Dimensional Stability of Lotus Leaf-like Nanostructure Superhydrophobic Bamboo by Modification Using Xylan

Xun Gao, Ling Su, Guiquan Jiang, Jiuyin Pang,* and Lin Lin

Xylan extracted from corncobs was used to modify bamboo and to improve its dimensional stability. A lotus leaf-like surface was prepared on the modified bamboo using a fresh lotus leaf and polydimethylsiloxane (PDMS) as the template and seal *via* soft lithography. The dimensional stability of bamboo was tested *via* anti-shrinkage efficiency (ASE), moisture excluding efficiency (MEE), weight percent gain (WPG), and its superhydrophobic property. The microstructures of lotus-like bamboo surface were analyzed *via* water contact angle (WCA), scanning electron microscopy, and atomic force microscopy (AFM). The study found that with increasing mass fraction of xylan content, the anti-swelling property and WPG of modified bamboo increased accordingly. When the mass fraction of xylan was 10%, its WPG was the largest (2.21%), and xylan had a better compatibilization effect on bamboo. The dimensional stability of bamboo was improved to a certain extent by xylan. Moreover, the anisotropy and superhydrophobicity of the lotus leaf-like bamboo treated by xylan were noticeably improved after modification, such that the WCA of the transverse, radial, and tangential sections were 157.5º, 145.5º, and 137.5º, respectively. This research lays a foundation for studies of dimensional stability of bamboo and the mechanism of modification to achieve hydrophobic properties.

Keywords: Dimensional stability; Superhydrophobicity; Anisotropy; Bamboo; Xylan; Soft lithography

*Contact information: Beihua University, Wood Material Science and Engineering Key Laboratory of Jilin Province, Jilin 132013, China; *Corresponding author: pangjiuyin@163.com*

INTRODUCTION

Bamboo belonging to the Bambusoideae, a subfamily of Gramineae, is an ideal natural forest resource, with advantages of fast growth, good toughness, and renewability. (Hattori 2017; Wang and Li 2019). Bamboo is mainly composed of cellulose, hemicellulose, and lignin. As an organic lignocellulosic material, bamboo has plenty of hydrophilic groups and an overall porous structure that has almost no resistance to moisture and possesses strong water absorbability (Wang *et al.* 2017a). When used or stored in moist conditions, bamboo undergoes damage by mildew, decay, cracking, and deformation. Bamboo is an anisotropic, heterogeneous material with characteristic variations along the radial gradient (Wang *et al.* 2017a). The structure of bamboo determines its physical properties, such as a relatively low dry shrinkage and wet swelling, which affects the dimensional stability of bamboo (Samanta and Singh 2019). When bamboo begins to shrink during drying or to swell when becoming wet, it can cause changes in the dimensions and shape of the bamboo, leading to defects such as cracking or warping (Nguyen *et al.* 2019). These may negatively influence the processing and utilization of bamboo. Therefore, it is necessary to conduct research to develop surface hydrophobic modification and to improve the dimensional stability of bamboo.

The hydrophobic modification of solid materials' surfaces can be achieved by changing the surface free energy and surface morphology (Liu *et al.* 2013). The micro/nano multi-scale hierarchical roughness structures of natural plant leaf surfaces endow the material with special wettability (Koch *et al.* 2010; Xia *et al.* 2012; Yuan *et al.* 2014). For example, the nanopapillae on the surface of the lotus leaf (*Nelumbo nucifera*) are covered with epicuticular wax crystalloids; this combination of structure and surface chemistry provides the lotus leaf with super-hydrophobic and self-cleaning properties (Ma and Hill 2006; Wang *et al.* 2017b; Sethi and Manik 2018). Taking inspiration from the biology of the lotus, the authors have successfully prepared lotus-leaf-like SiO_2 superhydrophobic bamboo surfaces based on the method of soft lithography using a fresh lotus leaf and poly-dimethylsiloxane (PDMS) (Schueller *et al.* 1999) as a template and seal transferring the surface topography of a lotus leaf onto the bamboo surface. This converted the bamboo surface from hydrophilic to hydrophobic surface, thus overcoming many of the problems caused by water absorption. Meanwhile, the hydrophobic properties of three different sections of bamboo were greatly improved after the hydrophobic modification treatment. However, the degree of hydrophobic improvement was not the same for all three sections; the bamboo still had obvious anisotropy in different sections. The anisotropy of the bamboo surface was related to the structure of bamboo itself. In addition, the transverse permeability of bamboo was poor. The air under the water droplets was closed into the cell lumen of the catheters and parenchyma cells, which was not easy to dissipate. Nevertheless, as to the radial section or tangential section, the air could easily escape along the cell lumen of catheters and fiber cells. It is well known that there is obvious anisotropy among different sections of wood. The variation of tangential sections ranges from 6% to 12%, while the radial and transverse sections are between 3% to 6%, and 0.1% to 0.35%, respectively. Bamboo has a similar anisotropy as wood. The anisotropy of bamboo also has characteristic variations along the radial gradient, making the different sections of bamboo exhibit differences in dry shrinkage and wet swelling, which can affect the dimensional stability of bamboo.

The general definition of dimensional stability is the degree of a sample's dimension or shape change under the action of temperature, humidity, other chemicals, or external forces (Yang *et al.* 2019). In the case of poplar wood, it has been shown that the dimensional stability can be improved and the hygroscopicity can be reduced by decreasing the adsorption points by acetylation of –OH groups (Chai *et al.* 2017). The common treatment methods of dimensional stability are covering with waterproof coating on material surfaces, phenolic resin treatment, polyethylene glycol treatment, heat treatment, acetylation treatment, the treatment of isocyanate, *etc.* (Dong *et al.* 2016; Wei *et al.* 2018). The bamboo can be chemically modified, which changes its characteristics (Giridhar *et al.* 2017). The xylan extracted from corncobs was used to treat bamboo in order to improve its dimensional stability in this work. Xylan (1,4-beta-D-xylan) is a kind of polysaccharide with a variety of substituent groups and is a major component of plant hemicelluloses. Corncobs, especially, have a high xylan content. Compared with other chemical treatments, xylan treatment is a new method that is harmless to humans and animals and does not pollute the environment. Xylan is a high molecular weight polymer that is not soluble in water, acid, alcohol, or ether; but it is soluble in dilute alkali solution. Therefore, the use of an alkali alcohol precipitation method is often used to extract xylan. Xylan is dispersed in the cell walls of plants, and the partial groups of the main chains are linked by the glycosidic bonds. These bonds are replaced by plant cell wall side chain substituents to form a dense structure that can effectively control the immersion or outflow of free water. Therefore, the dimensional stability can be effectively maintained to a certain extent. As a result, xylan is used to modify bamboo and make its cell walls filled, thus reducing the hydrophilic groups of the cell wall to form a dense structure, which can effectively prevent water flow into or out of the cell. Impregnating the bamboo with xylan can effectively reduce dry shrinkage and wet swelling of bamboo, which prevents cracking, warping, and deformation. Finally, the dimensional stability of bamboo can be improved to some degree. In addition to these hydrophobic properties, xylan solution also shows antibacterial and anticorrosion functions to a certain extent. In summary, xylan is a type of environmentally friendly chemical reagent that serves a variety of effects.

In this work, the bamboo was first treated with xylan to improve its dimensional stability, and then the treated bamboo surface underwent hydrophobic treatment by soft lithography using a fresh lotus leaf and PDMS as a template and seal, respectively, transferring over it a lotus leaf-like topography based on a micro/nano hierarchical structure. Soft lithography is especially suitable for replicating micro-nano structures of plant leaf surfaces. The PDMS is a low surface energy material containing $–CH_3$ groups; it has intrinsic deformability and hydrophobic properties (Guan *et al.* 2015). Meanwhile, the effects of the different mass fractions of xylan on the dimensional stability of bamboo were characterized by measuring the moisture absorption rate, volume expansion (contraction) rate, anti-swelling (shrinkage) efficiency (ASE), and moisture excluding efficiency (MEE) (García *et al.* 2012). The microstructures of the lotus-like bamboo surfaces were analyzed by scanning electron microscopy (SEM) and by atomic force microscopy (AFM). These explained the hydrophobic mechanism of rough surfaces. The successfully prepared bamboo samples not only could overcome the defects of dimensional differences caused by anisotropy, but also the modifications endowed the bamboo with a lotus-leaf-like superhydrophobic surface that could prolong the service life of bamboo. At the same time, this study could also provide a new direction for the study on the dimensional stability of wood, which would be of great practical value.

EXPERIMENTAL

Materials

Corncobs obtained from Shanghai Hanhong Ltd. (China) were used to extract xylan. Sodium hydroxide, ethanol, 3,5-dinitrosalicylic acid (DNS), sodium potassium tartrate, phenol, sodium sulfite, sulfuric acid, and xylose were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Moso bamboo (*Phyllostachys heterocycla* var. *pubescens*) slices of 20 mm × 20 mm × 10 mm (Length × Width × Height) were ultrasonically rinsed in deionized water for 30min and followed by acetone for 30 min, and then were oven-dried at 50 °C for 12 h. The PDMS and a curing agent, 184 silicone elastomer base, were purchased from DOW Corning Corporation of the United States (Midland, Michigan, USA). Polyvinyl butyral (PVB, MW 40,000 to 70,000), was purchased from Aladdin Industrial Corporation (Shanghai, China). All chemicals were used as received

Methods

Extraction of xylan

The corncobs were crushed and then screened below 60-mesh. A total of 50 g corncobs were added to water and boiled for 4 h. After the excess water was filtered out, the corncobs were extracted for 2 h according to the extraction temperature, alkali concentration, and solid-liquid ratio given in Tables 1 and 2. Then, the residue was filtered off. Next, 95% ethanol at a volume ratio of 1:3 was added to the filtrate and settled for 12 h. After filtering the liquid, the mixture was centrifuged at 8000 rpm for 10 min, and a relatively dry xylan was obtained after centrifuging four times.

Table 1. Factors and Levels of the Orthogonal Array

Number	Factors	Levels		
		1	2	3
1	Extraction Temperature (°C)	70	80	90
2	Alkali Concentration (%)	5	10	15
3	Solid to Liquid Ratio	5	1:5	1:10

Table 2. Orthogonal Experimental Design for the L9 (3^4) Orthogonal Array

Sample	Extraction Temperature (°C)	Alkali Concentration (%)	Solid to Liquid Ratio
1	70	5	1:5
2	70	10	1:7
3	70	15	1:10
4	80	5	1:7
5	80	10	1:10
6	80	15	1:5
7	90	5	1:10
8	90	10	1:5
9	90	15	1:7

Determination of Xylan Content

Preparation of DNS reagent

First, 6.3 g of 3,5-dinitrosalicylic acid and 262 mL of a 2 M sodium hydroxide solution were added to a 500 mL hot solution containing 185 g sodium potassium tartrate and stirred until all the sodium potassium tartrate was dissolved. Then, 5 g phenol and 5 g sodium sulfite were added, and the solution was stored in a cool dry place for a week.

Calibration of standard xylan curve

Xylan standard solutions (1 mg/mL) of 0 mL, 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL, and 1.0 mL were placed into 15 mL test tubes, and then made up to 1 mL with water. Then, 2 mL DNS reagents were added to these test tubes before heating in a boiling water bath for 2 min and adding water up to 15 mL after natural cooling. The absorbance was measured at a wavelength of 480 nm to determine the regression line equation, which is shown in Fig. 1.

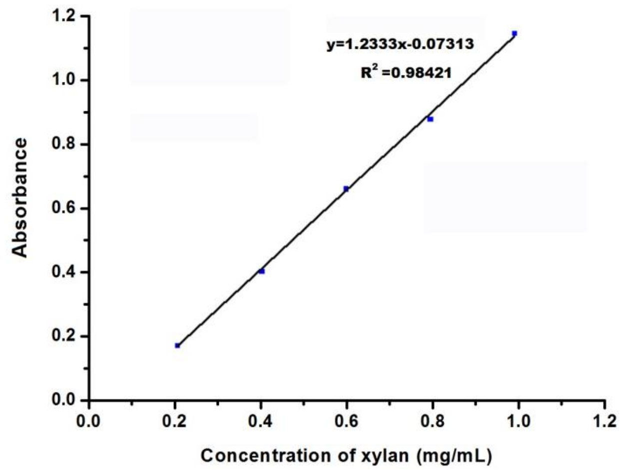

Fig. 1. Calibration of xylan curve

Determination of reducing sugar concentration by DNS method

First, 20 mL of 8% sulfuric acid solution was added to 20 mL xylan solution and kept at 121 °C for 1 h. The pH was then adjusted to 7.0 with 20% sodium hydroxide solution, and the mass concentration of the xylan was adjusted to 0.2 g/L to 2 g/L by adding water, and then the concentration of the neutralized solution was measured by the DNS method.

Then, 2 mL xylan solution and 3 mL configured DNS reagent were added to a 25-mL test tube in a boiling water bath for 5 min and added water up to 25 mL when the solution was cooled to room temperature. The absorbance was measured at 480 nm with an ultraviolet-visible spectrophotometer (Dor Yang UV755B; Duyang Precision Instrument Co., Ltd., Shanghai, China), and the reducing sugar concentration was calculated using the regression line equation.

It could be seen from Table 1 that the order of effect factors for the extraction of xylan was the extraction temperature > the alkali concentration > the solid:liquid ratio, and the optimum extraction process parameter was the extraction temperature at 70 °C, 10% alkali concentration, and solid-liquid ratio of 1:7; this extraction extent was 42.6%.

Preparation and treatment for the dimensional stability of bamboo

Firstly, 100 specimens of bamboo measuring 20 × 20 × 10 mm^3 were prepared from defect free bamboo (Xuancheng leye wood co. Led,, Xuancheng, China). After drying them to the absolute dry condition, the bamboo samples were weighed, measured by their radial, tangential, and longitudinal dimensions, and then their volumes were calculated. The measured specimens were treated to moisture absorption in a closed container with a temperature of 20 ± 2 °C and a relative humidity of 65%. The weight and size of the bamboo was measured after moisture absorption for 15 days, and then the moisture absorption rate (X) and volumetric swelling coefficient (S) were obtained.

The moisture absorption rate and volumetric swelling coefficient were determined based on the water-soaking method according to Eqs. 1 and 2,

$$X\,(\%) = 100(M_1 - M_0) / M_0 \qquad (1)$$

where M_1 (g) is the mass of sample after moisture absorption and M_0 (g) is the weight of oven-dried sample and,

$$S\ (\%) = 100(V_2 - V_1) / V_1 \quad (2)$$

where V_2 (mm^3) is the volume of the hygroscopic sample and V_1 (mm^3) is the volume of the oven-dried sample.

Secondly, the above 100 specimens were divided into 5 groups and dipped into xylan solutions with mass fractions of 2 wt%, 4 wt%, 6 wt%, 8 wt%, and 10 wt%, to be soaked for 15 days. Then, these modified specimens were treated with moisture absorption under a temperature of 20 ± 2 °C and a relative humidity of 65% for another 15 days. The weight and size of modified bamboo was measured the same way as the unmodified bamboo described above.

Thirdly, the moisture absorption rate and the volumetric swelling coefficient of the treated bamboo could be obtained by the above method. Lastly, the ASE (the percentage of size difference of the same sample after hygroscopic treatment), MEE (the percentage of the difference in the water discharge mass of the same sample after hygroscopic treatment), weight percent gain (WPG), and bulking efficiency (B) of the modified bamboo specimens were calculated using Eqs. 3 through 6,

$$ASE\ (\%) = 100(S_0 - S_1) / S_0 \quad (3)$$

where S_0 (%) and S_1 (%) are the volumetric swelling coefficients of unmodified and modified specimens, respectively. The MEE was determined as follows,

$$MEE\ (\%) = 100(X_0 - X_1) / X_0 \quad (4)$$

where X_0 (%) is the moisture excluding efficiency of unmodified sample and X_1 (%) is the moisture excluding efficiency of modified sample. The WPG was determined as follows,

$$WPG\ (\%) = 100(W_1 - W_2) / W_2 \quad (5)$$

where W_1 (g) and W_2 (g) are oven dried weight of chemically modified and unmodified wood specimens respectively. The B was determined as follows,

$$B\ (\%) = 100(V_T - V_C) / V_C \quad (6)$$

where V_T (mm^3) is the oven-dried volume of modified sample and V_C (mm^3) is the oven-dried volume of the unmodified bamboo sample.

Preparation and Characterization of the Lotus Leaf-like Structure Bamboo Sample

The lotus leaf-like superhydrophobic bamboo was prepared using a fresh lotus leaf and PDMS as a template and seal coating polyviny butyral (PVB) on both the unmodified and the modified bamboo surfaces *via* soft lithography with two replications, transferring over it a lotus leaf-like topography based on a micro/nano hierarchical structure which made the bamboo successfully translate from a hydrophilic surface to a hydrophobic surface, thus overcoming many of the problems caused by water absorption. The flow chart of the preparation and treatment for the dimensional stability of lotus leaf-like bamboo using xylan is shown in Fig. 2.

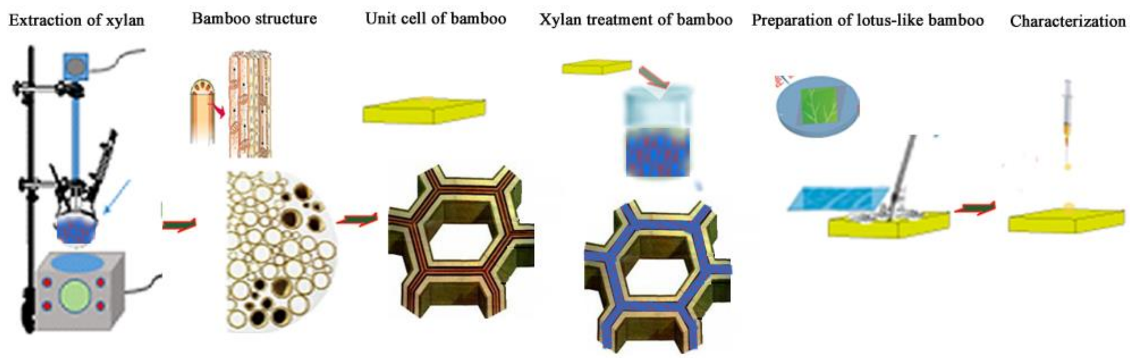

Fig. 2. Treatment for dimensional stability of lotus leaf-like bamboo by xylan

Bamboo surface microstructure was observed by SEM (Quanta 200; FEI Company). The microscopic morphology of the sample was observed by AFM (Nanoman VS, Veeco). Fourier transform infrared (FTIR) spectra for the lotus leaf-like bamboo was recorded using a FTIR spectrophotometer (Thermo Fisher Scientific Co., Ltd., Waltham, MA, USA). The water contact angle (WCA) of three different sections of the lotus leaf-like bamboo was measured using a JC2000C1 contact angle system (Powereach Co., Shanghai, China) at ambient temperature with a droplet volume of 5 μL. An average WCA value was determined by measuring five different positions of the sample.

RESULTS AND DISCUSSION

Range Analysis

Table 3. Process Parameters of Xylan Extraction

Sample	Extraction Temperature (°C)	Alkali Concentration (%)	Solid-to-Liquid Ratio	Extraction Rate (%)
1	70	5	1:5	42.05
2	70	10	1:7	42.64
3	70	15	1:10	34.34
4	80	5	1:7	32.72
5	80	10	1:10	32.12
6	80	15	1:5	25.88
7	90	5	1:10	34.35
8	90	10	1:5	34.05
9	90	15	1:7	34.90
T_1	39.682	36.376	33.998	
T_2	30.247	36.275	36.758	
T_3	34.435	31.713	33.609	
R	9.435	4.664	3.149	

The range analysis method is based on calculating the range (R-value) of each column in the orthogonal Table 3 through statistical methods. This method can be used to determine the major and minor orders between the processing parameters, in order to obtain the optimum combination of levels. For determining the optimum combination, it was assumed that a greater range corresponds to a factor with a greater impact. The calculation results are listed in Table 3. With respect to the extraction rate of the xylan, the R value corresponding to the extraction temperature, alkali concentration, and solid-to-liquid ratio were 9.435, 4.664, and 3.149, respectively. Clearly, the R-value corresponding to the extraction temperature was the maximum, and it is the minimum for the solid-to-liquid ratio. Thus, the following major and minor relationships between the processing parameters and the extraction rate of the xylan exit: the extraction temperature was predicted to have the strongest effect; the alkali concentration had the second-strongest effect; and the solid-to-liquid ratio had the weakest effect on the mechanical properties. The optimum extraction process parameters included a temperature of 70 ºC, an alkali concentration of 10%, and a solid-to-liquid ratio of 1:7.

Moisture Absorption Rate and Volumetric Swelling Coefficient Analysis

The moisture absorption percentage (X_1) and volumetric swelling coefficient (S_1) of the unmodified bamboo as well as X_2 (%) and S_2 (%) of the modified bamboo were calculated using Eqs. 1 and 2, as shown in Table 4. It was shown that the moisture absorption rate of the unmodified bamboo was nearly the same; all of which were less than those of the modified bamboo. That is because xylan has a variety of substituent groups, a major component of hemicelluloses, and hemicellulose has a strong ability to absorb moisture. The volumetric swelling coefficient of both unmodified bamboo and of modified bamboo increased with the increasing xylan content.

Table 4. Moisture Absorption Rate and Volumetric Swelling Coefficient of Bamboo Specimens

Samples	X_1 of Unmodified Bamboo (%)	S_1 of Unmodified Bamboo (%)	X_2 of Modified Bamboo (%)	S_2 of Modified Bamboo (%)
2% Xylan solution	9.7	2.59	11.82	2.93
4% Xylan solution	9.74	3.25	11.08	3.07
6% Xylan solution	9.66	2.43	11.56	2.95
8% Xylan solution	9.71	3.92	11.44	3.63
10% Xylan solution	9.72	6.03	11.47	4.86

Through *X* (%) and *S* (%), the results of ASE, MEE, WPG, and B of the modified bamboo specimens could be obtained, which are shown in Fig. 3 according to Eqs. 3 through 6.

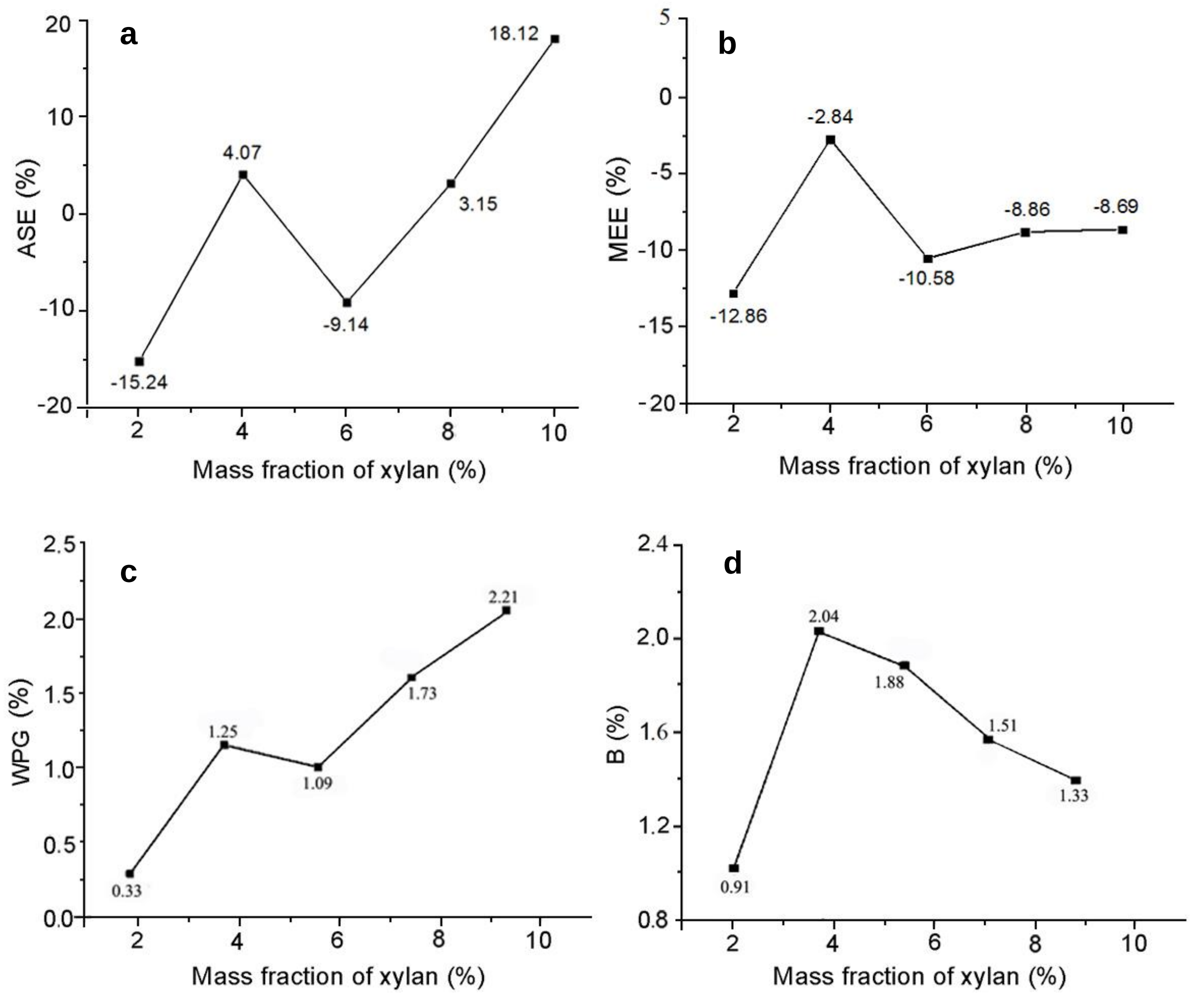

Fig. 3. (a) ASE, (b) MEE, (c) WPG, and (d) B of bamboo specimens modified by different mass fractions of xylan

It can be seen from Fig. 3a that the antishrinkage efficiency of bamboo showed an increasing trend with increased mass fraction of xylan. When the mass fraction of xylan increased to 10%, the ASE of modified bamboo was 18.1%. The xylan did not have an antishrinkage effect on bamboo at a low mass fraction; while in the case of a high mass fraction, xylan demonstrated antishrinkage properties. The reason was likely that in the case of a low mass fraction of xylan, the chemical loading of the bamboo specimens was low, and only a small amount of xylan entered the bamboo causing minimal antishrinkage for bamboo. However, when the mass fraction of xylan increased, the drug loading capacity of bamboo increased, resulting in a strong antishrinkage property. Meanwhile, as seen in Fig. 3b, MEE of the treated bamboo samples increased initially and then decreased, and finally it tended to stabilize with the increase of the mass fraction of xylan. The lowest and highest values were -12.9% as well as -2.8% in the presence of 2% xylan and 4% xylan, respectively. All the results were negative values with the average value being -8.8%, which indicated that xylan was able to absorb water, and could not prevent bamboo from absorbing moisture. In Fig. 3c, modified bamboo exhibited a high WPG that increased with the increasing mass fraction of xylan. The WPG of the 10% mass fraction of xylan treatment specimens was 2.2%. The WPG was related to the drug loading. When the mass fraction of the xylan solution increased, the drug loading also increased, resulting in a higher weight gain. In Fig. 3d, the B of the treated bamboo modified by xylan initially increased from 0.91in 2% xylan to 1.33 in 4% xylan with a maximum of 2.04%, and then it was reduced with an increasing mass fraction of xylan. The results showed that xylan had a compatibilizing effect on bamboo.

Figures 3a through 3d show that xylan had some inherent water absorption. When the mass fraction of xylan was low, the modified bamboo demonstrated no antiswelling properties, and the values of moisture excluding efficiency, weight percent gain, and bulking efficiency were also small. However, with the increasing mass fraction of xylan content, the antiswelling property and WPG increased; in addition, xylan had a better compatibilization effect than that of the low mass fraction of xylan.

Analysis by SEM and FTIR

The bamboo specimen treated by the 10% xylan solution was selected to modify its hydrophobic property by soft lithography using fresh lotus leaves as a template and PDMS as the seal with two replications. In Fig. 4a, the microstructure of the bamboo was distinctly observed, which showed a smooth surface. Figure 4b is the image of the modified bamboo surface with xylan.

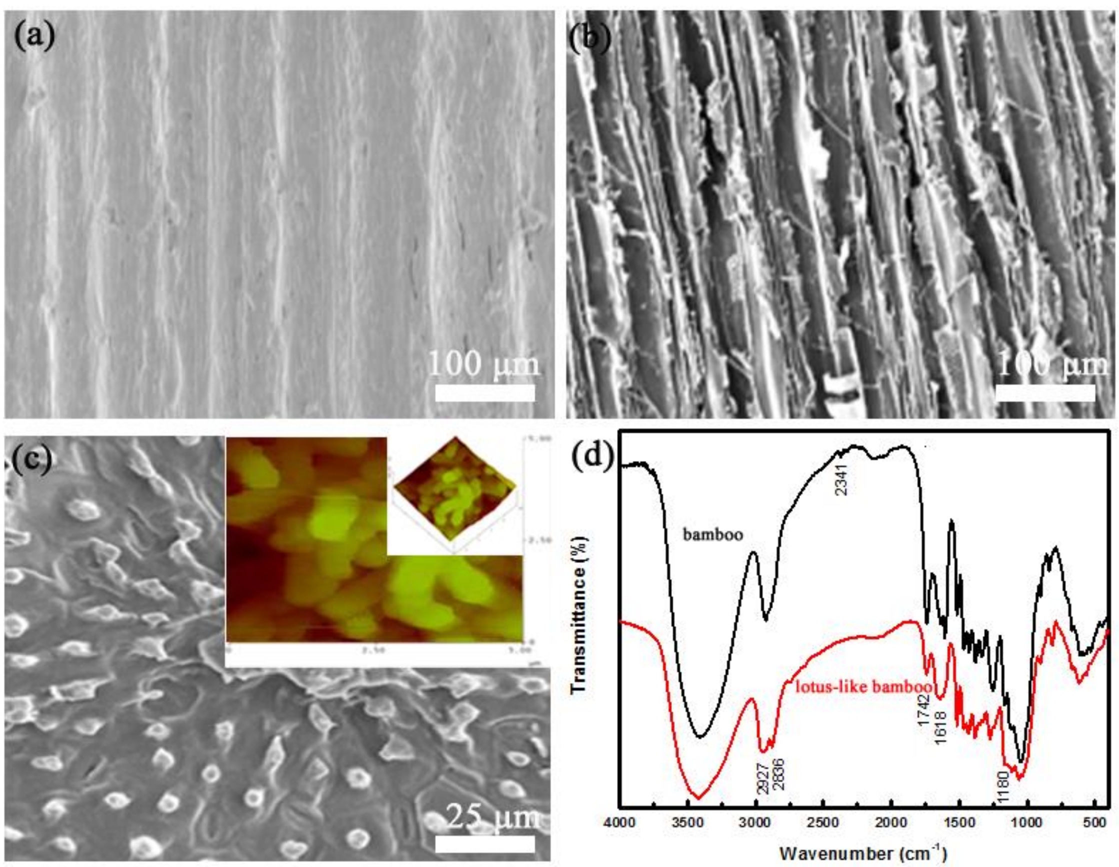

Fig. 4. The SEM images and FTIR of the samples: (a) bamboo surface, (b) xylan-treated bamboo surface, (c) modified lotus leaf-like bamboo surface, and (d) FTIR spectra

The surface of the bamboo became rougher after treatment with xylan. Figure 4c is the image of the lotus leaf-like bamboo surface, and its surface was uniformly textured with approximately 10-μm sized micro-nanopapilla. The inset is its corresponding AFM image, which showed a rough surface. Figure 4d presents the FTIR absorption spectra of bamboo and the lotus leaf-like bamboo treated with xylan. The absorption peak of bamboo at 2927 cm^{-1} was the $–CH_3$ symmetrical stretching vibrations of lignin. The absorption peak at 2836 cm^{-1} was caused by the $–CH_2$ asymmetrical stretching vibrations, and $–CH_2$ and $–CH_3$ groups were both low surface energy groups, which could provide a lower surface energy to bamboo surfaces to improve the wettability of bamboo.

Contact Angle and Scroll Angle Analysis

To test the improvement of anisotropy of three different sections of the modified bamboo, the WCA of the lotus leaf-like bamboo was measured, and the results are shown in Table 3 and Fig. 5 compared with the unmodified lotus-like bamboo. As shown in Table 3, the hydrophobic property of three sections of the modified lotus leaf-like bamboo was universally improved after modification treatment by xylan relative to the unmodified samples. Although an obvious anisotropy still existed in the three different sections, xylan treatment remarkably improved the anisotropy of bamboo.

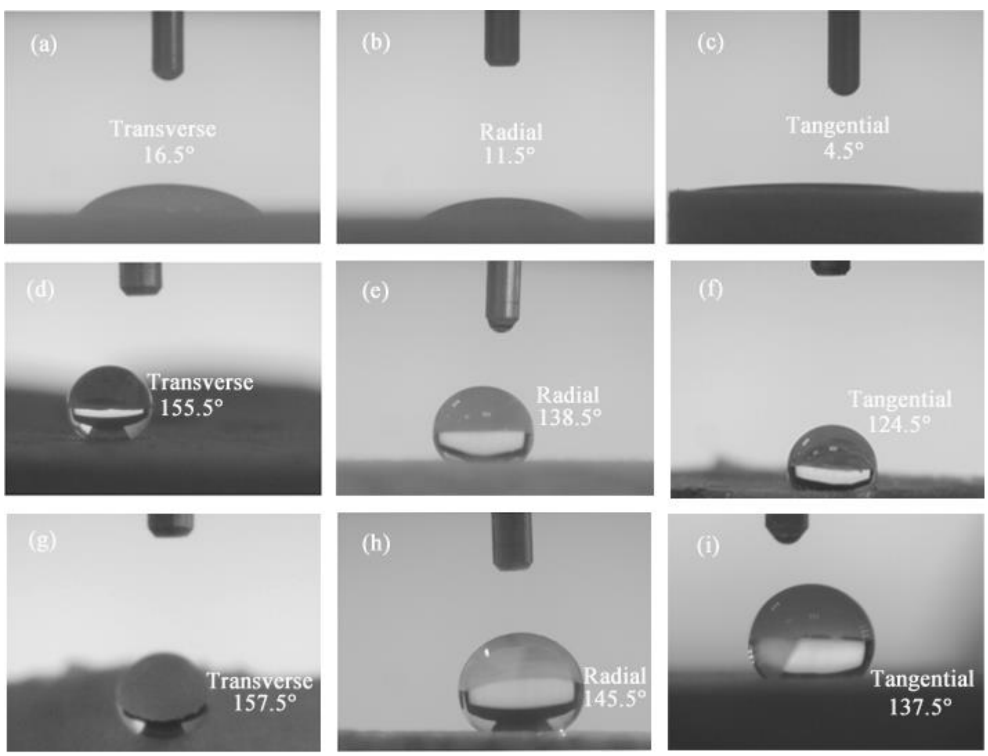

Fig. 5. The water contact angles (WACs) of the different sections of (a through c) bamboo, (d through f) unmodified lotus leaf-like bamboo, and (g through i) modified lotus leaf-like bamboo

Table 3. Contact Angle of Three Different Sections of Lotus Leaf-like Bamboo

Section	Unmodified Sample			Xylan-modified Sample		
	Maximum value	Minimum value	Average value	Maximum value	Minimum value	Average value
Transverse	157.5°	148.5°	155.5°	160.5°	153.5°	157.5°
Radial	141.5°	130.5°	138.5°	147.5°	141.5°	145.5°
Tangential	127.5°	118.5°	124.5°	140.5°	135.5°	137.5°

As shown in Fig. 5, images a through c were from unmodified bamboo, and the WAC of these three sections were all small, indicating strong hydrophilic properties. Images d through f are the WAC of the unmodified lotus leaf-like bamboo, whose infiltration changed greatly after modification treatment by soft lithography. The anisotropy of this bamboo can obviously be seen. Compared with Fig. 5d through 5f, Fig. 5g through 5i are the WCA of the modified lotus leaf-like bamboo treated by xylan. The WAC of transverse section, radial section, and tangential section were 157.5º, 145.5º, and 137.5º, respectively, which indicated great improvements.

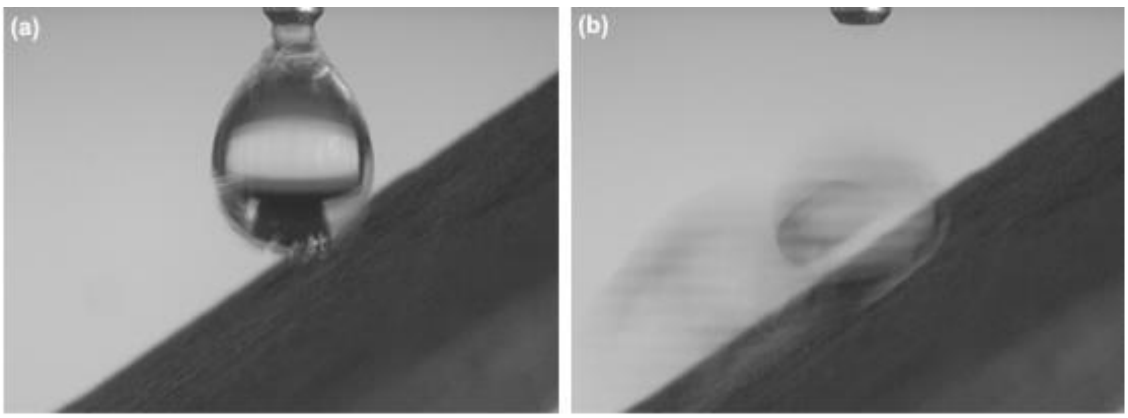

Fig. 6. WAC images of samples with (a) and (b) a rolling process of water on modified lotus leaf-like bamboo surface

Figure 6a and b are the process of rolling a water droplet on the second modified lotus leaf-like bamboo surface. The water droplet could roll away from the lotus leaf-like bamboo surface with a low scroll angle (SA) of < 10º, which showed the performances of superhydrophobicity and low adhesion. Xylan is dispersed in the cell walls of plants, and in the partial groups of the main chains linked by the glycosidic bonds are replaced by plant cell wall side chain substituents, so as to form a dense structure, which can effectively control the immersion or outflow of free water and drastically improve the dimensional stability and hydrophobic properties of the bamboo.

CONCLUSIONS

The modification with xylan is a relatively effective treatment method which could improve dimensional stability and superhydrophic properties of the modified bamboo. In this research, the effects of the modification on the properties of the modified bamboo were evaluated and the conclusions can be summarized as follows:

1. The orthogonal design method could be effectively used to optimize the processing parameters, and the extraction temperature was found to have the greatest effect on the extraction rate of the xylan, followed by the alkali concentration. A temperature of 70 °C, an alkali concentration of 10%, and a solid-to-liquid ratio of 1:7 were determined as the optimum parameters.
2. The xylan demonstrated water absorbability and could not prevent bamboo from moisture absorption. In a lower mass fraction of xylan solution, the treated bamboo demonstrated no antiswelling (shrinkage) property with small values of MEE, WPG, and B. However, with increasing mass fraction of xylan content, the antiswelling property and WPG of modified bamboo increased accordingly. The WPG of the 10% mass fraction of xylan treatment specimens was 2.21%, and xylan had a better compatibilization effect on the bamboo, which improved the dimensional stability of bamboo to a certain extent.
3. The SEM and AFM analyses showed that the lotus leaf-like bamboo surface was a polycrystalline material, and the lotus leaf-like topography played an important role in the fabrication of the superhydrophobic surface. The WCAs of transverse, radial, and tangential sections were 157.5º, 145.5º, and 137.5º. The xylan-treated bamboo specimens were superhydrophobically modified *via* soft lithography. The anisotropy of bamboo was remarkably improved, which could provide a good basis for the study of the modification of bamboo anisotropy.

ACKNOWLEDGEMENTS

The work was financially supported by the National Natural Science Foundation of China (31800480), Jilin Province Department of Education Fund (JJKH20190650KJ), Jilin Province Agricultural Sector Key Research and Development Projects (20190301045N Y), Jilin Provincial Development and Reform Commission Industrial Innovation Special Fund Project (2019C044-4), and the PhD Start up Fund of Beihua University.

REFERENCES CITED

Chai, Y., Liu, J., Wang, Z., and Zhao, Y. (2017). "Dimensional stability and mechanical properties of plantation poplar wood esterified using acetic anhydride," *BioResources* 12(1), 912-922. DOI: 10.15376/biores.12.1.912-922

Dong, Y., Yan, Y., Wang, K., Li, J., Zhang, S., Xia, C., and Cai, L. (2016). "Improvement of water resistance, dimensional stability, and mechanical properties of poplar wood by rosin impregnation," *European Journal of Wood and Wood Products* 74(2), 177-184. DOI: 10.1007/s00107-015-0998-6

García, J. J., Rangel, C., and Ghavami, K. (2012). "Experiments with rings to determine the anisotropic elastic constants of bamboo," *Construction and Building Materials* 31, 52-57. DOI: 10.1016/j.conbuildmat.2011.12.089

Giridhar, N., Pandey, K. K., Prasad, B. E., Bisht, S. S., and Vagdevi, H. M. (2017). "Dimensional stabilization of wood by chemical modification using isopropenyl

acetate," *Maderas. Ciencia y Tecnología* 19(1), 15-20. DOI: 10.4067/S0718-221X2017005000002
Guan, H., Han, Z., Cao, H., Niu, S., Qian, Z., Ye, J., and Ren, L. (2015). "Characterization of multi-scale morphology and superhydrophobicity of water bamboo leaves and biomimetic polydimethylsiloxane (PDMS) replicas," *Journal of Bionic Engineering* 12(4), 624-633. DOI: 10.1016/S1672-6529(14)60152-9
Hattori, T. (2017). "Biogeography of polypores in Malesia, Southeast Asia," *Mycoscience* 58(1), 1-13. DOI: 10.1016/j.myc.2016.09.004
Koch, K., Bhushan, B., and Barthlott, W. (2010). "Multifunctional plant surfaces and smart materials," in: *Springer Handbook of Nanotechnology*, Springer, Berlin, Heidelberg, Germany, pp. 1399-1436.
Liu, M., Wang, S., and Jiang, L. (2013). "Bioinspired multiscale surfaces with special wettability," *MRS Bulletin* 38(5), 375-382. DOI: 10.1557/mrs.2013.100
Ma, M., and Hill, R. M. (2006). "Superhydrophobic surfaces," *Current Opinion in Colloid & Interface Science* 11(4), 193-202. DOI: 10.1016/j.cocis.2006.06.002
Nguyen, Q. T., Nguyen, T., and Nguyen, N. B. (2019). "Effects of bleaching and heat treatments on *Indosasa angustata* bamboo in Vietnam," *BioResources* 14(3), 6608-6618. DOI: 10.15376/biores.14.3.6608-6618
Samanta, S., and Singh, T. J. (2019). "Effect of kevlar hybridization on dry sliding friction and wear behaviour of bamboo/epoxy composites," *Key Engineering Materials* 801, 89-94. DOI: 10.4028/www.scientific.net/KEM.801.89
Schueller, O. J., Zhao, X. M., Whitesides, G. M., Smith, S. P., and Prentiss, M. (1999). "Fabrication of liquid-core waveguides by soft lithography," *Advanced Materials* 11(1), 37-41. DOI: 10.1002/(SICI)1521-4095(199901)11:1<37::AID-ADMA37>3.0.CO;2-0
Sethi, S. K., and Manik, G. (2018). "Recent progress in super hydrophobic/hydrophilic self-cleaning surfaces for various industrial applications: A review," *Polymer-Plastics Technology and Engineering* 57(18), 1932-1952. DOI: 10.1080/03602559.2018.1447128
Wang, F., Li, S., and Wang, L. (2017a). "Fabrication of artificial super-hydrophobic lotus-leaf-like bamboo surfaces through soft lithography," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 513, 389-395. DOI: 10.1016/j.colsurfa.2016.11.001
Wang, F., Wang, L., Wu, H., Pang, J., Gu, D., and Li, S. (2017b). "A lotus-leaf-like SiO_2 superhydrophobic bamboo surface based on soft lithography," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 520, 834-840. DOI: 10.1016/j.colsurfa.2017.02.043
Wang, P. Y., and Li, D. Z. (2019). "*Dendrocalamus menghanensis* (Poaceae, Bambusoideae), a new woody bamboo from Yunnan, China," *PhytoKeys* 130, 143. DOI: 10.3897/phytokeys.130.33948
Wei, X., Tao, D., Sheng, X., and Zhang, M. (2018). "Modification of poplar wood using polyhexahydrotriazine and its effect on hygroscopicity," *Journal of Wood Chemistry and Technology* 38(3), 214-223. DOI: 10.1080/02773813.2018.1432654
Xia, D., Johnson, L. M., and López, G. P. (2012). "Anisotropic wetting surfaces with one-dimensional and directional structures: Fabrication approaches, wetting properties and potential applications," *Advanced Materials* 24(10), 1287-1302. DOI: 10.1002/adma.201104618

Yang, T., Ma, E., and Cao, J. (2019). "Synergistic effects of partial hemicellulose removal and furfurylation on improving the dimensional stability of poplar wood tested under dynamic condition," *Industrial Crops and Products* 139, Article ID 111550. DOI: 10.1016/j.indcrop.2019.111550

Yuan, Z. Q., Wang, X., Bing, J. P., Wang, M. L., and Huang, J. (2014). "Preparation of superhydrophobic surface on copper foils by a facile method," *Advanced Materials Research* 834-836, 42-45. DOI: 10.4028/www.scientific.net/AMR.834-836.42

Article submitted: October 10, 2019; Peer review completed: February 22, 2020; Revised version received: March 7, 2020; Accepted: March 8, 2020; Published: March 26, 2020.
DOI: 10.15376/biores.15.2.3443-3457