EXTRACTION OF BAMBOO SHOOT SHELL FIBERS BY THE ULTRASOUND-ASSISTED ALKALI-OXYGEN BATH METHOD

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Herein, bamboo shoot shell fibers were extracted by the ultrasound-assisted alkali-oxygen bath method. The effects of sodium hydroxide and hydrogen peroxide dosage, temperature and treating time on degumming properties were discussed. Taking the degumming rate as the index, the optimum technological parameters of alkali oxygen bath degumming were obtained by orthogonal experiments as follows: scouring temperature was 95 °C, alkali boiling time of 120 minutes, sodium hydroxide dosage of 20 g/L, hydrogen peroxide dosage of 24 mL/L, and the corresponding degumming rate was 70.07%. The structure of bamboo shoot shell fibers was examined by infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy. The results showed that pectin, lignin and hemicelluloses were effectively removed from bamboo shoot shell fibers after degumming.

Keywords: bamboo shoot shell fibers, ultrasonic, alkali-oxygen bath, degumming rate

INTRODUCTION

Natural cellulose fibers are abundantly available all over the world and easy to obtain. Cellulose and its derivatives are renewable, environmentally friendly, natural and biodegradable.[1-3] Due to its excellent mechanical properties, cellulose is often added into polymer matrix systems to prepare high-performance composites.[4,5] As a practically inexhaustible biopolymer, cellulose has been considered as a promising and sustainable raw material for the future chemical industry.[6,7]

Bamboo, as one of cellulose resources, is an economic, eco-friendly and sustainable material. In areas of the world facing growing shortages of wood,[8,9] bamboo products are increasingly used as wood substitutes.[10] Compared with most wood, bamboo shows similar or better physical and mechanical properties, and it can be processed into composite materials like wood, especially rare hardwood.[11,12] As one of the fastest growing woody plants in the world, bamboo has always been the most common plant for the production of various household products.[13]

The bamboo shoot shell is the outer skin of the bamboo shoot, which protects it. The bamboo shoot shell is a by-product of the bamboo shoot industry. As the growth cycle of bamboo is short, and the bamboo shoot shell, which is rich in cellulose, results in high yields, it has been considered to be applied in textile materials.[14] Bamboo shoot shell resources are very rich, but their utilization rate is very low. In recent years, bamboo shoot shell has been often seen abandoned on roadsides, which is not only a waste of valuable plant resources, but also seriously pollutes the environment. At present, much research is focused on medicinal uses of bamboo shell and edible bamboo fibers.[15,16] Moreover, bamboo shoot shell is a rich source of natural fibers, with properties similar to those of bast fibers.[17] The development of bamboo shoot shell fibers can not only mitigate the gap between the supply of raw materials for natural fibers and the demand, but can be also beneficial to the protection of the environment. The development of bamboo shoot shell fiber opens up a new way for the rational utilization of the bamboo shoot shell resource, and is also conducive to the development of textile fibers.

So far, there have been a large number of reports on the degumming of bast fibers.[18,19] As well known, the purpose of degumming is to obtain cellulose fibers with excellent performance. At present, the most commonly used degumming method is traditional high-temperature alkali boiling, followed by a bleaching process. This procedure is not only time-consuming, but also pollutes the environment with resulting wastewater. Moreover, the fibers obtained by this process often cannot achieve the expected performance.[20,21]

In the present study, the ultrasound-assisted alkali oxygen bath method was used to extract bamboo shoot shell fibers. This extraction method has the advantages of high degumming rate, environmental protection and simple operation. The morphology, chemical structure, crystallinity and thermal properties of the extracted bamboo shoot shell fiber were fully characterized by scanning electron microscopy, infrared spectroscopy and thermogravimetric analysis. The purpose of the study has been to provide a starting point for the development and application of bamboo shoot shell products.

EXPERIMENTAL

Materials

Mature naturally fallen bamboo shoot shells were collected from the bamboo forest in Wuhan City, Hubei Province. The chemicals used in the study, such as 98% sulfuric acid, NaOH, 30% H_2O_2, sodium metasilicate nonahydrate, sodium tripolyphosphate and others, were laboratory grade (Aladdin Chemical Registration Company, Shanghai, China), and used without further purification.

Pretreatment of bamboo shoot shell

The bamboo shoot shell was cut to a length of about 2.5 cm, and the impurities and fluff from the surface were removed with warm water (50 °C). The washed bamboo shoot shell was dried at 75 °C for 24 h. The chopped fiber segments were divided into four groups (5 g in each group), and were pretreated with ultrasound, at a bath ratio of 1:40, temperature of 45 °C, and ultrasonic frequency of 40 KHz. After the ultrasonic treatment with water for 20 min, the corresponding dosage of 3 g/L sodium hydroxide was added into the bath for 30 min. The samples were washed to neutral pH.[22]

Extraction of bamboo shoot shell fibers

Through a large number of prior experiments, it was found that the main factors affecting degumming are the amount of sodium hydroxide and hydrogen peroxide, temperature and time of the alkali oxygen bath treatment. The final range was determined by single factor experiments, and the orthogonal experiment was conducted to determine the optimal degumming process parameters, as shown in Table 2.

Degumming rate of bamboo shoot shell fibers

The degumming rate of bamboo shoot shell fibers was calculated by Equation 1:

$$\text{Degumming rate} = \frac{W_1 - W_2}{W_1} \times 100\% \quad (1)$$

where W_1 is weight of bamboo shoot shell fibers before degumming, W_2 is weight of bamboo shoot shell fibers after degumming.

Scanning electron microscopy

The microstructure of the bamboo shoot shell fibers before and after the treatment was analyzed by a Tescan Vega 3 Scanning Electron Microscope (Tesco, Czechoslovakia).

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was performed on the obtained fibers using a Vertex 70 type spectrometer, by the potassium bromide compression method. The spectra were recorded in the wavenumber range of 400-4000 cm^{-1}.

X-ray diffraction (XRD)

An X-ray diffractometer (D/Max-2550pc, RIGAKU, Japan) was used to determine the crystallinity of the bamboo shoot shell before and after the treatment. The experimental conditions were as follows: CuKa radiation (X-ray wavelength: 0.154 nm), tube voltage of 40 kV, tube current of 30 Ma, scanning angle 2θ 5-40° and scanning speed of 5 °/min.

Thermogravimetric analysis

About 5.0 mg of powdered sample was weighed and put into the sample pool of an SDT 2960 Differential Thermal Gravimetric Analyzer (DSC-TGA) (TA Instruments) for thermal performance measurement. The nitrogen flow rate was 50 mL/min, the heating rate – 10 °C min, and the temperature range – 20-600 °C.

RESULTS AND DISCUSSION

Degumming rate of bamboo shoot shell

Through the literature review and a large number of experimental studies, it has been found that the main factors affecting the degumming rate are the dosage of sodium hydroxide and hydrogen peroxide, the temperature and time of the process. The optimum degumming process was determined by the orthogonal test, using 4 factors and 3 levels. Table 1 shows the orthogonal factor level of the degumming experiment of bamboo shoot shell fibers, and Table 2 presents the orthogonal test results.

Table 1
Levels of orthogonal factors in degumming experiment of bamboo shoot shell fibers

Levels	Factors			
	A NaOH concentration (g/L)	B H_2O_2 concentration (mL/L)	C Temperature (°C)	D Time (h)
1	18	24	85	2
2	20	28	90	2.5
3	22	32	95	3

Table 2
Orthogonal design factors and test data of degumming bamboo shoot shell fibers

No.	A	B	C	D	Test indicator Degumming rate (%)
1	1	1	1	1	61.5%
2	1	2	2	2	67.0%
3	1	3	3	3	68.5%
4	2	1	2	3	61.0%
5	2	2	3	1	59.5%
6	2	3	1	2	68.5%
7	3	1	3	2	64.5%
8	3	2	1	3	56.5%
9	3	3	2	1	53.0%
k_1	64.11	61.47	61.16	57.26	
k_2	62.37	60.24	59.66	65.59	
k_3	57.80	62.56	63.45	61.43	
R	6.31	2.32	3.79	8.33	
Main→Secondary	DACB				
Optimal scheme	$A_1B_3C_3D_2$				

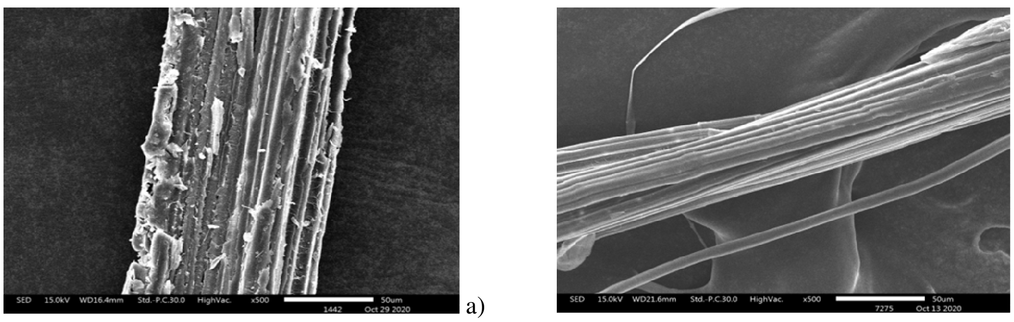
Firstly, the bamboo shoot shell fiber was pretreated and degummed by ultrasonic waves, and a certain amount of sodium hydroxide was added to bath, which made the structure of the material loose and thus improved the subsequent degumming effect. The bamboo shoot shell fibers were degummed by alkali and hydrogen peroxide in the same dissolving bath. Alkali could dissolve hemicelluloses and gum in the bamboo shoot shell, while also removing other impurities. At the same time, it can provide an alkaline reaction environment for hydrogen peroxide. Properly stirring during the addition of the hydrogen peroxide solution prevents the bubbles generated by the hydrogen peroxide from producing an upward force, pushing the fibers to move from bottom to top. Stirring by an external force is required to ensure the fibers come in full contact with the solution. A higher degumming rate of bamboo shoot shell fibers and better fiber quality can be obtained under such conditions.

The results showed that during the degumming pretreatment process, when the ultrasonic time was 50 min and the alkali addition was 3 g/L, the degumming rate of the bamboo shoot shell fibers was high. The experiment of the alkali oxygen scouring process of bamboo shoot shell fibers in the same bath as the alkali oxygen treatment revealed that the alkali oxygen scouring time is 120-180 min, the mass concentration of alkali liquor is 18-22 g/L, and the mass concentration of hydrogen peroxide is 28 g/L. If the NaOH concentration is too high, the performance of the bamboo shoot shell fiber will decline.

It can be seen from Table 2 that the order of the factors affecting the degumming rate is D > A > C > B. The optimal values obtained by the orthogonal test are the following: alkali concentration of 20 g/L, hydrogen peroxide concentration of 32 g/L, temperature of 95 °C, treatment time of 2.5 h. The corresponding degumming rate of the bamboo shoot shell fibers was of 70.07%.

Morphological structure

Figure 1 shows the surface morphology of the bamboo shoot shell fiber. It can be seen from Figure 1 that the surface of the untreated bamboo shoot shell fibers is rough, with many nodal lines, and there are many colloidal particles on the surface. After the treatment, the nodal pattern on the surface of the bamboo shoot shell fibers is obviously reduced, the gum is basically removed, and the surface becomes smooth. It can be seen that the bamboo shoot shell fibers are actually a fiber bundle formed by the association of multiple single fibers, whose appearance is similar to that of ramie fibers. There are grooves and cracks on the surface of the bamboo shoot shell fibers. The surface structure of the bamboo shoot shell fibers is conducive to water transmission, which means that the fabric made from bamboo shoot shell fibers will have excellent moisture permeability.



a) b)

Figure 1: Surface morphology of raw (a) and degummed (b) bamboo shoot shell fibers

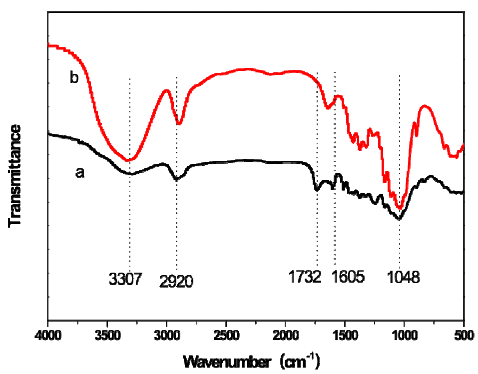


Figure 2: FTIR spectra of raw (a) and degummed (b) bamboo shoot shell fibers

FTIR analysis

Figure 2 illustrates the infrared spectra of the bamboo shoot shell fibers before and after the treatment. The strong absorption peak at 3307cm^{-1} is caused by the stretching vibration of the -OH group, the absorption peak at 2920 cm^{-1} belongs to the stretching vibration of the C-H group, that at 1732 cm^{-1} corresponds to the stretching vibration peak of C=O of the acetyl group, and the absorption peak at 1605 cm^{-1} is assigned to the C-C of the aromatic ring. The symmetric stretching vibration peak at 1732 cm^{-1} is the characteristic peak of lignin.[23]

The absorption peak at 1048 cm^{-1} is caused by the C-O stretching vibration of the C-O-C ring. Compared with the untreated bamboo shoot shell fiber, the peak value of the degummed bamboo shoot shell fiber at 2905 cm^{-1} is lower, indicating that the hemicellulose content is lower, and the peak intensity at 1732 cm^{-1} and 1605 cm^{-1} is weaker, indicating that the lignin content is lower. The strength of the peak at 3308 cm^{-1}, attributed to cellulose, increased. The analysis of the infrared spectra shows that the bamboo shoot shell fibers mainly contained cellulose, lignin and hemicelluloses.

X-ray diffraction analysis

Figure 3 shows the X-ray diffraction patterns of the bamboo shoot shell fibers before and after the treatment. As may be remarked, the XRD patterns of the fibers before and after degumming are basically the same. For the degummed fiber, the diffraction peaks shifted a little, but the crystal form belonging to cellulose I did not change.[18] After degumming, the diffraction peaks of the bamboo shoot shell fiber reached 2θ values of 16.2, 22.2 and 34.8°, corresponding to the 101, 002 and 040 planes, respectively.

By using the X-ray diffraction analysis software MDI Jade 6.0, the crystallinity of the bamboo shoot shell fibers before the treatment was determined to be of about 43.5%, while after the treatment it reached 58.7%. This is mainly due to the removal of lignin, hemicelluloses, water soluble matter and pectin from the fibers, thus the proportion of the crystalline region increased, so the crystallinity of the fibers enhanced.

Thermal performance

Figure 4 presents the TG and DTG curves of the bamboo shoot shell fibers before and after degumming. It can be seen from Figure 4 (A and B) that, both before and after the degumming treatment, the bamboo shoot shell fibers underwent the first stage of weight loss, of about 4%, from 30 to 210 °C. This weight loss is explained by the evaporation of adsorbed water from the fiber (intra- and intermolecular dehydration reactions), as well as the degradation of volatile matter in bamboo shoot shell fiber.

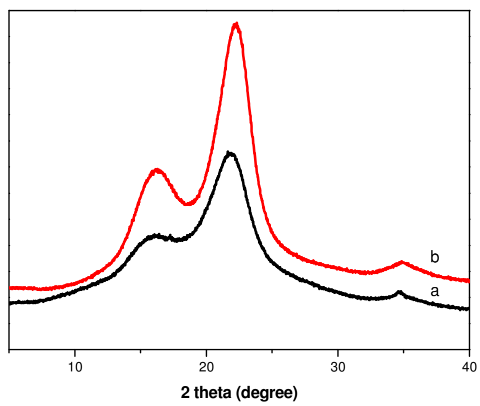


Figure 3: X-ray diffraction patterns of raw (a) and degummed (b) bamboo shoot shell fibers

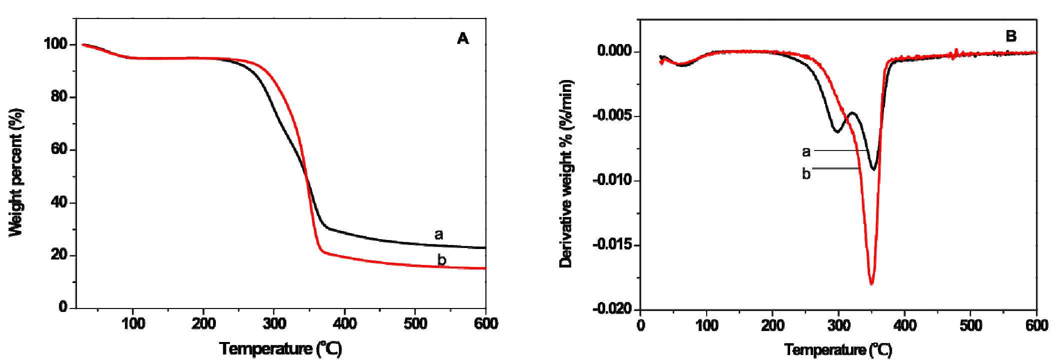


Figure 4: TG (A) and DTG (B) diagrams of raw (a) and degummed (b) bamboo shoot shell fibers

From 230 °C to 270 °C, a weight loss of about 5% was recorded, which was mainly due to the degradation of hemicelluloses. In the range of 270-380 °C, the weight loss increased sharply, which was mainly due to the decomposition of cellulose. It may be remarked that for the degummed bamboo shell fiber, the temperature range for the significant weight loss stages is higher. This can be explained by the fact that the crystallinity of the degummed bamboo shell fiber is higher than that of the raw material, which indicates that the thermal stability of the bamboo shell fiber is improved after the degumming treatment.

CONCLUSION

In the present study, bamboo shoot shell fibers were extracted by the ultrasound-assisted alkali-oxygen bath method. The extracted bamboo shoot shell fibers presented smooth surface, good quality and high cellulose content. In terms of chemical composition, the bamboo shoot shell fibers contained cellulose, hemicelluloses, lignin, pectin, waxy fats and other substances. The degumming of bamboo shoot shell fibers was performed to remove hemicelluloses and lignin. After the experimental study, it could be concluded that the degumming effect of the ultrasonic pretreatment on bamboo shoot shell fiber is remarkable. The addition of a certain amount of sodium hydroxide to the ultrasonication process and the "hollow effect" generated by the ultrasonic waves improve the effects of subsequent degumming, while using hydrogen peroxide and sodium hydroxide in the same bath can remove more gum. Bamboo shoot shell is rich in cellulose and thus is a potential natural fiber resource, while the approach proposed in this study offers a possibility to valorize it. This method can also be applied to other raw biomass materials and this will be investigated in future research.

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