Changes in Surface Properties of Heat-Treated *Phyllostachys pubescens* Bamboo

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The wetting phenomena and surface energetic behavior in heat-treated bamboo were studied. The bamboo specimens were heat-treated at temperatures of 100, 140, and 180 °C for 4 h, and an untreated sample served as a control. The sessile drop technique was used to estimate the surface contact angles of the control and heat-treated bamboo samples. The contact angle data were then used to determine the surface free energies using the Lifshitz-van der Waals/acid-based approach. The results revealed that the heat treatment process affects surface wettability. Heat treatment at 100 to 180 °C increased the contact angle of distilled water and formamide, but heat treatment did not cause any increase in the contact angle of diiodomethane. The hydrophobic characteristics of the bamboo surfaces also increased under heat treatment, and the surface free energy and the polarity of the bamboo decreased. Surface analysis by XPS of the samples heat-treated at 180 °C showed a decreased O/C ratio and increased C1 peak, indicating that more lignin and extractives were situated on the bamboo surface. Changes in wettability can greatly impact the use of the material, particularly with respect to the adhesion of paints and coatings.

Keywords: Bamboo; Heat treatment; Contact angle; Surface free energy; Equilibrium moisture content

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INTRODUCTION

Bamboo, a fast-growing and highly productive material, is widely used to produce composites such as bamboo plywood, laminated bamboo lumber, bamboo scrimber, bamboo particle board, and bamboo fiber-reinforced polymers. These materials have extensive applications in furniture, flooring, building, and civil engineering fields, especially in China and India (Lee and Liu 2003; Okubo *et al.* 2004; Sulaiman *et al.* 2006; Yu 2011; Mahdavi *et al.* 2012).

Phyllostachys pubescens bamboo is the most common bamboo species in China and is widely used in the Chinese bamboo industries. It is an important part of the Chinese economy. Statistically, 70% of all Chinese bamboo is *Phyllostachys pubescens*. According to the Forestry Bureau, in 2012 alone the total output of bamboo in China was approximately 16.44 million bamboo, and the output of the number *Phyllostachys pubescens* bamboo plants was approximately 11.15 million (The Annual report 2012).

Bamboo products in the current market are divided into two categories: natural color and carbonized color. Heat treatment is typically applied to deepen the color of the bamboo material (carbonized bamboo); this style of bamboo is considered high-end and is very popular as furniture and decorative material. Bamboo enterprises in China have developed a rather wide variety of carbonized bamboo furniture. The surface properties of specific types of bamboo greatly impact the way they are glued in such applications. Glue joint destruction or coating delamination of the bamboo often starts from the bonding surface or interface (Zhang 1995). Previous studies have explored relevant changes in the surface properties of bamboo after a variety of treatments, such as high-temperature drying, high-temperature processing, and boric acid processing (Yu *et al.* 2007)

Microwave softening treatment and microwave plasma (MWP) treatment also have varying degrees of influence on the surface properties of bamboo (Du *et al.* 2007; Jiang *et al.* 2008). Research regarding the specific effects of heat treatments on bamboo, however, is still lacking. According to our previous research, heat treatment on bamboo improves its homogeneity of color distribution, decay resistance, and resistance to natural weather; however, heat treatment at excessive temperatures causes degradation of the hemicelluloses and reduction of the pH value. The authors also observed a drastic reduction in modulus of rupture (MOR) accompanied by smaller changes in modulus of elasticity (MOE) when specimens were heat-treated at 100 to 220 °C for 1 to 4 h (Zhang *et al.* 2013a,b).

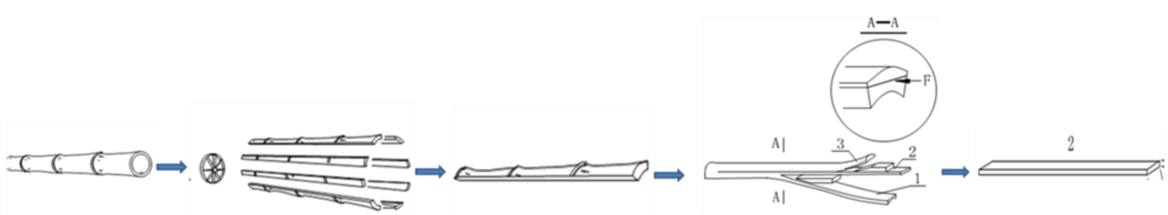
Bamboo is composed of cellulose, hemicelluloses, and lignin, as well as extractives and a small amount of inorganic components (Zhao and Yu 2002). When bamboo is exposed to high temperatures, the layers near the physical surface undergo chemical processes that modify the surface and endow new characteristics. Effective utilization of bamboo is strongly related to the favorable surface properties, which in most cases must involve successful adhesive bonding and coating.

The primary goal of this study was a thorough investigation of the effects of heat treatment on bamboo wetting phenomena and surface energy, as well as the specific mechanisms that cause changes in either factor. Mass loss and equilibrium moisture content were measured to understand the relevant changes. X-ray photoelectron spectroscopy (XPS) was applied to investigate the surface chemical composition of the bamboo samples.

EXPERIMENTAL

Materials

Five-year-old *Phyllostachys pubescens* bamboo was obtained from Zhejiang, China, for use as raw material. The bamboo was sawed into a tube and then split longitudinally into arc tubes. A sketch of the sampling process is shown in Fig. 1. Specimens had dimensions of 80 mm × 10 mm × 3 mm. The moisture content of the bamboo specimens was 8%, measured after the samples were air dried in Beijing.



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

Fig. 1. Sketch of the sample processing: (a) raw bamboo; (b) radial splitting; (c) bamboo strips; (d) tangential splitting; (e) bamboo sliver; 1) near the bamboo inner skin; 2) near the bamboo outer skin; 3) outer skin; A-A) Cross section: F) Cutting face

Methods

Heat treatment

Samples were heat treated in an electric oven for 4 h at 100, 140, or 180 °C. The treated samples were cooled down to room temperature then conditioned to specific equilibrium moisture content (EMC) in a room maintained at a constant temperature of 20 °C and 65% relative humidity (RH) for 28 days.

Equilibrium moisture content of the specimens after treatments is presented in this report on an oven-dried basis. Oven-drying: 105±2 °C for 48 h; cooling: over silica gel in desiccators; accuracy of weighting: ± 0.001 g. Equilibrium moisture content was calculated according to the formula,

$$EMC = 100 \times (m_i - m_{od})/m_i \quad (1)$$

where m_i is the initial mass of bamboo sample, which is the weight of the sample in an environment maintained at a constant temperature of 20 °C and 65% relative humidity, and m_{od} is the weight of the oven-dried sample.

Contact angle measurement

Advancing contact angles were determined by the Wilhelmy method according to previously reported procedures (Gardner *et al.* 1991; Wålinder and Johansson 2001; Pétrissans *et al.* 2003). The sessile drop technique, which is commonly used to observe the profile of a drop deposited on the surface of a solid, was employed to estimate the apparent contact angle of distilled water, diiodomethane, and formamide on both control and heat-treated bamboo specimens. Measurements were performed at room temperature (20 °C) at 40% to 50% RH with the help of an OCA20 instrument (Data Physics contact angle measuring apparatus, Germany). The contact angle was measured every 0.04 s. An automatic micro syringe was used to dispense an approximately 5-μL drop of distilled water, diiodomethane, or formamide. Five replicate specimens from each material sample were selected for the contact angle measurements; three points on each specimen were measured. Thus, the total number of tests for each specimen was 15.

Lifshitz-van der Waals and acid-base component determination

Direct measurement of surface free energy of solids is not feasible and necessitates indirect evaluation. This evaluation is based on Young's equation,

$$\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl} \quad (2)$$

where θ is the equilibrium contact angle, γ_{lv} and γ_{sv} are the surface free energies of the liquid/vapor and solid/vapor interfaces, and γ is the interfacial energy of the solid/liquid interface.

Based on the contact angle values of liquids of known surface free energies, it is possible to analyze changes in the polar, non-polar, and acid-based components of the surface free energy of bamboo using the Lifshitz-van der Waals/acid-based (LW-AB) approach. Surface free energy is the sum of the Lifshitz-van der Waal component and the acid-base component:

$$\gamma = \gamma^{LW} + \gamma^{AB} \quad (3)$$

The acid-base component can be expressed in terms of electron-accepting and electron-donating components as follows:

$$\gamma^{AB} = 2\sqrt{\gamma^{+}\gamma^{-}} \quad (4)$$

where γ^{+} and γ^{-} are electron-accepting and electron-donating components, respectively. According to previous research, the solid/liquid interface energies are equal to the following,

$$\gamma_{sl}^{LW} = \left(\sqrt{\gamma_{lv}^{LW}} - \sqrt{\gamma_{sv}^{LW}}\right)^2 \quad (5)$$

$$\gamma_{sl}^{AB} = 2(\sqrt{\gamma_{sv}^{+}\gamma_{sv}^{-}} + \sqrt{\gamma_{lv}^{+}\gamma_{lv}^{-}} - \sqrt{\gamma_{sv}^{+}\gamma_{lv}^{-}} - \sqrt{\gamma_{sv}^{-}\gamma_{lv}^{+}}) \quad (6)$$

where the subscripts s, l, and v denote solid, liquid, and vapor phase, respectively. Combining Eqs. 4 through 6 and 2 forms the following equation:

$$(1 + \cos\theta)\gamma_{lv} = 2(\sqrt{\gamma_{sv}^{LW}\gamma_{lv}^{LW}} + \sqrt{\gamma_{sv}^{+}\gamma_{lv}^{-}} + \sqrt{\gamma_{sv}^{-}\gamma_{lv}^{+}}) \quad (7)$$

Using three test liquids of different polarity (one non-polar and two polar) with known surface free energy components, it is possible to determine the Lifshitz-van der Waals and the acid-base components of the bamboo samples.

The surface free energy components of the test liquids were obtained by use of a Krüss Processor Tensiometer (model K100 T Krüss, Germany) database and are presented in Table 1.

Table 1. Physical Properties and Surface Free Energy Components of the Test Liquids

Liquid	Density (g/cm^3)	Viscosity (mPa s)	Surface free energy (mJ/m^2)		
			γ_{lv}^{d}	γ_{lv}^{p}	γ_{lv}
Water	1.00	1.0	21.8	51.0	72.8
Formamide	1.13	3.6	39.0	19.0	58.0
Diiodomethane	3.33	2.8	50.8	0	50.8

XPS analysis

Samples were prepared with a cutter blade by removing chips of approximately 5 mm × 2 mm × 1 mm from the larger face of the blocks to minimize the required time to obtain appropriate vacuum conditions in the XPS analysis chamber. All preparation was performed just before analysis, avoiding all contact with bare hands. Samples were immediately placed in the vacuum chamber of the apparatus.

XPS analyses were carried out with a PHI QUANTERA-II system (Ulvac-PHI, Inc., Japan) spectrometer with a hemispherical energy analyzer using a monochromatic Al Kα source (1486.6 eV). All spectra were recorded at a 45° take-off angle. The analyzed area was approximately 100 µm. Because the bamboo samples behaved as non-conducting materials, a charge neutralizer was necessary to correct binding energies using adventitious aliphatic carbon (BE at 284.8 eV) as an internal reference. Spectra were analyzed using the XPS peak (Version 4.1) software.

RESULTS AND DISCUSSION

Contact Angle Changes

The effects of heat treatment on the wettability properties of *Phyllostachys pubescens* bamboo were assessed by measuring the contact angles of distilled water, formamide, and diiodomethane on the surface of the samples. Wettability values, given as contact angles of the different test liquids 1 s after the drops were deposited on the surface of the test bamboo, are presented in Table 2.

The contact angles of distilled water and formamide on the heat-treated specimens were higher than on the untreated specimens. Furthermore, after heat treatment at higher temperatures, a clear increase in contact angle occurred. Heat treatment did cause slight changes in the contact angle of diiodomethane, however, because distilled water and formamide are polar liquids, while diiodomethane is dispersive.

Table 2. Average Contact Angles of the Test Liquids 1 s After the Drop was Deposited on the Control and Heat-Treated Bamboo Surfaces (Coefficient of Variation Shown on Parentheses)

Treated temperature (°C)	Contact angle(°)		
	Distilled water	Formamide	Diiodomethane
Control	49.74 (6.44)	24.70 (7.90)	40.37 (9.71)
100 °C	57.97 (5.66)	25.72 (9.80)	39.34 (10.18)
140 °C	79.85 (6.06)	48.00 (6.68)	36.27 (5.65)
180 °C	104.01 (4.20)	63.91 (4.79)	42.46 (9.25)

The contact angles for distilled water were higher after heat treatment compared to the control specimens, an increase from 49.74° for untreated bamboo to 104.01° for bamboo treated at 180 °C. A higher contact angle indicates lower surface wettability (Gardner *et al*. 1991; Du *et al*. 2007). Results thus suggest that heat treatment at 100 to 180 °C actually decreased the wettability of the bamboo surface.

Surface Free Energy

Calculations of bamboo samples' surface free energies were performed using contact angles of distilled water, formamide, and diiodomethane. Results are shown in Table 3. Diiodomethane was selected as a non-polar test liquid to avoid problems inherent to the polarity of bamboo.

Table 3. Surface Energy of the Control and Heat-Treated Bamboo

Surface energy (mJ/m^2)	Control	100 °C	140 °C	180 °C
r_{tot}	52.38	51.93	44.39	39.79
r_{sv}^{LW}	39.42	39.94	41.43	38.35
r_{sv}^{AB}	12.96	11.99	2.95	1.44
r_{sv}^{+}	1.92	3.04	0.84	0.53
r_{sv}^{-}	21.86	11.91	2.59	0.98

For a treatment temperature of 100 °C, no major change was observed compared to the control specimens. After treatment at higher temperatures, a clear decrease in the total surface free energy occurred.

In all cases, the Lifshitz-van der Waals (LW) component was observed to be the primary surface free component compared to the acid-base (AB) component. Behavior of these two components changed after heat treatment; where the LW component increased slightly after heat treatment at temperatures of 100 to 140 °C, it decreased slightly when the samples were heat-treated at 180 °C. Conversely, the AB component decreased at various levels after treatment at 140 °C. Between the two components of acid-base contribution, the electron-donating component was more strongly influenced, decreasing sharply as treatment temperature increased.

Equilibrium Moisture Content of Specimens

To better understand the reasons behind the observed changes in properties, contact angle was compared to equilibrium moisture content for control and heat-treated specimens.

Figure 2 shows the effects of treatment temperature on equilibrium moisture content of the specimens. Equilibrium moisture content decreased after heat treatment. No noticeable change was observed for treatment temperature below 140 °C; obvious changes in equilibrium moisture content were observed for samples treated above 140 °C.

As shown in Fig. 2, heat treatment at 140 °C was the cut-off point. When samples were heat-treated in a range of temperatures between 100 and 140 °C, no noticeable changes in equilibrium moisture content were observed. Hemicelluloses, for one, degrade under heat treatment at temperatures above 160 °C (Esteves *et al.* 2007). Thus, during heat treatment in the temperature range of 100 to 140 °C, the chemical components in the bamboo did not change much. Changes in contact angle may have been related to the evaporation of water in the bamboo and the degradation of extractives as they moved toward the bamboo surface.

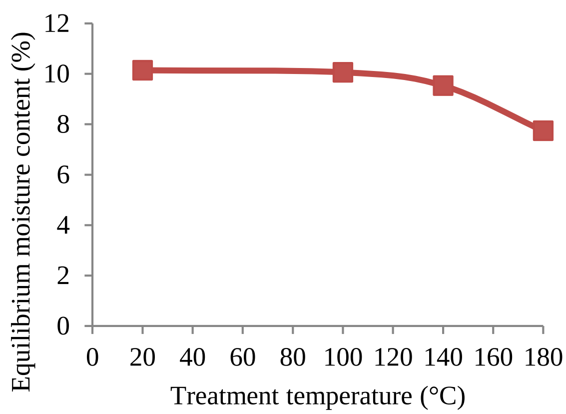


Fig. 2. Equilibrium moisture content of bamboo before and after heat treatment

When samples were heat-treated at 180 °C, equilibrium moisture content changed noticeably compared to the control samples. This can be explained by the degradation of the chemical components. After heat treatment, free -OH groups existed in the bamboo decreased and amorphous regions in the bamboo micro fibrils partially crystallized. The crystallinity of cellulose increased, resulting in the formation of internal hydrogen bonds and ether bonds in the cellulose. The bamboo then became water repellent, decreasing its equilibrium moisture content. It seems possible that there was an indirect relationship between contact angle and equilibrium moisture content in the samples.

XPS Analysis

Free hydroxyl groups are the main active groups on the surface of bamboo and show a close relationship with surface free energy. Changes in chemical functional groups on the bamboo surface are an impetus for changes in bamboo surface free energy after heat treatment. XPS, which was used in these tests, is commonly applied to investigate the surface chemical composition of lignocellulose materials (Nguila *et al.* 2006; Tuong *et al.* 2011).

To evaluate the influence of oxygen content on surface properties, control samples and samples heat-treated at 180 °C for 4 h underwent XPS analysis. Typical C1s XPS survey spectra of the samples are presented in Fig. 3. High-resolution scans of the XPS spectra of C1s and O1s levels are also presented, decomposed into four and two components, respectively. A quantitative determination of the O/C ratio was calculated using the total areas of these peaks and their respective photoemission cross-sections.

Figure 3 shows C1s carbon spectra deconvoluted into four components. The C1 peak is attributable to carbon linked to carbon, or hydrogen present in lignin and extractives. The C2 peak corresponds to carbon-oxygen bonds present in hydroxyl or ether groups of lignin and polysaccharides of bamboo. The C3 peak corresponds to carbon doubly bonded to oxygen, which formed as a result of hemiacetal carbon present in cellulose and hemicelluloses, and to a lesser extent, to carbonyl groups. The C4 peak corresponds to carbonyl of carboxylic acid or ester functions present in bamboo.

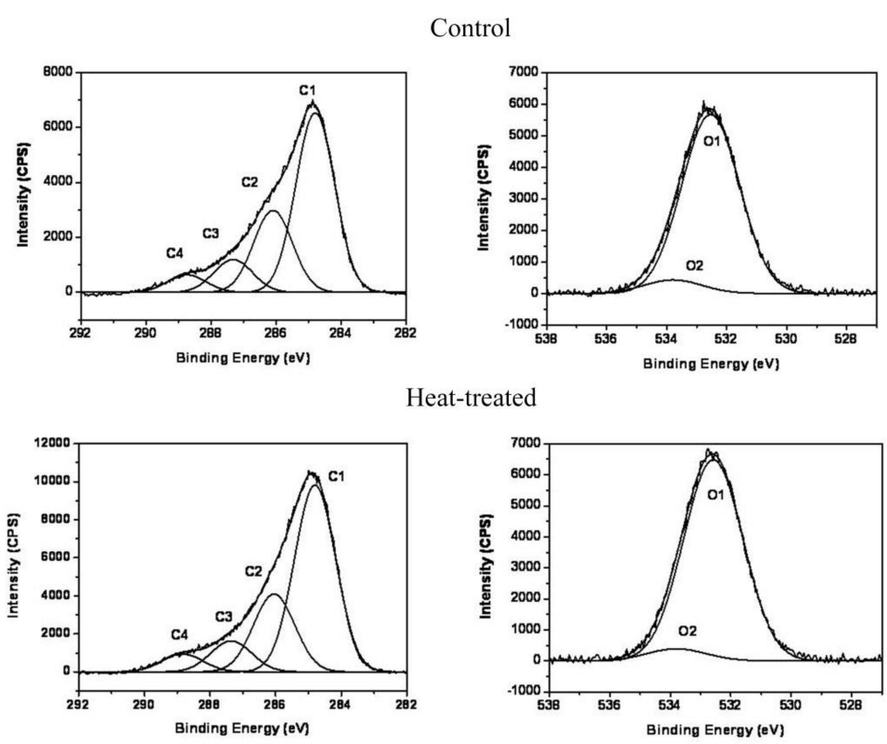


Fig. 3. C_{1S} and O_{1s} XPS survey spectra of control and heat-treated samples

Table 4 summarizes the oxygen and carbon atom concentrations and the abundance of each deconvoluted oxygen and carbon signal in the samples. As mentioned above, the main components of bamboo are cellulose, hemicelluloses, and lignin, along with minor amounts of extractives and inorganics. The O/C ratio reflects the content of lignin and extractives on the bamboo surface (Hua *et al.* 1993). Heat treatment at 180 °C led to a decreased O/C ratio. The C1 peak area increased from 57.54% in the control sample to 59.59% in the samples treated at 180 °C for 4 h, and the C2 and C3 peaks simultaneously decreased, indicating that the hydroxyl group content and hemicelluloses in heat-treated bamboo were reduced because the carbohydrates only contributed to C2 and C3.

Table 4. XPS Spectral Parameters

Sample	O1S%	C1S%	O/C	C1%	C2%	C3%	C4%
Control	26.58	73.42	0.36	57.54	26.28	10.53	5.64
Heat treated	21.35	78.65	0.27	59.59	24.81	9.85	5.74

This decreased oxygen content likely explains the weaker electron-donating component observed in heat-treated samples. The affinity of bamboo for water was considerably reduced as a result of hemicellulose degradation, which caused hydrogen bonds to form within the acidic hydrogen atoms of water molecules through the electron pairs present on the oxygen atoms of their hydroxyl groups.

CONCLUSIONS

1. Bamboo becomes considerably hydrophobic after heat treatment in a range of temperatures between 100 and 180 °C. In this study, heat treatment was observed to increase the contact angle of water and formamide on the bamboo surface, but showed little effect on the contact angle of diiodomethane. Heat treatment between 100 and 180 °C for 4 h led to decreased total surface free energy of the bamboo specimens as temperature increased.
2. Equilibrium moisture content results suggest that when samples were heat-treated in a range of temperatures between 100 and 140 °C, changes in contact angle were likely related to water evaporation and the degradation of extractives as they moved toward the bamboo surface. Samples heat-treated at 180 °C showed more noticeable changes in equilibrium moisture content, however. This is can be explained by the degradation of the chemical components. XPS surface analysis showed that the C1s peak components within the area of the C1 peak increased, indicating where more lignin and extractives were situated on the bamboo surface.
3. The results obtained in this study can be used to predict and understand the wettability of heat-treated bamboo with various surface coatings because wettability profiles significantly impact the use of the material, particularly the adhesion of paints and coatings.

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