DEGUMMING BAMBOO SHOOT SHELL FIBERS USING A TERNARY DEEP EUTECTIC SOLVENT

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In this study, cellulose fiber was extracted from bamboo shoot shell with a deep eutectic solvent (DES). The deep eutectic solvent used was prepared by the fusion of choline chloride (ChCl), oxalic acid (OA) and ethylene glycol (EG) at 80 °C. Based on the degumming rate, the influence of temperature and time on the DES degumming system was determined. Based on the scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TG) results, it was confirmed that the DES system can remove colloids from bamboo shoot shell, increasing the thermal stability and heat resistance of bamboo shoot shell fiber, and improving its crystallinity. It was proved that the DES system can effectively remove lignin and hemicelluloses, and retain cellulose in bamboo shoot shell.

Keywords: bamboo shoot shell, deep eutectic solvent, degumming, cellulose

INTRODUCTION

Natural cellulose fibers have received wide research interest among academia and industries. Thus, various new sources of cellulose have been explored, as well as new applications for this material. Natural cellulose fibers have many special properties that make them applicable in many areas, such as composite materials, textiles, nanomaterials – to mention just a few.[1] Bamboo shoot shell (BSS) is an agricultural waste generated from bamboo shoot processing. Researchers have found that BSS has high cellulose content, with high development prospects, and meets the needs of today's society for sustainable development.[2] At present, the BSS, as a by-product obtained during the bamboo shoot harvest, is often arbitrarily discarded or burned.[3] With the rapid development of the bamboo shoot industry, improper disposal of bamboo shells can cause serious environmental pollution, while a large amount of resource is wasted.[4] The main components of plant fibers are cellulose, hemicelluloses and lignin.

The degumming process is mainly intended to retain cellulose, while removing lignin and hemicelluloses. For cellulose products, removing part of the lignin will effectively improve the performance of the product.[5] From a molecular point of view, cellulose is a slender chain-like crystal structure formed by the parallel arrangement of repeating units, which is composed of hundreds of β-(1-4) glucoside bonded by hydrogen bonds. As the main structure in plant cell walls, the presence of cellulose determines the strength and stiffness of plant tissues.[6] There are many common ways to extract cellulose, including hydrolysis bleaching extraction with acidic or alkaline solvents, TEMPO oxidation, ionic liquids, organic solvents and deep eutectic solvents, steam hydrolysis and other methods, at a certain temperature and time, as well as microwave or ultrasonic assisted extraction of cellulose.[7]

In recent years, the pretreatment with deep eutectic solvents (DES) has received great attention. DES can be formed simply through a hydrogen bond donor (HBD) and a hydrogen bond acceptor

(HBA) at a certain temperature and time.[8] Interestingly, in the process of preparing DES, two or three components with high melting points themselves can form a clear transparent liquid at a lower temperature.[9] Common HBAs include choline chloride and betaine, and common HBDs mainly refer to urea, carboxylic acids and polyols. The main reason why DES have attracted wide interest is that they have some similar properties to ionic liquids, but can solve the related shortcomings of ionic liquids. They are easy to synthesize, inexpensive, biodegradable and have little impact on the environment. In addition, DES can be combined with other technologies to produce excellent results and have great development prospects.[10]

This paper aims to find utilization for bamboo shell resources. DES have been selected due to their environmentally friendly characteristics. The effects of DES on the degumming of bamboo shoots shell and the content of cellulose achieved were investigated. Also, the effect of the reaction temperature and time on the degumming of bamboo shoot shell using DES was investigated. Finally, the bamboo shell fibers were characterized by scanning electron microscopy (SEM), Fourier infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

The materials used were waste and mature natural bamboo shoot shells collected from the bamboo plantation of Wuhan Textile University. Choline chloride (AR 98%) was purchased from Aladdin, oxalic acid (AR 99.5%) and ethylene glycol (AR 99.5%) were received from Sinopharm Chemical Reagent Co., and used without further purification.

Preparation of deep eutectic solvents

To ensure the normal use of choline chloride, a certain amount of choline chloride was weighed and dried in an oven at 105 °C for 2 h. Choline chloride, oxalic acid and ethylene glycol with a molar ratio of 1:1:2 were stirred in an oil bath at 80 °C until a uniform, transparent and clear liquid was formed. The obtained DES was stored in an oven to remove residual moisture.

Degumming process

To remove the surface impurities, the BSS was washed with deionized water, and then oven dried, and finally crushed with a grinder. In order to remove lignin and hemicelluloses, 2 g BSS was treated with 40 g of DES. Different reaction times (0.5, 1, 1.5, 2, 2.5 and 3 h) and reaction temperatures (70, 80, 90, 100, 110 and 120 °C) were designed to determine the effects of reaction time and temperature on the system. The optimum process parameters were determined by single factor experiments.

Calculation of degumming rate

The degumming rate was selected to evaluate the degumming effect, and the formula for calculating the degumming rate of fibers was the the following:

$$\text{Degumming rate} = \frac{W_0 - W_1}{W_0} \times 100\% \quad (1)$$

where W_0 is the mass of bamboo shoot shell, W_1 is the mass of bamboo shoot shell fiber after the degumming treatment.

Composition determination

In order to determine the changes occurring in the samples because of the treatment, the composition of cellulose, hemicelluloses and lignin in the samples was determined before and after the treatment. The holocellulose, α-cellulose, and lignin contents in the specimens were determined according to ASTM D1104-56, ASTM D1103-55T, and NREL/TP-510-42618, respectively.[11-12]

Determination of holocellulose

1 g of sample was weighed for measurement, 1.25 g sodium chlorite, 32.5 mL of deionized water and 0.5 mL of acetic acid were added successively for reaction at 70 °C for 4 h, washed until neutral, and then oven-dried until constant weight. The resulting weight was the amount of holocellulose.

Determination of α-cellulose

12.5 mL of 17.5% sodium hydroxide solution was added to the obtained holocellulose, soaked for 30 min, and 30 mL of deionized water was added to continue to react for 30 min, and then washed until neutral and dried. The resulting weight was the cellulose content of the sample.

Determination of lignin

0.3 g of sample was added to 3 mL of 72% concentrated sulfuric acid, stirred in a water bath at 30 °C for 1 h, 84 mL of deionized water was added, the sample was placed in an autoclave at 121 °C for 1 h, washed to neutral, and then dried. The final product was the lignin from the raw material.

Characterization

The morphology of the samples was examined using scanning electron microscopy (SEM) (JSM-6510LV, JEOL Ltd., Japan) with magnification of 2000x. Before scanning, the surface of the samples was sputter coated with a thin layer of gold.

The powders of all samples were dispersed on KBr pellets and then the spectra of the samples were recorded on a Nicolet iS50, Thermo Fisher, USA. All the samples were recorded in the range of 4000-400 cm^{-1} with 16 scans in each case, at a resolution of 4 cm^{-1}.

In order to investigate the crystallinity of untreated and treated BSS cellulose, the milled sample powders were analyzed at ambient temperature by step scanning on an X-ray diffractometer (PANalytical Empyrean, Panaco, Netherlands). The samples were scanned in the 2θ range of 10-45° and a scan rate of 8 °/min. The crystallinity index (CrI) of the material was calculated using Equation (2):

$$CrI\ (100\%) = (I_{200}\text{-}I_{am}) / I_{200} \times 100 \quad (2)$$

where CrI represents the relative degree of crystallinity, I_{200} is the maximum intensity of the (200) lattice diffraction at 2θ=22.8°, and I_{am} is the minimum intensity of diffraction at around 2θ=18°.

Thermogravimetric analysis was employed to investigate the thermal stability of fibers before and after the treatment. TG analysis of all the powdered samples was performed using a TG 209F1 Libra. Samples of approximately 5 mg were placed in a platinum crucible under nitrogen atmosphere, and were heated at a heating rate of 10 °C/min within the range of 30 to 700 °C.

RESULTS AND DISCUSSION

Effect of temperature and time on degumming rate

Figure 1 shows the effect of temperature and time on degumming efficiency. As can be seen from Figure 1 (a), under the constant conditions of mass ratio of BSS to DES, and reaction time of 2 h, the degumming rate of bamboo shell fiber increases continuously with the increase of temperature. A significant increase is recorded between 70 °C and 100 °C, and levels off beyond 100 °C. As can be seen in Figure 1 (b), at the constant temperature of 100 °C, the degumming rate of bamboo shell continuously increases with the increase of treatment time, rising significantly between 0.5 h and 2 h, and then stabilizing beyond 2 h. As has been observed, the bamboo shell fiber reacts more thoroughly with DES with the increase of time. The principle of degumming is to dissolve the lignin, separating it into acid-soluble lignin and acid-insoluble lignin, and the hemicelluloses, which are converted into constituent five-carbon sugars, under the treatment with DES.[13] It can be seen that the degumming efficiency is the highest when the reaction temperature is 100 °C and the time is 2 h in this DES system.

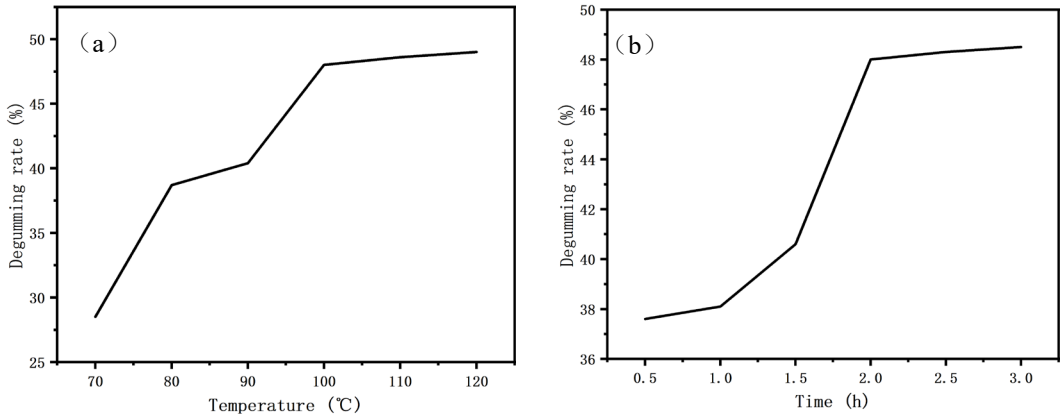

Figure 1: Effects of (a) temperature and (b) time on degumming rate

Chemical composition

Table 1 shows the chemical composition of untreated and DES treated bamboo shells under optimal conditions. The contents of α-cellulose, hemicelluloses and lignin of the untreated sample were 41.12%, 34.10%, and 15.50%, respectively. Meanwhile, for the sample treated under optimal conditions, the contents of α-cellulose, hemicelluloses and lignin were 46.32%, 24.74%, and 8.5%, respectively.

Table 1
Chemical composition of bamboo shoot shell before and after degumming treatment

Samples	Holocellulose (%)	α-Cellulose (%)	Hemicelluloses (%)	Lignin (%)
Untreated	67.13±0.94	30.67±1.96	36.33±2.05	15.50±1.03
DES treated	71.06±0.64	46.01±1.22	24.74±1.49	8.50±1.54

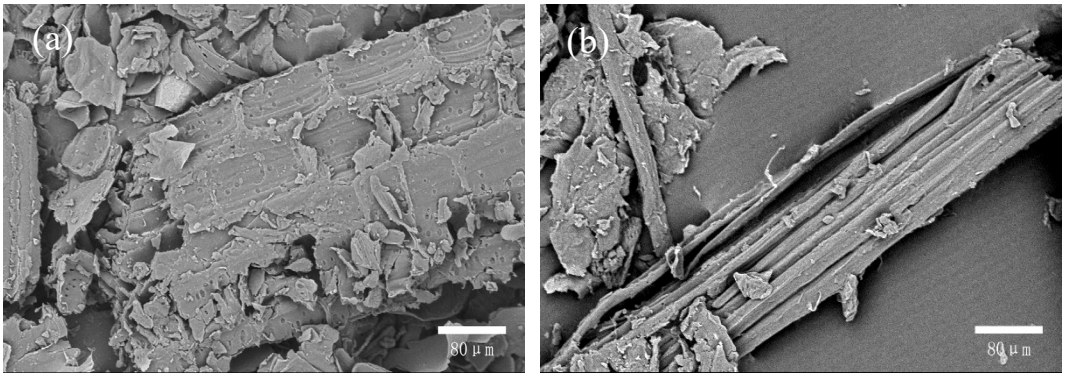

Figure 2: SEM images of (a) untreated BSS and (b) treated BSS

As can be observed, the α-cellulose contents in the treated bamboo shell significantly increased, while the contents of hemicelluloses and lignin decreased, compared with the untreated bamboo shell, which indicates that the DES can be successfully used for degumming of bamboo shoot shells and can effectively dissolve lignin.[14]

Microstructure analysis

Figure 2 shows the SEM images of the bamboo shoot shell samples before and after the processing. It can be seen from Figure 2 (a) that the surface of the initial bamboo shell is rough and uneven, there is a significant amount of colloids on the surface of the fiber and they are bonded together. Meanwhile, Figure 2 (b) reveals that the surface of the bamboo shoot shell after the DES treatment becomes obviously smoother, and the clearly exposed fibers can be easily identified.

FTIR analysis

Figure 3 describes the FTIR spectra of BSS before and after the degumming treatment. The spectra allow observing structural changes in cellulose, hemicelluloses and lignin occurring because of the treatment. Both treated and untreated samples show wide large absorption peaks in the range of 3000~3600 cm^{-1}, and the characteristic absorption peak appeared at 3340 cm^{-1}, which was caused by the stretching vibration of the -OH bonds in cellulose, hemicelluloses and lignin. The transmission peak at 2917 cm^{-1} corresponds to the stretching vibration of C-H bonds present in the cellulose and hemicelluloses structures. Compared with the raw bamboo shells, the peak intensity of the DES-treated sample is higher, being affected by the condensation of lignin. The phenomenon of lower lignin content being accompanied by a higher intensity peak has also been reported previously.[15]

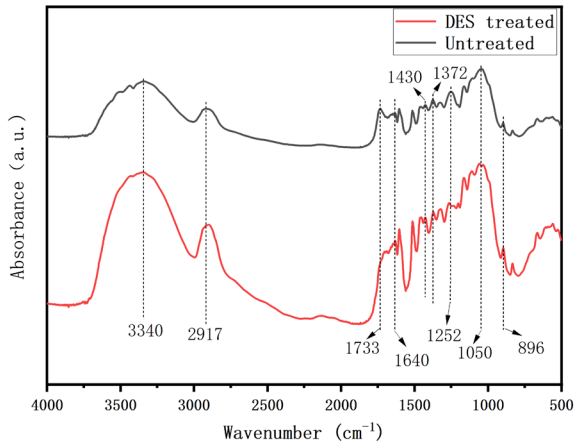

Figure 3: FTIR spectra of bamboo shoot shell before and after degumming

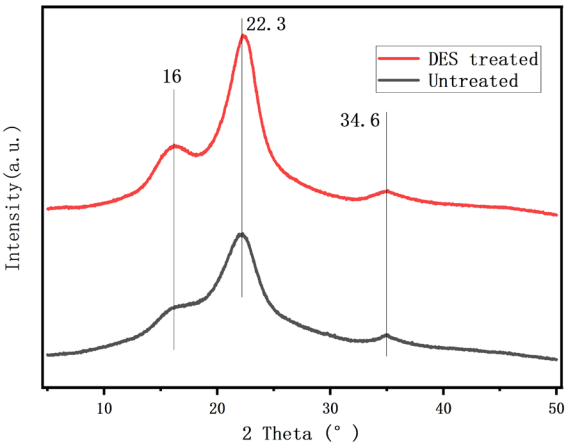

Figure 4: X-ray diffractograms of bamboo shoot shell before and after degumming

The characteristic absorption peaks at 1733 cm^{-1} corresponds to the stretching vibrations of the carboxyl group belonging to the hemicelluloses.

It can be seen from the figure that after the DES treatment, the peaks in this region are significantly weakened or disappeared completely, proving that

the hemicelluloses are effectively removed by the degumming process.[16] The absorption peak at 1640 cm^{-1} represents the bending vibration of absorbed water in cellulose. The absorption peak at 1430 cm^{-1} represents the crystal structure of cellulose I, and the one at 1372 cm^{-1} represents the bending vibration of C-H, the strength of which reflects the hydrogen bonding in cellulose.[17] The intensity of these peaks did not change significantly, indicating that the cellulose component of the raw material was not destroyed by the DES treatment. The absorption peak at 1252 cm^{-1} represents the C-C, C-O, C=C stretching vibration of lignin, and the reduction of this peak confirms that the lignin content of bamboo shells is reduced after the treatment.[18] The peaks at 1050 cm^{-1} and 896 cm^{-1} represent the stretching vibration of cellulose C-O-H and the stretching vibration of cellulose β-(1-4) glucoside bond, respectively. The existence of these peaks confirmed that the cellulose content of BSS treated with DES is not greatly affected.[19]

Crystallinity analysis

Figure 4 shows the XRD patterns of bamboo shell fiber before and after the treatment. It can be seen from the XRD patterns of both treated and untreated samples that the diffraction peaks of bamboo shell are at 2θ=16°, 22.3° and 34.6°, which correspond to the crystal planes of (110), (200) and (004), typical of cellulose type I structure.[20] The presence of these three peaks proves that the treatment of bamboo shell fibers with DES did not affect the crystal structure of cellulose.[21] The crystallinity of the untreated bamboo shoot shell is 47.51%, while after the DES treatment it increases to 54.11%. This indicates that most of the lignin and hemicelluloses in the treated bamboo shell fiber were removed.

Thermal stability

The TG and DTG curves of BSS are shown in Figure 5. The thermal degradation of BSS is divided into three stages. The first stage is the initial decomposition that occurs before 200 °C, during which the evaporation of water and part of volatile substances in the BSS fiber occurs. The second stage is the main thermal decomposition stage, which occurs between 200 °C and 400 °C. In this stage, cellulose, hemicelluloses, and lignin begin to decompose, and the decomposition of cellulose is caused by the breaking of the carbon chain of cellulose, causing the cellulose to begin to depolymerize, decomposing into glucose units.[22] During this period, the decomposition of hemicelluloses and lignin occurred between 210 °C ~ 320 °C and 320 °C ~ 400 °C, respectively.

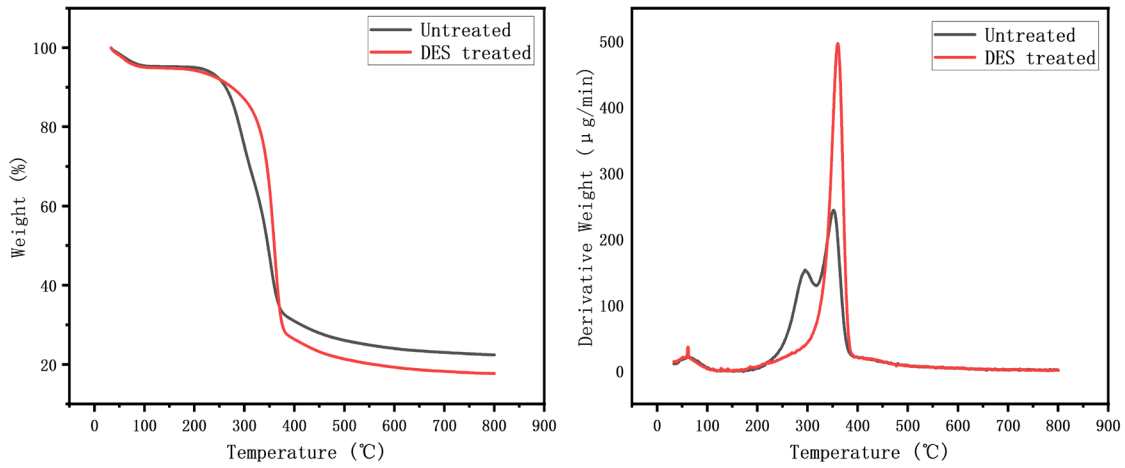

Figure 5: TG and DTG curves of bamboo shoot shell before and after degumming

Table 2
Thermal properties of bamboo shoot shell samples

Sample	T_{onset} (°C)	T_{max} (°C)
Untreated	284	352
Treated	327	360

The final stage is after 400 °C, the residue of bamboo shell gradually carbonizes at temperatures above 400 °C. After TG analysis, the residual weight of raw bamboo shell material after

carbonization was 22.4%, while that of the DES treated sample was 17.7%. This also shows that, in addition to removing most of the lignin and hemicelluloses through the process of DES treatment, a large number of impurities were also removed.

Table 2 summarizes the initial degradation temperature (T_{onset}) and maximum degradation temperature (T_{max}) of BSS obtained by TG and DTG analyses. It can be clearly seen from Table 2 that the raw untreated BSS began decomposing at about 284 °C and reached the highest degradation temperature at about 352 °C. After the DES treatment, BSS begins decomposing at about 327 °C, and reaches the highest degradation temperature at about 360 °C. This indicates that the thermal stability of the bamboo shell was enhanced by the DES treatment. The higher maximum degradation temperature after the DES treatment confirms that the colloids between the bamboo shell fibers have been removed, leading to enhanced crystallinity, and thus, higher heat resistance.[23]

CONCLUSION

In this study, bamboo shoot shells were degummed with a deep eutectic solvent, prepared using choline chloride, oxalic acid and ethylene glycol as reaction solvents, in order to extract cellulose. By exploring the influence of temperature and time on the degumming process, the optimum process parameters were determined. Thus, a BSS to DES mass ratio of 1:20, temperature of 100 °C and reaction time of 2 h yielded the best degumming results. SEM, FTIR, XRD and TG analyses indicated that the cellulose content of bamboo shoot shell significantly increased after degumming, while the lignin and hemicelluloses components were to a great extent removed. Thus, it can be concluded that the prepared DES system proved suitable for the desired purpose. Moreover, deep eutectic solvents can be recycled and continue to be used under certain conditions, reducing solvent consumption, saving resources, and thus being less harmful for the environment and meeting the needs of sustainable development of today's society.

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