.36% respectively, while the swelling rates of bamboo untreated were 2.48%, 2.64% and 2.23% respectively of the three cycles. The shrinkage rates of treated bamboo were 1.03%, 1.09% and 1.45% respectively of the three cycles, while the part of untreated bamboo were up to 2.31%, 2.34% and 2.52% respectively.

The ASE of bamboo after moisturizing was showed in Fig4a, and ASE after water soaking of bamboo was showed in Fig4b. The moisture ASE was 47.1% at first cycle, second cycle was up to 52.9%, and the third was 34.2%. The water soaking ASEs of bamboo were 52.2%, 30.4% and 26.4% respectively. The up-trend of swelling rate of treated bamboo went through water soaking test was related to the flowing-away of PAm/PVA semi-IPN, and the rate of flowing-away of first cycle was 6.1%, the second was 2.1%, and the third was less than 1%.

4. Conclusions

In this research, the semi-IPN of PAm/PVA was successfully synthesized, in which PAm was scattered in PVA through the microscopy analysis. Meanwhile, the FTIR showed that there was -H bond exiting in the PAm/PVA semi-IPN. The bamboo impregnated in chemical solution was tested through the dimensional stability. As shown from the results of dimensional stability test, swelling and shrinkage rate of bamboo treated by PAm/PVA semi-IPN were much lower than those of the untreated ones, which indicated that the PAm/PVA semi-IPN in situ structure inside bamboo played an important role in improving dimensional stability.

Acknowledgments

The work was financially supported by the National Natural Science Foundation of China (31270589).
References

[1] He Xingwei, Fu Shenyuan, Daiyue Ping, Jin Chunde, Wang Fapeng. Research on surface characteristics of bamboo with bionic super-hydrophobic Chinese rose/TiO2. World Bamboo and Rattan, 15(5): 11-15. 2017.

[2] D. Ohrnberger. Introduction - The Bamboos of the World, Bamboos of the World, (1999) 1–6.

[3] Wang, F.P., L. Song, Li Wang. "Fabrication of artificial super-hydrophobic lotus-leaf-like bamboo surfaces through soft lithography." Colloids and Surfaces A: Physicochemical and Engineering Aspects, 513: 389-395. 2017.

[4] F. P. Wang, L. Wang, H. P. Wu, et al. A lotus-leaf-like SiO2 superhydrophobic bamboo surface based on soft lithography. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 520: 834-840. 2017.

[5] S. Amada, Y. Ichikawa, T. Munekata, et al. Fiber texture and mechanical graded structure of bamboo. Composites Part B: Engineering, 28 (1997) 13-20.

[6] Y. J. Li, L. X. Du, C. Kai, et al. Bamboo and High Density Polyethylene Composite with Heat-Treated Bamboo Fiber: Thermal Decomposition Properties. Bioresources, 8(1): 900-912. 2013.

[7] F. Farn, M. T. Paridah, U. M. KAnwar, et al. Enhancing mechanical properties and dimensional stability of phenolic resin-treated plybamboo. Journal of tropical forest science, 29(1): 19-29. 2017.

[8] J. L. Xie, J. Q. Qi, T. X. Hu, et al. Effect of fabricated density and bamboo species on physical-mechanical properties of bamboo fiber bundle reinforced composites. Journal of materials science, 51(16): 7480-7490. 2016.