Changes in the Chemical Properties of *Phyllostachys iridescens* Bamboo with Steam Treatment

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This study explored the chemical properties of heat-treated bamboo. Oriented bamboo fiber mats (OBFMs) of *Phyllostachys iridescens* bamboo, as units of a bamboo fiber-reinforced composite (BFRC), were heat-treated in saturated steam at 0.40 MPa (150 °C) for 110, 140, or 170 min. After heat treatment, the color of oriented bamboo fiber mats changed noticeably. The chemical properties of the bamboo were examined. The results revealed that the contents of holocellulose and hemicelluloses decreased, while the contents of α-cellulose and water extractives and buffering capacity increased. The pH value decreased compared with control samples. The change in the chemical properties of the OBFMs would have an effect on the properties of the BFRC.

Keywords: Phyllostachys iridescens bamboo; Steam treatment; Chemical properties

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INTRODUCTION

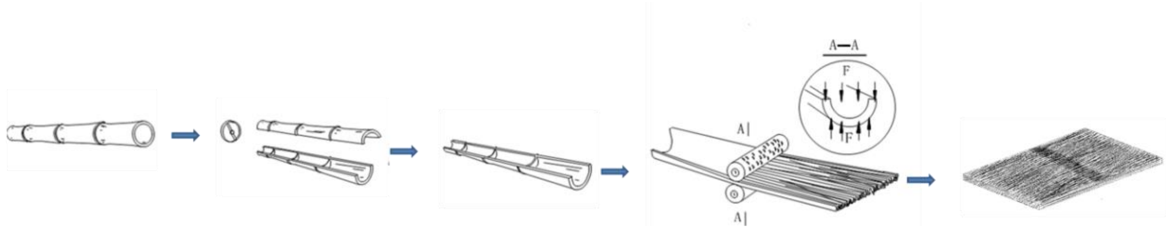
Phyllostachys iridescens is a well-known bamboo species endemic to China. It can be used for bamboo shoots, timber, and in ornamental applications. Heat-treated bamboo possesses new properties such as higher dimensional stability, while its strength is considerably reduced (Tjeerdsma *et al.* 1998; Shao *et al.* 2003; Tjeerdsma and Militz 2005; Qin 2010; Tuong and Li 2010; Zhang *et al.* 2013a). Heat treatment also affects the bamboo's components, such as cellulose, hemicelluloses, lignin, and extractives (Zhang *et al*. 2013b).

In this study, *Phyllostachys iridescens* bamboo was formed into oriented bamboo fiber mats (OBFMs) (Yu 2011). Then, steam treatment was applied to create different colors to enhance the bamboo's value. OBFMs were heat-treated at a steam pressure of 0.40 MPa for 110, 140, or 170 min. The chemical composition, water extractives, and pH value of the OBFMs were then studied. Heat treatment changed the properties of OBFMs; this will affect the properties of bamboo fiber-reinforced composite (BFRC). This work considered the properties of OBFMs. The properties of BFRC will be considered in future research.

EXPERIMENTAL

Materials

Phyllostachys iridescens bamboo aged 4 to 5 years was obtained from Anhui province. The bamboo was sawn into a tube with a length of 2600 mm and then split longitudinally into two semicircular bamboo tubes. Thereafter, the inner nodes were removed and the semicircular bamboo tube was pushed into a fluffer along the grain direction. The bamboo tubes were fluffed along the longitudinal fiber direction to form a series of dotted and/or linear cracks along the fiber direction. In other words, a section of arrowroot was separated, but the clinging fiber remained in the bamboo tubes. Consequently, a structural net of OBFMs was formed by the interlaced bamboo bundle fibers, which consisted of less than five vascular bundles and several ground tissues (see Fig. 1). The OBFMs were dried in an oven to an approximate moisture content of 10%. The OBFMs were easier to saturate with phenol formaldehyde resin and also easier to achieve the effects of steam-treatment.



(a) (b) (c) (d) (e)

Fig. 1. Process flow diagram for OBFMs: (a) row bamboo; (b) splitting; (c) semicircular bamboo tube; (d) fluffing; (e) bamboo fiber mat. Inset: A-A: Semicircular bamboo tubes; F: Cross face

Fig. 2. Surface features of OBFM

Methods

Heat treatment

Oriented bamboo fiber mats (OBFMs) with a moisture content of 9% to 10% were immersed in carbonation equipment, which consisted of a horizontal carbonization furnace (THLφ1200X4300, made in China) set at steam pressures of 0.40 MPa (151 °C) for durations of 110, 140, or 170 min. A steam pressure of 0.40 MPa is the commonly used carbonization pressure in the Chinese bamboo enterprise. The oriented bamboo fiber mats (OBFMs) used for each treatment weighed 50 kilograms. The samples were used for the chemical experiments and as units of bamboo fiber-reinforced composite (BFRC). After heat treatment, the OBFMs were reconditioned to reach equilibrium.

Color measurement

The color of OBFMs was measured with a spectrophotometer (Konica Minolta CR-400, Japan) under a D65 light source and an observer angle of 10 degrees. The sensor head of the spectrophotometer was 8 mm in diameter. Color was expressed according to the CIE ($L^*a^*b^*$) system. The differences in ΔL^*, Δa^*, and Δb^* and the total color change (ΔE^*) were calculated using the following formulas,

$\Delta L^* = L^* - L_0^*$

$\Delta a^* = a^* - a_0^*$

$\Delta b^* = b^* - b_0^*$

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where L^* represents lightness, with values ranging from 0 (black) to 100 (white). The parameters a^* and b^* describe the chromatic coordinates on green-red (a^*) and blue-yellow (b^*) axes. L_0^*, a_0^*, and b_0^* are the reference values, obtained as the average of 20 untreated specimens. Color was measured for each group at 20 points near the outer bamboo culms. The results were then averaged.

Chemical properties of OBFMs

The bamboo flour used for chemical analysis was made according to GB/T 2677 1-93 (1993). Samples for each treatment were sawn into small pieces and milled. Powdered samples were sieved into three fractions; the middle fraction (0.25 to 0.42 mm) was used for chemical determinations. The measurements for the contents of holocellulose, α-cellulose, hot water extractives, pH value, and buffering capacity were performed according to GB/T 2677.10-1995, GB/T 744-1999, GB/T 2677.8-94, GB/T 2677.4-93, GB/T 6043-1999, and GB/T 17660-1999. The specific methods mentioned in our previous paper were employed (Zhang *et al.* 2013b).

The method of testing pH value are as follows: The bamboo powders (approximately 3 g, ±0.1 mg) were placed in 50-mL beakers. A total of 30 mL of distilled water that was boiled and cooled down to room temperature was added to the powders. The mixture was let stand for 15 min after being stirred for 5 min, and then stirred again for 5 min before it was let stand for another 5 min. The acidity of UB-10 was used to determine the pH values. Prior to each titration, the pH meter was calibrated with a standardized buffer solution to a pH of 4. Each sample was analyzed twice.

Testing for buffering capacity was carried out based on GB/T 17660-1999, as follows: The aqueous extract for pH value of reflux extraction liquid and buffering capacity measurement was prepared by refluxing 25 g of dry bamboo powder in 200-mL of distilled water for 20 min. Two sets for each sample were prepared. After refluxing, the mixture was filtered through filter paper. After calibration, exactly 50 mL of bamboo extract solution was pipetted into a 150-ml breaker. The pH of the extract solution was measured, and then titrated to a pH of 3 (for alkaline buffering capacity) or 11 (for acid buffering capacity) with 0.0125 mol/L H_2SO_4 or 0.025 mol/L NaOH solutions. The pH of the constantly stirred solutions was measured after each incremental addition of acid or alkali. All pH and buffering capacity measurements were conducted by using an acidity of UB-10. Prior to each titration, the pH meter was calibrated with a standardized buffer solution to a pH of either 4 or 9, depending on the buffering capacity measurement to be made.

Statistical analysis

A one-way statistical analysis (ANOVA) was performed on the data to evaluate the effect of steam treatment on the color with SAS software (Version 8.0, SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

Color Change of the Oriented Bamboo Fiber Mats

The effect of chemical changes induced by steaming could be observed with the naked eye after heat treatment (Fig. 3). The specimens became visibly darker, and the color changed to a relatively more pleasant reddish hue after steam treatment. The visual observations described above were confirmed by the objective color measurement.

(a) (b)

Fig. 3. The surface color of OBFM. (a): before heat treatment; (b): after heat treatment

The color changes of samples are shown in Table 1. The lightness decreased continuously with increasing duration, but the change was not significant when samples were heat-treated for durations between 110 and 170 min. The red color, represented by the a^* co-ordinate, increased rapidly when samples were heat-treated for 110 min, and then a relative decrease was found when samples were treated for durations of 140 min and 170 min.

The initial values of the yellow color of bamboo were relatively high. After heat treatment, the yellow hue (b^* co-ordinate) showed a similar trend as L^*. Significant changes were found when the materials were treated for 110 min. Lower values were detected with increasing treatment duration, but no significant change in yellow hue was found when samples were heat-treated between 140 and 170 min.

Table 1. Results of Color Measurement

Pressure (MPa)	Duration (min)	Color in CIE system			Color difference			
		L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE^*
Control		62.6 ^{A} (3.9)	2.9 ^{A} (14.1)	26.2 ^{A} (6.1)				
0.40	110	36.5 ^{B} (9.8)	11.1 ^{B} (9.9)	19.8 ^{B} (13.1)	-26.1	8.2	-6.4	28.1
0.40	140	36.6 ^{B} (3.0)	9.6 ^{C} (7.3)	17.5 ^{C} (9.9)	-25.9	6.7	-8.7	28.1
0.40	170	36.4 ^{B} (10.6)	9.9 ^{C} (5.4)	18.1 ^{C} (10.8)	-26.1	6.9	-8.1	28.2

Coefficient of variation (CV) is given in parentheses. All data in variance and one-way ANOVA tests were assessed at a confidence level $p < 0.05$. Values followed by a different letter within a column are statistically different at $p = 0.05$ (ANOVA single factor and t-test).

As L^*, a^*, and b^* were affected by steam treatment, the final color change (ΔE^*) was significant, as shown in Table 1. The color modification achieved by steam treatment is considered to be a major advantage compared to surface treatment by pigmented stains or finishes. However, color modification by steaming is not recommended for outdoor application (Fengel and Wegener 1984). In terms of bamboo color changes, more research is required.

Changes in Chemical Composition

The chemical composition of the heat-treated samples differed from that of the control samples, as shown in Table 2. Changes in chemical composition are observable, especially for longer treatment duration. The most noticeable content decrease in relation to the original value was observed for hemicellulose.

Table 2. Changes in Chemical Composition of Bamboo

Treatment duration (min)	Holocellulose (A, %)	α-cellulose (B, %)	Hemicelluloses (A-B, %)	Hot water extractives (%)
Control	67.4	44.3	23.1	5.7
110	59.3	46.8	12.5	8.8
140	56.9	45.6	11.6	11.2
170	57.5	45.4	12.1	12.2

Hemicelluloses (%) = Holocellulose (%) - α-cellulose (%)

Results in Table 2 consider two important aspects of the tested materials. One is the molecular mass of analyzed substances. High molecular mass substances (holocellulose, α-cellulose) were compared with low molecular mass (hemicelluloses, hot water-soluble substances). The other is the parameter of treatment duration (110, 140, and 170 min).

When samples were treated at 0.40 MPa for 110 to 170 min, a decrease in the holocellulose content with increasing treatment duration was found. However, the change was slight when the samples were steam treated for 140 and 170 min. The α-cellulose content increased after heat treatment; the increase range was between 2.4% and 5.6%. According to research on wood, other components accompanying wood cellulose are involved in the increase of crystallinity after heat treatment (Bhuiyan *et al*. 2000). When OBFMs were heated for 140 and 170 min, a relative decrease in the content of α-cellulose was found compared with samples treated for 110 min. Therefore, this warrants further research.

Changes in hemicellulose and hot water-soluble substance contents after treatment are also shown in Table 2. These are substances of relatively low molecular mass. Hemicellulose content was calculated by subtracting α-cellulose content from holocelluose content. The decrease in hemicellulose content compared to the control sample was approximately 45.9% to 51.3% for treatment duration of 110 to 170 min. Hemicelluloses are less resistant to thermal degradation than lignin because of their low molecular weight and branching structures (Fengel *et al.* 1984). The content of substances soluble in hot water increased by almost 54.0% after heat-treatment for 110 min, followed by a relative increase for a longer duration. The samples treated for 170 min showed 2.1 times as many soluble substances as the control sample. The increase in water extractives showed that steam treatment resulted in many more small soluble molecules because of the degradation of hemicelluloses and cellulose. The results were similar to those found for *Neosinocalamus affinis* bamboo (Zhang *et al.* 2013b). Because of the difference in the bamboo chemical composition, the changes in *Phyllostachys iridescens* bamboo after heat treatment were also different from that of *Neosinocalamus affinis* bamboo.

The Effect of Steam Treatment on pH and Buffering Capacity

As shown in Table 3, the pH value was clearly decreased after heat treatment compared with that of the control sample, reaching a maximum reduction of 22.4%. When samples were treated at 0.40 MPa between 110 and 170 min, the change in pH value between them was lower than 0.3, which was not significant. The results are similar to our previous research for *Neosinocalamus affinis* bamboo.

Table 3. Results of pH Value and Buffering Capacity of Bamboo Fibrous Veneers

Duration (min)	pH Value	Buffering capacity (mmol L^{-1})		
		Acid buffering capacity	Alkali buffering capacity	Buffering capacity
Control	5.3	0.38	0.93	1.31
110	4.2	0.33	1.59	1.92
140	4.1	0.39	2.15	2.54
170	4.4	0.47	1.96	2.43

When samples were treated at 0.40 MPa for durations of 110 and 170 min, the alkali buffering capacity increased compared with that of the control sample. When the samples were heat treated at 0.40 MPa for 110 min, the alkali buffering capacity was 1.7 times that of the control sample. A relative increase was found when the samples were heat-treated for longer durations. However, the alkali buffering capacity reached a maximum value when the samples were heat-treated at 0.40 MPa for 140 min.

The acid buffering capacity was 0.9 times that of the control sample when specimens were heat treated at 0.40 MPa for 110 min, followed by a relative increase when samples were heat treated for longer durations; the values reached a maximum when samples were heat-treated at 0.4 MPa for 170 min.

Knowledge of the pH and buffering capacity of bamboo is an important factor for better understanding the gluing process. The change in pH and buffering capacity may affect the gel time of the material.

CONCLUSIONS

1. The surface color of OBFM became darker after steam treatment. The total color change ΔE^* increased with increasing duration. These results are useful in practice when customers require certain colors of bamboo products.
2. Steam treatment at 0.40 MPa for 110 to 170 min causes a decrease in the holocellulose and hemicelluloses content. However, the α-cellulose and the hot water-soluble substance contents increased.
3. As the units of bamboo fiber-reinforced composite (BFRC), the changes in the color and chemical properties of the oriented bamboo fiber mats (OBFMs) also affect the properties of bamboo fiber-reinforced composite (BFRC). Overall results from this study demonstrate that steam treatment of oriented bamboo fiber mats affects the properties of bamboo fiber reinforced composites.

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REFERENCES CITED

Bhuiyan, M. T. R., Hirai, N., and Sobue, N. (2000). "Changes of crystallinity in wood cellulose by heated treatment under dried and moist conditions," *J. Wood Sci*. 46(6), 431-436. DOI: 10.1007/BF00765800.

Fengel, D., and Wegener, G. (1984). *Wood-Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, Berlin. DOI: 10.1002/pol.1985.130231112.

GB/T 2677.1-93 (1993). "Fibrous raw material of sampling for analysis," China Standards Press, Beijing.

Qin, L. (2010). *Effect of Thermo-treatment on Physical, Mechanical Properties and Durability of Reconstituted Bamboo Lumber*, Ph.D. dissertation, Chinese Academy of Forestry, Beijing (in Chinese).

Shao, Z. P., Zhou, X. H., Wei, T., Zhou, J., and Cai, F. Y. (2003). "The strength variance of bamboo blanks heat-treated with different methods," *China Forest Products Industry* 30(3), 26-29 (in Chinese).

Tjeerdsma, B. F., and Militz, H. (2005). "Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood," *European Journal of Wood and Wood Products* 63(2), 102-111. DOI: 10.1007/s00107-004-0532-8.

Tjeerdsma, B. F., Boonstra, M., Pizzi, A., Tekely, P., and Militz H. (1998). "Characterization of the thermally modified wood: Molecular reasons for wood performance improvement," *Holz als Roh-und Werkstoff* 56(3), 149-153. DOI: 10.1007/s001070050287.

Tuong, V. M., and Li, J. (2010). "Effect of heat treatment on the change in color and dimensional stability of acacia hybrid wood," *BioResources* 5(2), 1257-1267. DOI: 10.15376/biores.5.2. 1257-1267.

Yu, W. J. (2011). "Development of bamboo-fiber based composites," *China Wood Industry* 25(1), 6-8, 29 (in Chinese).

Zhang, Y. M., Yu, Y. L., and Yu W. J. (2013a). "Effect of thermal treatment on the physical and mechanical properties of *Phyllostachys pubescens* bamboo," *European Journal of Wood and Wood Products* 71(1), 61-67. DOI:10.1007/s00107-012-0643-6.

Zhang, Y. M., Yu, W. J., and Zhang, Y. H. (2013b). "Effect of steam heating on the color and chemical properties of *Neosinocalamus affinis* bamboo," *Journal of Wood Chemistry and Technology* 33(4), 235-246. DOI:10.1080/02773813.2013.779714.

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