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# Influence of freezing and thawing cycles on bamboowood's surface properties

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"Replacing wood by bamboo" is a research hotspot in the current field of wood science. Performing freezing and thawing cycles on moso bamboo chips and bamboo surface feature analysis before and after freezing and thawing cycles, results indicated that at freezing temperature of -16—-20ºC, freezing time of 6 h, thawing time of 1.5 h, ice melting temperature of the bamboo chips of 60 ºC, and 4 cycles, the surface glue absorption of moso bamboo could reach up to 11.01% with an increasing rate up to 92.41%. Plan B could be used to increase bamboo wood's specific surface area by 267.06%. Pore volume was increased by 37.65%. Mean pore size was reduced by 62.87%. In cross section, the interval between primary tissues and vascular bundle was slightly enlarged, so that adhesive distribution would be evener. Relevant height of diffraction peaks in cellulose crystalline region was reduced by 106 cps and relevant crystallinity was lowered by 1.4%.

**Keywords:** Bamboo wood; Freezing and thawing disposal; Permeability; Surface performance

## INTRODUCTION

Bamboo is an environmentally friendly natural renewable material, with fast growth rate, excellent tenacity and abrasive resistance. Within 3-5 years, it may find broad utilization. There are abundant bamboo woods in China, which are excellent materials to replace woods to manufacture artificial boards [1,2]. At present, bamboo-based artificial boards mainly include bamboo plywood, reconsolidated bamboo and glued laminated bamboo, etc., which are composed of bamboo materials, glued by phenolic resin and produced by assembling and hot-pressing [3-5]. Bamboo wood has lots of lipids and saccharides, resulting in poor permeability of bamboo surface [6]. As a result, how to improve permeability of bamboo surface and make close-grained bamboo wood become a porous material to improve bonding performance and enhance internal bonding strength of bamboo-based artificial boards has been the research hotspot in recent years.

Freezing and thawing cycles form ice crystals to expand cellular structure of bamboo wood, increase specific surface area, so as to expand its pores, loosen cytoderm, promote moisture movement in the drying process, improve diffusion rate, enhance surface performance of bamboo wood, and improve dipping effects of adhesives [7-9]. In the paper, the authors discussed the optimal process of bamboo wood freezing and thawing cycle through parallel experiments, used modern analysis to study the changes of bamboo wood's surface features before and after freezing and thawing cycle, and provided theoretical basis that freezing and thawing cycle can improve bamboo wood's surface permeability.

## EXPERIMENTAL

### *Experimental Materials*

Bamboo chip: 5 year-old crude moso bamboo, string bamboo chip with removed tabasheer and bamboo green; thickness 2±0.2 mm, moisture content 30%; bamboo comes from Sanming Yong'an Forest Farm in Fujian, lifting 1.5-2 m.

Adhesive: phenolic resin, viscosity 36 mPa.s, pH value 10-12, solid content 25%.

### *Test Facilities*

Refrigerator (BCD-257SL, Qingdao Haier), electrically heated thermostatic water bath (DK-98-1, Tianjin Tester), specific surface area and aperture tester (ASAP2020HD88, American Micromeritics), scanning electron microscope (S-3400N, Japan Hitachi), X-ray diffraction analyzer (DX270, Japan Hitachi)

### *Test Methods*

Bamboo wood's freezing and thawing cycle: on the basis of previous studies [10-11], the freezing temperature was set up as -16—-20 ºC, ice melting time 1.5 h, ice melting temperature 60 ºC, cycle index 4 times, freezing time 3 h, 6 h and 9 h; glue-absorbing quantity of phenolic resin was measured according to GB/TF14074-2006 Detection Methods of Wood Adhesive and Resin. The test was repeated 5 times. The result was the mean of all tests.

To find out the effect of freezing and thawing cycle on bamboo wood's permeability, the influence of freezing and thawing cycle on bamboo wood's surface performance was analyzed as follows:

(1) Specific surface area and aperture were tested. Nitrogen was used as absorbing medium. BET method was applied to calculate the specific surface

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area of the samples. With integrals, the pore volume between pore size distribution intervals was calculated. Mean pore size was calculated as 4V/A (V is the pore volume, A is the specific surface area in $m^2/g$). Changes in cellular structure before and after freezing and thawing cycle were followed. The influence of freezing and thawing cycle on bamboo wood's specific surface area, aperture, pore volume, etc., was studied.

(2) Scanning electron microscope was used to analyze the main microstructural features of bamboo wood surface before and after freezing and thawing cycle. Microcosmic structure chart in all directions for bamboo wood was observed, photographed and recorded.

(3) X-ray diffraction analysis was used to study bamboo wood's microcrystalline structure features before and after freezing and thawing cycle. By continuous scanning, X-ray diffraction peak chart of the samples was obtained. According to the empirical formula, cellulosic crystallinity was calculated to determine changes of crystallinity [12-13].

$$X_c = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%$$

$X_c$: crystallinity, $I_{002}$: diffraction intensity of crystal face $I_{am}$: diffraction intensity in amorphous region. Scanning range: 10°-80°; step length: 0.02°; scanning speed: 5°/min; tube flow and pressure: 40mA, 40kV.

## RESULTS AND DISCUSSION

### *Glue-absorbing test of freezing and thawing cycle*

As shown in Table 1, with the extension of the freezing time, bamboo wood's glue-absorbing capacity increased. When freezing time was 6 h, the glue-absorbing capacity reached the maximum. By comparing with bamboo wood's glue-absorbing capacity with unfreezing treatment, it was improved by a factor of nearly two. However, after a freezing time of 9 h, the glue-absorbing capacity was reduced and its stability was also reduced. Nevertheless, by comparing with the control group, the glue-absorbing capacity was still improved by 61.09%, because with the extension of the freezing time, the internal structure of bamboo wood retained the micromechanical force generated by freezing and thawing cycle, so that bamboo wood's organizational structure was occupied by moisture. Therefore, it caused adverse effects on phenolic resin glue.

The above-mentioned test indicated that the optimal treatment procedure of bamboo wood's freezing and thawing cycle was 1.5 h, ice melting temperature of 60ºC, 4 cycles, frozen time of 6 h, (Table 1, scheme B).

### *Bamboo wood's surface feature analysis before and after freezing and thawing cycle*

#### Bamboo wood's specific surface area

As shown in Table 2, bamboo wood's specific surface area after freezing and thawing cycle in scheme B significantly increased by 267.06%.

Bamboo wood's pore volume after freezing and thawing cycle increased to $2.23 \times 10^{-4}$ $cm^3/g$ from the untreated $1.62\times10^{-4}$ $cm^3/g$ (an increase by 37.65%). However, pore size decreased by 62.87% after freezing and thawing cycle, indicating that freezing and thawing cycle may have an important influence on the changes in bamboo wood's specific surface area, pore volume and mean pore size. After a freezing and thawing cycle, bamboo wood's specific surface and pore volume were obviously improved. With a freezing and thawing cycle, a circular hole with a smaller diameter was obtained, so that the micropore number was increased. To sum up, the freezing and thawing cycle contributes to expanding bamboo wood's microcellular structure, so as to improve bamboo wood's surface permeability.

#### Scanning Electron Microscope Analysis of Bamboo Wood's Fiber Structure

As shown in Figure 1, the internal pore diameter of bamboo wood was smaller after a freezing and thawing cycle of scheme B and the overall interspace was expanded. Bamboo wall's vascular

**Table 1.** Test results of glue-absorbing capacity before and after freezing and thawing cycle

| Freezing time/h | Glue-absorbing capacity/% | | | | | | |
|---|---|---|---|---|---|---|---|
| | Specimen 1 | Specimen 2 | Specimen 3 | Specimen 4 | Specimen 5 | Mean | Increasing rate |
| Untreated | 6.12 | 5.88 | 5.07 | 5.52 | 6.01 | 5.72±0.46 | - |
| 3 (Scheme A) | 6.45 | 6.73 | 6.42 | 6.67 | 6.71 | 6.60±0.16 | 15.31 |
| 6 (Scheme B) | 10.81 | 11.23 | 10.51 | 11.12 | 11.36 | 11.01±0.32 | 92.41 |
| 9 (Scheme C) | 8.71 | 9.24 | 10.11 | 8.98 | 9.89 | 9.39±0.61 | 61.09 |

**Tab. 2** Testing results of samples' specific surface area before and after freezing and thawing cycle

| Indicators | Blank group | Freezing and thawing group | Changing rate |
|---|---|---|---|
| Specific surface area/$\times10^{-2}m^2/g$ | 0.85 | 3.12 | 267.06% |
| Pore volume /$\times10^{-4}cm^3/g$ | 1.62 | 2.23 | 37.65% |
| Mean pore size/nm | 73.14 | 27.16 | -62.87% |

**Table 3** Test results of relative crystallinity before and after freezing and thawing cycle

| Categories | Diffraction angle/2θ° | Relative strength/cps | Relative crystallinity/% |
|---|---|---|---|
| Blank group | 22.62 | 1071 | 39.7 |
| | 16.74 | 640 | |
| Freezing and thawing (Scheme B) | 22.50 | 965 | 38.3 |
| | 16.47 | 588 | |

bundle distribution without a freezing and thawing cycle was loose, presenting an irregular shape. Moreover, there were a few elementary tissues. The cross section was close to an oval. Bamboo wood's cross section after freezing and thawing cycle was slightly expanded between elementary tissues and vascular bundle. Most of parenchyma cells were encircled around vascular bundle. Moreover, cells were large. The arrangement was compact and well-aligned and the cross section was close to roundness.

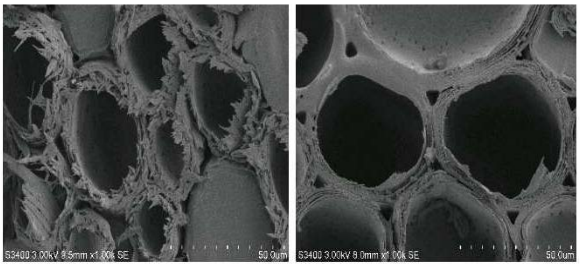

**Fig. 1** Scanning electron microscope comparison of the cross section before and after bamboo wood's freezing and thawing cycle

As shown in Figure 2, the pores of bamboo wood cells without freezing and thawing cycle were small and closely arranged. Bamboo wood after a freezing and thawing cycle was evenly distributed with some glue solution between elementary tissues and cells. There were obvious cell intervals between parenchyma cells. Some phenolic resin glue adhesive could enter into the cell cavity of the parenchyma cells through the cell pores, so as to fill in parenchyma cells.

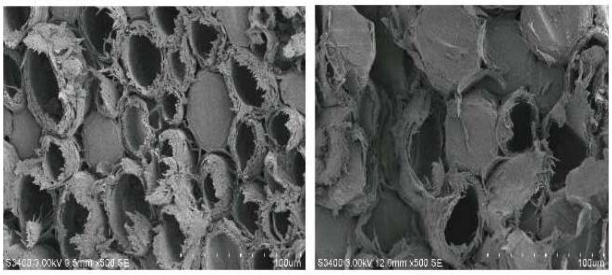

**Fig. 2** Scanning electron microscope comparison of the glue-absorbing cross section before and after bamboo wood's freezing and thawing cycle

XRD diffraction analysis of bamboo wood's microstructure

As shown in Figure 3, after a freezing and thawing cycle of scheme B, the relative strength of the diffraction peak in the cellulosic crystalline region changes, because cellulose underwent hydrolysis and pyrolysis during the freezing and thawing cycle, so that cellulosic crystalline region was destroyed to some extent. As for freezing and thawing cycle, there was a prominent crystal diffraction peak around 22.50° for the diffraction angle 2θ. There was a weaker crystal diffraction peak around diffraction angles 16.47° and 35.05°.

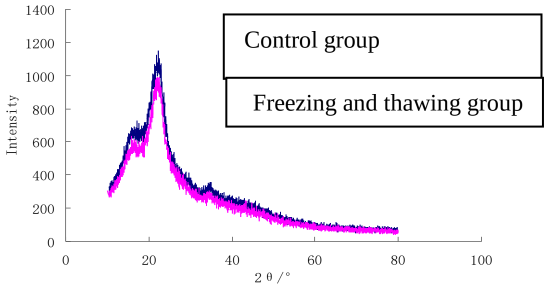


**Fig. 3** XRD diffraction pattern before and after bamboo wood's freezing and thawing cycle

As shown in Table 3, after freezing and thawing cycle of scheme B, the relative crystallinity of cellulose was reduced to some extent. This was greatly beneficial to improve bamboo wood's glue-absorbing capacity. Due to the freezing and thawing cycle, bamboo wood's structure was looser and more scattered. The scattered bamboo wood's structure was good for permeation of adhesive, so as to improve glue-absorbing properties of bamboo wood.

CONCLUSIONS AND PROSPECTS

(1) Freezing and thawing cycle could improve the permeability of bamboo wood. With 4 cycles at ice melting time of 1.5 h and thawing temperature of 60ºC the optimal frozen time was 6 h. When the frozen time exceeded 8 h, boh the permeability and stability of bamboo wood decreased. Moreover, long time was not good for cost control.

(2) Freezing and thawing cycle made bamboo wood's surface features to change as follows: specific surface area increased by 267.06%; pore volume increased by 37.65%, and the mean pore size decreased by 62.87%. The interval between cross section's elementary tissues and vascular bundle was slightly enlarged, so that the adhesive was evenly distributed in bamboo's elementary tissues and cellular intervals. The relative height of the diffraction peak in the cellulosic crystalline region decreased by 106 cps and the relative crystallinity decreased by 1.4%.

(3) In the future, consideration should be given

to age and terrain clearance of bamboo wood. Response surface analysis and orthogonal test should be used to further refine the permeability of bamboo wood.

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