Preparation and Characterization of Aldehyde-Functionalized Cellulosic Fibers through Periodate Oxidization of Bamboo Pulp

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Cellulosic fibers were efficiently disintegrated from bamboo pulp as raw material and then oxidized using sodium periodate to introduce dialdehyde groups on their surfaces. The resultant fibers were characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). FT-IR spectra demonstrated that the characteristic absorption band of aldehyde groups was present at 1735 cm^{-1}, confirming that aldehyde groups were successfully introduced. XRD showed that the nature of bamboo pulp fibers changed slightly after oxidation, except in the reduction of crystallinity. The aldehyde content increased with the sodium periodate content and reached a maximum of 1.41 mmol/g. The yield loss maximum was 32.4 wt%. TGA results showed that the temperature at the initial and final decomposition of the oxidized fibers was subject to the periodate dosage and that the thermal stability decreased to some extent.

Keywords: Bamboo pulp fibers; Periodate oxidization; FT-IR; XRD; TGA

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INTRODUCTION

Lignocellulosic biomass represents a renewable, abundant, and inexpensive source of raw materials for the chemical industry to develop biofuels, renewable chemicals, and biomaterials. Cellulosic fibers isolated from lignocellulosic biomass can be used as reinforcing elements in polymeric matrices, and they are considered highly promising fillers in preparing sustainable composite materials (Xie *et al.* 2016). Currently, wood is the primary source of cellulosic fibers. However, its utilization in such fibers might have consequences involving the exploitation and protection of forests, even for fast-growing species (Catto *et al.* 2014). Therefore, it is important to discover alternative resources to replace wood.

Bamboo is one of the fastest growing woody plant biomasses, and it contains 57 to 65 wt% cellulose, 27 to 30 wt% hemicellulose, and 4.9 to 5.0 wt% lignin (Shimokawa *et al.* 2009; Yamashita *et al.* 2010; Sun *et al.* 2011; Sun *et al.* 2013; He *et al.* 2014; Pejic *et al.* 2015). Bamboo pulp fibers are more homogenous in structure and properties than man-made regenerated cellulose fibers (Qin *et al.* 2010; Teli and Sheikh 2012). With such advantages, bamboo is a promising candidate for the production of cellulosic fibers.

In addition, bamboo resource utilization reduces the demand for wood flour and the environmental impacts associated with wood fiber harvesting (Li *et al.* 2016).

However, cellulosic fibers made from wood, bamboo, or other biomass materials cannot fulfill the advanced material demands on production and application. There is a critical need to improve the physical and chemical properties and expand applications of cellulosic fibers. Several different strategies have currently been developed, such as mechanical treatment, surface modification, and blending (Larsson *et al.* 2014). The most efficient method is oxidation with periodates, which cleaves the pyranose ring and introduces aldehyde groups at both the C-2 and C-3 positions on cellulose molecules. The derived aldehyde groups can further react with amino, hydroxyl, and carboxyl groups, resulting in new functional chemical bonds, further broadening the potential applications for cellulosic fibers (Heinze and Liebert 2001; Calvini *et al.* 2006; Potthast *et al.* 2007; Zhang *et al.* 2008). However, there has been a shortage of systematic research on the periodate modification of bamboo fibers.

In this work, cellulosic fibers disintegrated from bamboo paper pulp were oxidized *via* sodium periodate. The effects of $NaIO_4$ added during the reaction on the content of aldehyde groups and yield loss of the oxidized fibers were investigated. Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA) were then applied to characterize the oxidized fibers.

EXPERIMENTAL

Materials

Bleached bamboo paper was obtained from the Yongfeng Paper Pulp Factory (Sichuan, China). Analytical grade sodium periodate ($NaIO_4$) and glycerin were obtained from Aladdin (Shanghai, China) and used without further purification. Deionized water was used throughout the experiment.

Methods

Sodium periodate oxidation of bamboo pulp fibers

Bamboo paper was ground, passed through a 60-mesh sieve to select the final fibers, and then dried in a vacuum dryer for 12 h at 40 °C to completely remove moisture. A total of 0.5 g of bamboo pulp fibers were added to the aqueous solution of sodium periodate in a 250-mL flask. The reaction vessel was covered with aluminum foil to prevent the photo-induced decomposition of sodium periodate, and the mixture was stirred with an electric blender at 500 rpm in a water bath at the desired temperature. After completion of the 4 h oxidation reaction, the product was filtered and then immersed in 0.1 M glycerin aqueous solution for 24 h, during which the water was refreshed every 12 h to thoroughly remove any of the residual reagent. The resultant pulp fibers were dried in a vacuum dryer at 40 °C for 48 h and preserved for characterization.

Determination of yield loss

The formation of soluble fragments, a result of the cellulose destruction, was determined by measuring the yield loss using the direct gravimetric method (Pejic *et al.* 2015), and calculated using Eq. 1,

$$Yield\ loss\ (\%) = \frac{M_0 - M_t}{M_0} \times 100\% \quad (1)$$

where M_0 and M_t are the absolute dry weights (g) of the sample before and after the oxidation treatment, respectively.

Aldehyde content

The aldehyde content of the oxidized fibers was determined using sodium hydroxide titration (Veelaert *et al.* 1997). A 25 g solution with 1.0 wt% of oxidized fibers was weighed, and 0.1 M NaOH solution was used to adjust the pH to 5.0. The 0.05 g/mL $NH_2OH \cdot HCl$ solution was prepared and also adjusted to pH 5.0 using 0.1 M NaOH. Then, 10 mL of $NH_2OH \cdot HCl$ solution was added to the oxidized pulp solution, which was placed in a 40 °C water bath for 4 h. The titration was performed using 0.1 M NaOH, and the amount of NaOH consumed when the pH value of the solution reached 5.0 was recorded.

The aldehyde content was calculated according to Eq. 2,

$$\text{Aldehyde content (\%)} = \frac{C_1 \times (V_1 - V_2) \times 162}{M \times 1000} \times 100\% \quad (2)$$

where C_1 denotes the concentration of NaOH solution (M), V_1denotes the amount of NaOH consumed by oxidized fibers (mL), V_2 denotes the amount of NaOH consumed by pulp fibers (mL), and M denotes the sample weight (g).

Fourier-transform infrared spectroscopy (FT-IR)

Dried fiber samples were ground with pre-dried KBr powder and then compressed into disks for FT-IR testing. The absorption spectra were recorded using a Nicolet 6700 (Thermo Scientific, USA) spectrometer with a resolution of 4 cm^{-1} and 32 scans. The scanning range was in the wavenumber range of 4,000 to 400 cm^{-1}.

X-ray diffraction (XRD)

X-ray diffraction patterns of the bamboo pulp fibers were recorded using a XRD-6000 detector (Shimadzu, Japan) at a voltage of 40 kV, a current of 30 mA, and a scan rate of 2°/min. The crystallinity of the bamboo pulp fibers before and after oxidation was calculated using the method for peaks separation and Gaussian peak fit with the software Peakfit V. 4.12 (Lu *et al.* 2007), as shown in Eq. 3,

$$X_c(\%) = \frac{I_c}{I_a - I_c} \times 100\% \quad (3)$$

where X_c was the crystallinity of the fiber samples, I_a was the diffraction intensity of the amorphous peak, and I_c was the sum of all crystal peak diffraction intensities.

Thermogravimetric (TG) Analysis

Thermogravimetric analysis was carried out on a STA 409PC thermal analyzer (Netzsch, Germany). Samples of approximately 10 mg were heated from 20 to 600 °C at a heating rate of 10 °C/min under a constant nitrogen flow of 50 mL/min.

RESULTS AND DISCUSSION

Periodate Oxidation of Bamboo Pulp Fibers

Due to its polyhydric alcohol structure, cellulose is very sensitive to various oxidizing reagents. The chemical structure of cellulose is changed in a way that hydroxyl groups are oxidized into the corresponding aldehyde structure, *i.e.*, an aldehyde, a ketone, or a carboxyl moiety. Periodates, as specific oxidants, oxidize the vicinal hydroxyl groups at C-2 and C-3 in an anhydroglucose unit (AGU) of cellulose, thereby forming two aldehyde groups (Coseri *et al.* 2013), as depicted in Fig. 1. The oxidation reaction proceeds though a cyclic diester of AGU with vicinal hydroxyls, and subsequently undergoes an intermolecular redox process with C-C bond cleavage, according to a concerted mechanism (Nevell 1957), finally resulting in the production of the bamboo pulp cellulose dialdehyde groups.

In this study, the dialdehyde cellulosic fibers were obtained from bamboo pulp by way of sodium periodate oxidation. It was reported in previous studies that the pH, temperature, and time influence the preparation of periodate-oxidized cellulose (Varma and Kulkarni 2002; Liu *et al.* 2012; Liu and Xu 2014; Sun *et al.* 2015). The present study focused on the effect of the periodate dosage at a range of 0 to 50 mg/mL and pH 5. The temperature (45 °C) and reaction time (4 h) were constant throughout all experiments.

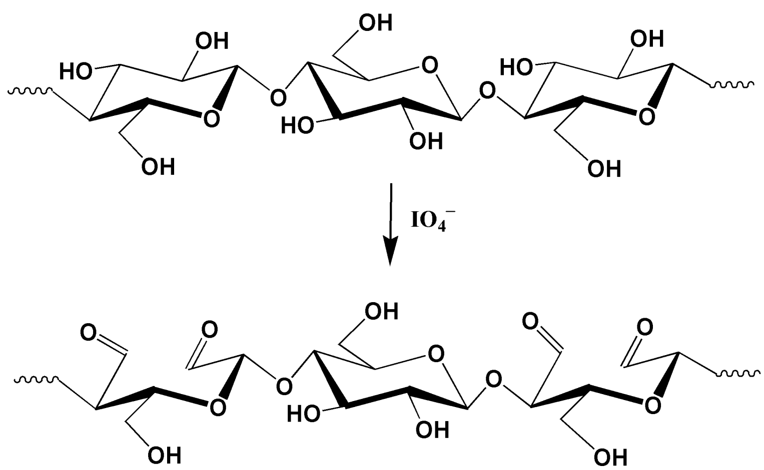

Fig. 1. Schematic of preparation of cellulose oxidized by periodates

FI-IR Analysis

To determine the variation in functional groups of the unoxidized and oxidized pulp fibers at varying $NaIO_4$ concentrations, FT-IR spectra were analyzed (Fig.2). The broad peak at 3425 cm^{-1} was attributed to the stretching vibration of the -OH group, and the peak at 1376 cm^{-1} was assigned to the -OH group bending vibration. The intense absorbances at 2928 cm^{-1} and 2860 cm^{-1} were due to the $-CH_2$ stretching vibration, and the peak at 1429 cm^{-1} corresponded to the $-CH_2$ bending vibration. Absorption peaks at 1072 cm^{-1} were related to the anti-symmetric stretching vibrations of the C-O-C group. The absorbance band at 994 cm^{-1} was attributed to the C-O stretching vibration. The presence of a broad band at 895 cm^{-1} was the result of the glycosidic linkages. All of these peaks are the characteristic absorption bands of cellulose composed of bamboo pulp fibers. Following the oxidation, the characteristic absorption band of aldehyde groups was present at 1735 cm^{-1}, confirming that aldehyde groups were successfully introduced onto the surface of bamboo pulp fibers by sodium periodate oxidation.

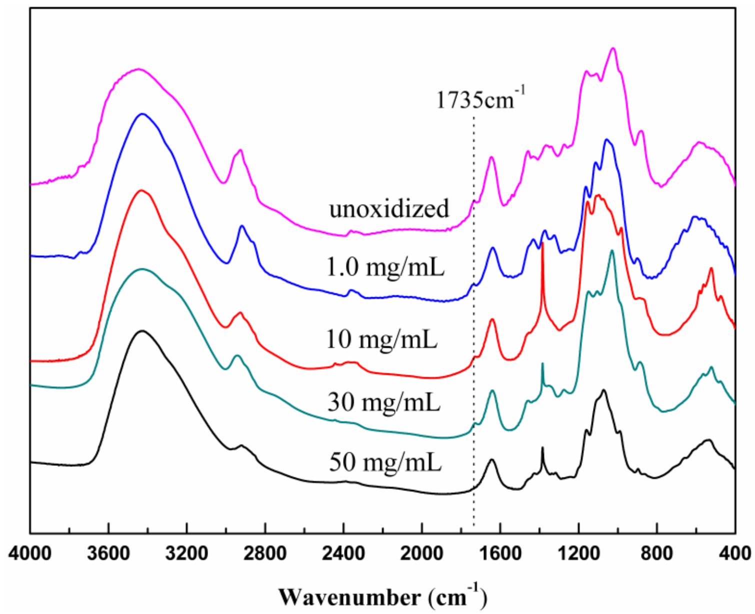

Fig. 2. FT-IR spectra of the unoxidized and oxidized bamboo pulp fibers

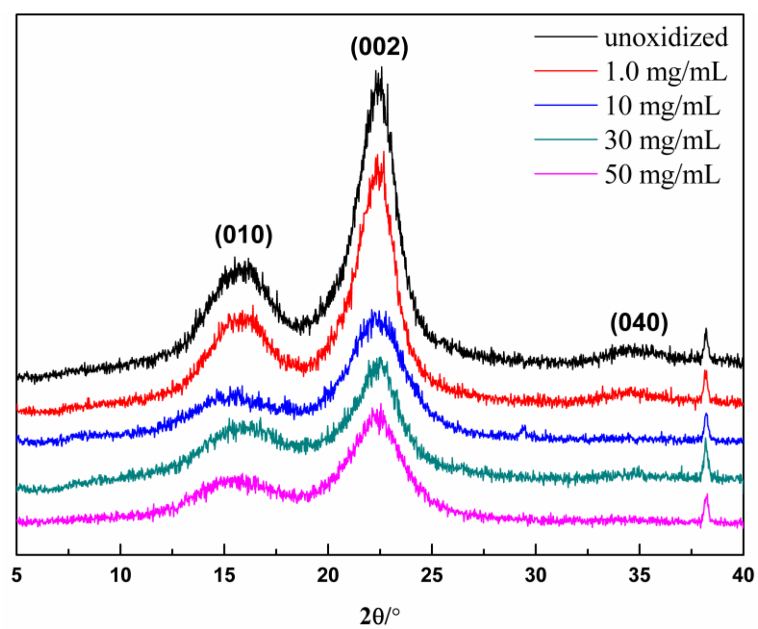

Fig. 3. XRD patterns of bamboo fibers with and without $NaIO_4$ oxidation

XRD Analysis

The X-ray diffraction patterns of bamboo pulp fibers oxidized by varying concentrations of sodium periodate are presented in Fig. 3. The bamboo pulp fibers possessed characteristic peaks of cellulose I with a sharp high peak (002) at 22.6°, and two weaker peaks (010 and 040) centered at 16.2° and 34.1°, respectively (French 2014).

For the oxidized fibers, the diffraction peak angles hardly changed, indicating that sodium periodate caused little change to the nature of bamboo pulp fibers. However, a noticeable reduction in the diffraction intensity peaks was observed, implying the crystallinity may have been disrupted by the oxidation treatment to some degree. The oxidized fibers with 1.0 mg/mL, 10 mg/L, 30 mg/mL, and 50 mg/mL $NaIO_4$ reduced the relative crystallinity to 61.39%, 51.48%, 48.60%, and 47.53%, respectively, compared to the relative crystallinity of the unoxidized fibers (64.33%). The $NaIO_4$ oxidation was due to the opening of the glucopyranose rings and destruction of the ordered structure of bamboo pulp fibers (Li *et* al. 2011), which led to the observed decrease in relative crystallinity. In addition, the higher the $NaIO_4$ concentration, the lower the crystallinity should be, which agrees with Liu and Xu's previous research (2014).

Aldehyde Content and Yield Loss

The aldehyde content and yield loss of oxidized fibers were measured *via* sodium hydroxide titration and the gravimetric method, respectively. The results are presented in Fig. 4. The figure shows the aldehyde content of the oxidized bamboo pulp fibers with varying concentrations of sodium periodate. The results clearly indicate that the $NaIO_4$ dosage had a crucial role in the oxidized reaction; it directly affected the aldehyde content on the sample surfaces. There was a remarkable increase in the content of aldehyde groups corresponding to the gradual increases in $NaIO_4$ dosage. The aldehyde content was more than 20x more when the concentration was raised from 1.0 to 50 mg/mL, especially from 0.06 to 1.41 mmol/g.

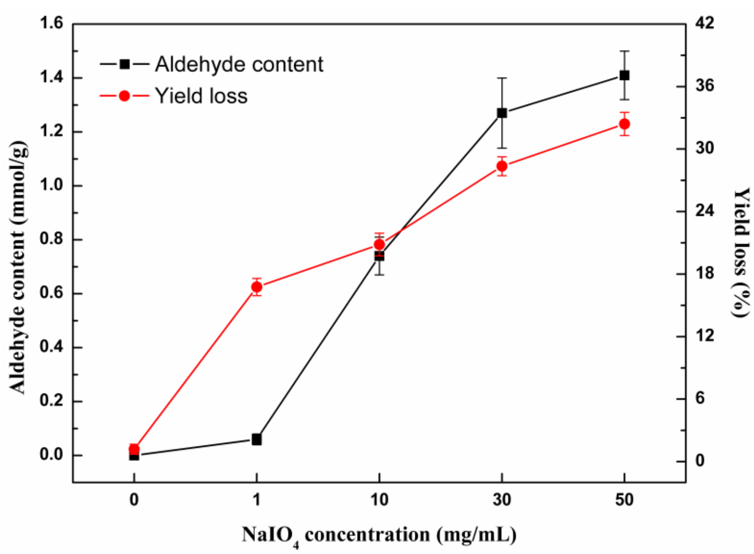

Fig. 4. Aldehyde content and yield loss

However, with the oxidative cleavage of the bonds between the C-2 and C-3 of the glucopyranose units caused by the sodium periodate oxidation, undesired oxidative/hydrolytic cleavages of glycoside bonds also took place, resulting in yield loss (Liu *et al.* 2012). As shown in Fig. 4b, the yield loss, like the aldehyde content, also increased with increasing $NaIO_4$ dosages. When the $NaIO_4$ dosage was equal to 50 mg/mL, the yield loss reached up to 32.4 wt%. Therefore, ways to decrease the yield loss should be further investigated.

TG Analysis

Figure 5 shows thermogravimetric curves of bamboo pulp fibers that were unoxidized or oxidized with different $NaIO_4$ concentrations. The TGA curves of the oxidized and unoxidized fibers were similar in some ways and were divided into three distinct stages.

During the first stage (10 to 160 °C), the adsorbed water and other residue solvents were vaporized.

In the second stage (160 to 360 °C), the crystal portion of bamboo pulp fibers was destroyed, while the cellulose simultaneously generated thermic degradation, so that amorphous regions were enhanced and the polymerization degree of cellulose decreased. The unoxidized bamboo fibers started to decompose at 247°C and terminated at around 360 °C, whereas the fibers oxidized with 50 mg/mL of $NaIO_4$ rapidly degraded at 162°C towards the uncertain termination of decomposition. The loss weights of bamboo fibers in the second stage both with and without periodate treatment were around 73.99% and as low as 46.81%, respectively.

The final stage occurred when the crystal portion of bamboo cellulose had been entirely destroyed, at the moment bamboo pulp fibers thoroughly decomposed. The temperatures at the initial and final decomposition of the oxidized fibers were lower than those of the unoxidized fibers, and the oxidation treatment weakened intermolecular bonding action in oxidized bamboo cellulose. This demonstrated that the thermal stability of the oxidized bamboo pulp fibers increased to some extent. In addition, the obtained results were in agreement with the aforementioned X-ray diffraction data. Thus, the crystallinity of the oxidized bamboo pulp fibers was slightly reduced compared with the unoxidized fibers.

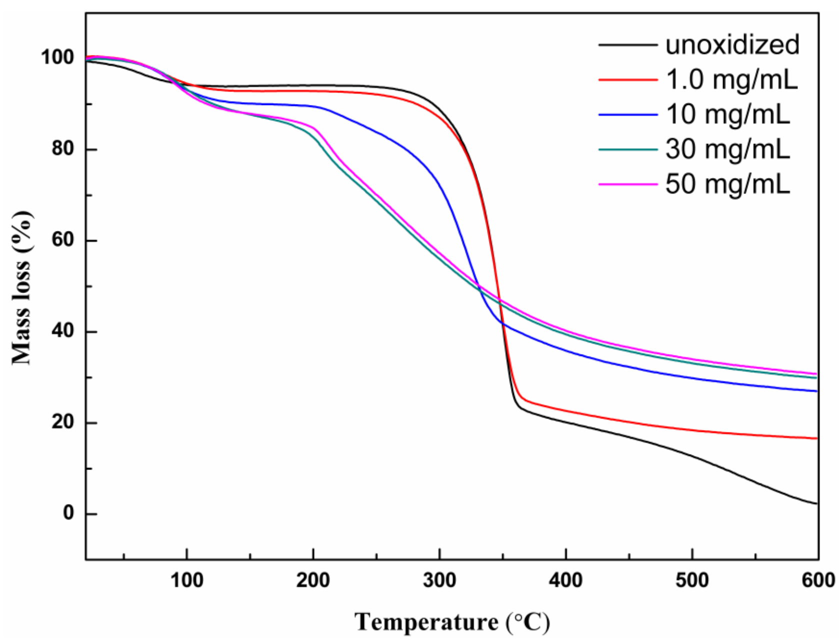

Fig. 5. TGA curves of bamboo fibers with and without $NaIO_4$ oxidization

CONCLUSIONS

1. Cellulosic fibers disintegrated from bamboo paper pulp were successfully oxidized using sodium periodate, thus introducing dialdehyde groups onto the surfaces.
2. The nature of bamboo pulp fibers changed slightly after oxidation. However, the crystallinity reduced accordingly with periodate content.
3. The aldehyde contents were positively related to the periodate content, and the content reached a maximum of 1.41 mmol/g. The maximum undesirable yield loss was 32.4 wt%.
4. The temperature at the initial and final decomposition of the oxidized fibers was subject to the periodate content. The thermal stability decreased to some extent.

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