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Influence of HNO_3/H_3PO_4–$NANO_2$ mediated oxidation on the structure and properties of cellulose fibers

Yunhui Xu[a,*], Xin Liu[b], Xuelan Liu[c], Jiulong Tan[a], Hongling Zhu[a]

[a] College of Light-Textile Engineering and Art, Anhui Agricultural University, Hefei, Anhui 230036, China
[b] College of Natural Sciences, Anhui Agricultural University, Hefei, Anhui 230036, China
[c] Key Laboratory of Zoonoses of Anhui Province, Anhui Agricultural University, Hefei, Anhui 230036, China

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ABSTRACT

The bamboo pulp cellulose fiber was oxidized with HNO_3/H_3PO_4–$NaNO_2$ mixture to obtain oxidized cellulose containing different levels of carboxyl content and with high yields. The effects of HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation on structure and properties of the fiber were investigated. The results showed that an increase in carboxyl content and weight loss of oxidized fibers appeared with increasing oxidation time. Compared with the original cellulose, the oxidized fibers had lower crystallinity (29–40%) and thermal stability. The patterns of ^{13}C NMR, X-ray diffraction and other testing methods revealed that the oxidation mostly occurred at C6 primary hydroxyl groups of cellulose. Moreover, an oxidized fiber with 94.14–98.59% of high yields and 1.13–3.56% of carboxyl content was obtained in the range of oxidation time from 15 to 60 min, while its mechanical properties did not change significantly. This work presented some detailed information about structure–property correlations of oxidized bamboo pulp cellulose fibers and was useful in planning applications of these products.

1. Introduction

The unrenewable resources of petroleum and coal become increasingly exhausted, so there is a growing attention to utilize natural biopolymers. In this regard, fiber plants consisting of cellulose, hemicelluloses and lignin acquire enormous significance as rich biomass and chemical feedstock since they are containing many functional groups suitable to chemical derivatization (Khullar, Varshney, Naithani, & Soni, 2008). Bamboo is a woody herbaceous plant and consists of many vascular bundles and xylem. Cellulose pulp prepared from bamboo is around 57–66%, and especially α-cellulose gets about 26–43% that is comparable with that of softwoods and hardwoods (He, Cui, & Wang, 2008; Shanmughave, 2003). Compared with other counterpart timber species, bamboo is an abundant renewable natural resource capable of fast growth (3–5 years), high productivity and holocellulose content (64–70%), and easy propagation, which is not like wood to suffer insect infestation. Bamboo pulp cellulose fiber is a novel kind of green and environment-friendly fiber that has been successfully industrialized in China. At present, the regenerated bamboo cellulose fiber is produced in the form of dissolving pulp of bamboo cellulose by using viscose or Lyocell spinning procedure. However, it is very different from traditional viscose fiber in the raw material and process. Bamboo pulp fiber has markedly different properties from cotton and wood fibers, such as lustrous looking, soft and cool feelings, good drapability, high water and perspiration adsorption, abrasion resistance, good dyeability, anti-ultraviolet, and excellent thermal conductivity (Ma, Huang, Chen, Cao, & Chen, 2011; Shen, Liu, Gao, & Chen, 2004). Bamboo pulp cellulose fibers have already attained an increasingly important position in the clothing and medical textile industry.

Chemical modification of polysaccharides is an important approach for preparation of new materials with improved performance and value-addition (Liu & Sun, 2008; Schurz, 1999). In principle, chemical modification of native and regenerated cellulose fibers by selective oxidation reactions of primary and secondary hydroxyl groups of the pyranose ring in cellulose offers an attractive means for acquisition of new properties by introduction of aldehyde and carboxyl active groups to a polymer surface (Gert, Torgashov, Zubets, & Kaputskii, 2005; Montanari, Roumani, Heux, & Vignon, 2005). The partial oxidation renders cellulose bioabsorbable in human, on such way introduced functionalities further

* Corresponding author. Tel.: +86 551 6578 6459; fax: +86 551 6578 6331.
E-mail address: xuyunhui@ahau.edu.cn (Y. Xu).

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broadens the potential applications of these biodegradable polymers, and it has been applied in medical devices such as absorbable adhesion barriers and hemostatic agents, scaffold in tissue engineering, drug delivery matrix, biosensors, etc., while the hemostatic properties and absorption of oxycellulose can be adjusted by the degree of oxidation (Hon, 1996).

Oxidized cellulose containing carboxyl groups is commercially available by reacting cellulose with NO_2 or N_2O_4 in the gaseous form or as a solution in an appropriate organic solvent (Ashton, 1968; Bertocchi et al., 1995; Wu, He, Huang, Wang, & Tang, 2012). Other oxidants usually applied to produce monocarboxy cellulose include HNO_3, HNO_3–$NaNO_2$, HNO_3/H_2SO_4–$NaNO_2$, H_3PO_4–$NaNO_2$ and H_3PO_4–$NaNO_2$–$NaNO_3$, etc. (Bertocchi et al., 1995; Gert, Shishonok, Zubets, Torgashov, & Kaputskii, 1995; Painter, Cesaro, Delben, & Paoletti, 1985; Wanleg, 1956). The reaction with HNO_3 alone or a mixture of H_3PO_4–$NaNO_2$ requires heating at high temperature, these cause extensive hydrolysis of cellulose and low yield of oxycellulose. The HNO_3–$NaNO_2$ can prepare oxycellulose with 14–18% carboxyl content, but requires a long oxidation time. The mediated oxidation of HNO_3/H_2SO_4–$NaNO_2$ is quicker compared to that with HNO_3–$NaNO_2$ alone and achieves the oxidized product with up to ~21% carboxyl content. However, the yield of oxycellulose was decreased to about 20–30% due to further hydrolysis by strong acid of H_2SO_4. Oxidation of primary hydroxyl groups of celluloses using a mixture of HNO_3/H_3PO_4–$NaNO_2$ as an oxidant has become one of the interesting routes to introduce carbonyl and carboxyl functionalities into polysaccharides (Kumar & Yang, 2002; Painter et al., 1985; Wang, Xiang, & Zou, 2009). The advantages of HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation of polysaccharides are the followings: high selectivity and yield, just modest degradation of celluloses through out the oxidation process, and this oxidation proceeds under aqueous mild conditions around room temperature (Kumar & Yang, 2002; Saito, Okita, Nge, Sugiyama, & Isogai, 2006). On the other hand, the HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation can effectively introduce carboxyl and carbonyl functional groups into fibrous celluloses and activate the cellulose polymers for further chemical modification. It has also been investigated that oxidized celluloses may integrate with proteins, dyes, enzymes, or amine drugs by coupling with their amino functions to synthesize new type cellulose-based polymers with special performance and application (Alinovskaya, Yurkshtovich, & Kaputskii, 1989; Kaputskii et al., 1995; Kumar & Deshpande, 2001).

In the previous literature (Gert et al., 1995; Kumar & Yang, 2002; Wang et al., 2009; Wei, Kumar, & Banker, 1996), the HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation of natural cellulose is detailedly investigated. However, the study on HNO_3/H_3PO_4–$NaNO_2$ oxidation of C6 primary hydroxyls in regenerated cellulose of bamboo pulp fibers has not been conducted yet. In our paper, bamboo pulp fibers are used to obtain information about impact of HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation on molecular structure and properties of regenerated cellulose fibers. It is taken HNO_3/H_3PO_4–$NaNO_2$ as oxidant to oxidize regenerated bamboo pulp fibers under various conditions, collected water-insoluble fractions were analyzed in terms of weight loss values, carboxyl contents, fiber fineness and mechanical properties. The changes in internal structure of oxidized bamboo pulp fibers were evaluated by determination of crystallinity, thermal behavior and surface morphology. The significance of this study is to understand the individual roles of introduced functionalities and changed fiber structure in the properties of the oxidized bamboo pulp fibers, and achieve a novel biofiber with active carboxyl groups, which can react with other functional groups for further surface modification and be utilized in textile and paper industry, medical and packing materials.

2. Experimental

2.1. Materials

Bamboo pulp spinning yarns (Lyocell Bamboo Fiber Co., Ltd., Shanghai, China) were used as a regenerated cellulose fiber, which was bleached and scoured. Its color was white with a fineness of 37.59 tex. Sodium nitrite, 68% (w/w) nitric acid solution, 85% (w/w) phosphoric acid solution and acetone were purchased from Aladdin Chemical Reagent Co., USA, and other chemicals were obtained from Wako Pure Chemicals, Co., Japan, as analytical grades and used without further purification.

2.2. Preparation of HNO_3/H_3PO_4–$NaNO_2$ oxidized bamboo pulp fibers

The samples of bamboo pulp yarns were soaked in 0.25 M NaOH aqueous solution for 20 min at room temperature to remove the oil and impurities, and then washed with deionized water cleanly. Subsequently, a sample of bamboo pulp yarns (3.0 g) was immersed in a 90 ml mixture solution of nitric acid and phosphoric acid. Once the bamboo pulp fibers were entirely soaked, 0.63 g and 1.26 g (i.e. 0.7% and 1.4%, w/v) of sodium nitrite were respectively added immediately. The reaction vessel was covered with a petri dish to prevent reddish brown fumes to the air and then the mixture solution was oscillated gently at the absence of light and room temperature, for 15, 30, 45, 60, 120, 180, 300, 360 and 480 min. After that, the fibers were rinsed thoroughly with deionized water several times and soaked in 0.2% (w/w) of propanetriol solution for 15 min to remove the oxidant. It was finally washed with acetone and air-dried for about 30 min at 60 °C and cooled down to room temperature.

2.3. Measurements and analyses

2.3.1. Determination of weight loss

The formation of soluble fragments, as a result of the cellulose chain scission caused by oxidation treatment, was determined by measuring the weight loss of oxidized bamboo pulp fibers by applying the direct gravimetric method (Koblyakov, 1989).

2.3.2. Carboxyl (COOH) groups determination

The amount of carboxyl groups present in the oxidized products was determined according to the reported procedure (Yackel & Kenyon, 1942). The carboxyl groups of the oxidized cellulose react with the salts of weaker acids such as calcium acetate, forming a salt of the oxidized cellulose and releasing an equivalent amount of the weaker acid. For determination of carboxyl content in oxidized bamboo pulp fibers, the following method was developed. The fiber samples (0.5 g) were cut up to particles, and then treated with 0.01 M HCl for 1 h for obtaining in the acidic form by replacement of its cations by hydrogen ions, followed by washing with deionized water. In the next step to the oxidized fibers 50 ml of a 2% (w/w) calcium acetate solution were added. After frequent ultrasonic shaking for 30 min, to facilitate completion of the interchange, the mixture was titrated with 0.1 M standardized sodium hydroxide, using phenolphthalein as an indicator. The volume of NaOH solution consumed was corrected for the blank. The carboxyl content in the sample was calculated as follows:

$$\text{Carboxyl content}\,(\%\text{w/w}) = \frac{0.1\ \text{M} \times V_{\text{NaOH}} \times MW_{\text{COOH}}}{m \times (1 - w/100)} \times 100\%, \quad (1)$$

where 0.1 M is the normality concentration of NaOH, V_{NaOH} is the volume (ml) of NaOH solution used in titration after correcting for

the blank, m is the weight of oxidized bamboo pulp fibers (mg), and w is the moisture content of the fibers (%).

2.3.3. Aldehyde (CHO) groups determination

The aldehyde content in oxidized products was determined by the method described by Saito and co-workers (2004). The oxidized bamboo pulp fibers were further oxidized with sodium chlorite at pH 4–5 for selective conversion of the aldehyde groups in the samples to carboxyl ones, and carboxyl content was determined by above mentioned calcium acetate method. Cellulose slurry with 10% consistency was prepared beforehand, and then this slurry (20 g) was added to a mixture containing $NaClO_2$ (1.81 g), 5 M CH_3COOH (20 g), and water (57 ml). Oxidation was performed by stirring the mixture at room temperature for 48 h, followed by washing thoroughly with deionized water by filtration. The carboxyl groups formed by the post $NaClO_2$ oxidation of the HNO_3/H_3PO_4–$NaNO_2$ oxidized cellulose were regarded as aldehyde groups present in the starting oxidized bamboo pulp cellulose.

2.3.4. Carbonyl groups determination

The amount of carbonyl groups in oxidized bamboo pulp fibers was measured according to the hydroxylamine method (Kumar & Yang, 2002). A 50 ml of hydroxylamine hydrochloride was prepared by dissolving 50 g of NH_2OH–HCl in 120 ml of 1 M sodium hydroxide solution and then diluting to 1000 ml with water. Subsequently, this NH_2OH–HCl solution and 0.5 g oxidized fibers were placed in a 250 ml round-bottom flask connected by a manifold and with a stopcock for evacuation using a water pump. Then the stopcock was closed and the mixture was reacted by heating at 50 °C for 2 h. When cooling to room temperature, a 25 ml aliquot of the reaction supernatant was taken to titrate with a 0.1 M HCl solution to pH 3.2. Using a 25 ml hydroxylamine hydrochloride solution as a blank titration was conducted in the same manner. The carbonyl content in the oxidized fibers was calculated using the equation.

$$\text{Carbonyl content (\%w/w)} = \frac{0.1\ \text{M} \times (V_2 - V_1) \times MW_{CO}}{m} \times 100\%, \quad (2)$$

where 0.1 M is the concentration of HCl, V_1 and V_2 are the volumes (ml) of 0.1 M HCl consumed in titrations of blank and sample solutions, respectively, m is the dry weight of oxidized sample (mg).

2.3.5. Ketone groups analysis

The ketone group content in oxidized fibers sample was determined by subtracting the aldehyde group content from the carbonyl content confirmed as described above.

2.3.6. Determination of fineness of oxidized bamboo pulp fibers

Fineness of the oxidized fibers in tex was measured as per standard method (SRPS F.S2.212, 1963) by dividing the mass of fibers by their known length.

2.3.7. Morphology analysis

Scanning electron microscopy (SEM) was used to observe longitudinal surface morphology. The samples were coated with gold. The instrument was a Japan JEOL JSM-6700F field emission-type scanning electron microscope with an accelerating voltage of 5 kV.

2.3.8. Solid state ^{13}C-CP/MAS NMR analysis

Solid state ^{13}C NMR spectra of the oxidized bamboo pulp fibers were recorded using a Bruker AVANCE III-400 (100.4 MHz) superconducting nuclear magnetic resonance spectrometer (Switzerland) with cross polarization and magic angle sample spinning under the following conditions: spinning rate 5 kHz, pulse delay 3 ms, contact time 5 ms and compensate time 20 ms.

2.3.9. FT-IR spectroscopy

The Fourier transform infrared (FT-IR) spectra of samples were obtained on a Nicolet NEXUS-870 FT-IR spectrophotometer (Madison, USA) using KBr pellets, and samples were analyzed in the range of wavelength from 4000 to 400 cm^{-1} with the result of 24 scans at the resolution of 4 cm^{-1}.

2.3.10. X-ray diffraction analysis

X-ray diffraction (XRD) patterns of the bamboo pulp fibers were performed by the reflection method using a RINT 2027 X-ray detector diffraction system (Rigaku Corporation, Tokyo, Japan) with a Cu Kα target and β Ni filter at a voltage of 40 kV, a current of 30 mA, a scan rate of 2°/min and 2θ range of 5–45°. The crystallinity degree (X_c) and crystalline index (CrI) of the fibers sample were calculated by the method of peaks separation and Gaussian peak fit with the Peakfit data processing software (Ver. 4.12, Seasolve Software Inc., Framingham, MA, USA) according to Eqs. (3) and (4), respectively:

$$X_c(\%) = \frac{S_c}{S_c + S_a} \times 100\%, \quad (3)$$

$$\text{CrI} = \frac{I_{002} - I_{am}}{I_{002}}, \quad (4)$$

where S_c is the sum of all crystal areas, and S_a is the amorphous area. I_{002} is the maximum intensity (in arbitrary units) of the 0 0 2 lattice diffraction and I_{am} is the diffraction intensity of amorphous peak at about 18° of 2θ.

2.3.11. Thermal analysis

Thermogravimetry (TG) and differential thermogravimetry (DTG) analysis were carried out on 4–6 mg samples using a SDT Q600 TG/DSC thermal analyzer (TA Instrument Corp., USA) at a heating rate of 10 °C/min from 20 to 800 °C with a constant nitrogen flow of 100 ml/min.

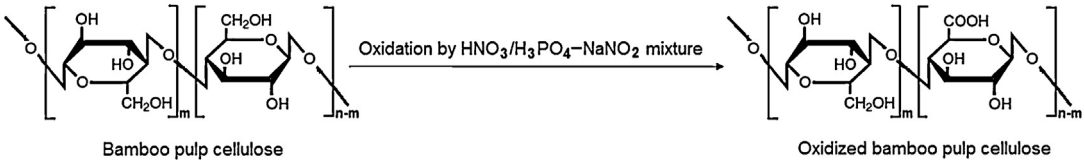
2.3.12. Mechanical properties

The tensile breaking strength and elongation of bamboo pulp fibers were taken on a YG021A electronic single yarn strength tester (Ningbo Textile Instrument Factory, China). The gauge length of the yarn sample was 200 mm, and speed was 200 mm/min. The fiber samples were conditioned in a room at 20 °C and a relative humidity of 65% for 48 h before measurement.

3. Results and discussion

3.1. Effect of volume ratios of HNO_3 and H_3PO_4 on the oxidation of bamboo pulp fibers

For obtaining monocarboxy bamboo pulp cellulose (seen in Scheme 1), the impacts of HNO_3/H_3PO_4–$NaNO_2$ oxidation on



Scheme 1. HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation of bamboo pulp cellulose.

Table 1
Effect of different ratios of HNO_3 and H_3PO_4 (or H_2SO_4) on oxidation of bamboo pulp cellulose.

Oxidation no.	HNO_3:H_3PO_4 (or H_2SO_4) (v/v)	Weight loss[a] (%)	Carboxyl content[b] (%)	Carbonyl content[c] (%)
Oxidation system: HNO_3/H_3PO_4–$NaNO_2$[d]				
A	11:1	16.34	7.93	1.83
B	4:1	15.29	8.82	2.17
C	2:1	17.02	9.71	2.69
D	1:1	17.80	8.48	2.08
E	1:2	19.03	8.96	2.26
F	1:4	18.68	8.64	2.13
Oxidation system: HNO_3/H_2SO_4–$NaNO_2$				
G	11:1[e]	56.92	8.75	3.12

[a] Represents average value of 3 determinations, standard deviation (%) range ±0.68–1.19.
[b] Represents average value of 3 determinations, standard deviation (%) range ±0.14–0.47.
[c] Represents average value of 3 determinations, standard deviation (%) range ±0.11–0.91.
[d] All oxidations were proceeded at room temperature for 6 h with a bath ratio of 1:30 (w/v) of bamboo pulp fiber to acid solution and about 1.4% (w/v) of $NaNO_2$.
[e] Corresponds to the same ratio used by Wanleg (1956). The ratio of bamboo pulp fiber, acid mixture and $NaNO_2$ was as same as the HNO_3/H_3PO_4–$NaNO_2$ reaction system.

bamboo pulp fibers were assessed by determining the carboxyl group content, weight loss, fiber fineness and mechanical properties of fiber samples. In general, since commercial HNO_3 contains small amounts of nitrogen oxides including NO, NO_2, N_2O_3 N_2O_5, etc., the oxidation of polysaccharide compounds by HNO_3 alone is sluggish and frequently requires a catalyst (e.g., H_2SO_4), an initiator (e.g., NO_2 or HNO_2), and/or heating at high temperature (Ogata, 1978). In this study, the HNO_3/H_3PO_4–$NaNO_2$ mixture system oxidation of regenerated cellulose was investigated. The carboxyl content and weight loss of bamboo pulp cellulose oxidized with different ratios of HNO_3 and H_3PO_4 at ambient temperature for 6 h are summarized in Table 1. The data presented in Table 1 display that the ratio of HNO_3 and H_3PO_4 used in the reaction did not have a significant effect on the oxidation of bamboo pulp fibers, and the HNO_3/H_3PO_4–$NaNO_2$ oxidation with the ratio of 2:1 (HNO_3:H_3PO_4) obtained the maximum carboxyl content of 9.71% and a low weight loss of 17.02%. For comparison purpose, the result of the oxidation conducted using the HNO_3/H_2SO_4–$NaNO_2$ reaction system reported by Wanleg (1956) is also presented in Table 1. The oxidation with a mixture of HNO_3/H_2SO_4–$NaNO_2$ produced the oxycellulose with 8.75% carboxyl content, whereas the weight loss of oxidized bamboo pulp cellulose was found to be very high (about 56.92%). An addition in concentration of H_2SO_4 to speed the oxidation rate would cause further degradation of cellulose and hence a further decrease in the yield of oxycellulose (Wanleg, 1956). As shown in Table 1, the reaction system of HNO_3 in combination with H_3PO_4 and $NaNO_2$ can achieve the oxidized bamboo pulp fibers with a high carboxyl content (7.93–9.71%) and in a relatively low weight loss (15.29–19.03%). These results reveal that the HNO_3/H_3PO_4–$NaNO_2$ mixture produced oxycellulose in high yields due to slight hydrolysis of cellulose by a weak acid of H_3PO_4.

As seen in Table 1, the HNO_3/H_3PO_4–$NaNO_2$ oxidized bamboo pulp celluloses corresponding to different ratios of HNO_3 and H_3PO_4 contained 7.93%, 8.82%, 9.71%, 8.48%, 8.96%, and 8.64% carboxyl contents, respectively. The amounts of carbonyl groups determined in these oxidized fibers were 1.83%, 2.17%, 2.69%, 2.08%, 2.26%, and 2.13%, while the carboxyl contents in the samples, after further oxidation with sodium chlorite, corresponded to 7.91%, 8.80%, 9.71%, 8.47%, 8.96%, and 8.63%, respectively. These data illustrate that the oxycellulose by HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation contained no aldehyde groups and the carbonyl content formed in the oxidized samples was only due to ketone groups. Simultaneously the HNO_3/H_2SO_4–$NaNO_2$ mixture oxidized bamboo pulp fibers separately contained 8.75% carboxyl content and 3.12% ketone content, and the analysis of carboxyl content in the oxidized fibers with sodium chlorite treatment indicated no aldehyde groups. According to the oxidation mechanism for alcohols reported by Ogata (1978) the nitrogen oxides have been broadly implicated as the oxidants in the oxidation of polysaccharide compounds by HNO_3, solely or in the presence of an acid and $NaNO_2$, furthermore, several different pathways may cause the generation of these species of nitrogen oxides in situ. During the HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation, this reaction is initiated via abstracting a α-hydrogen atom of C6 site from cellulose by such odd-electron species of NO_2 and NO, giving the product of Cell—C(•)H—OH, further attack by NO_2• and subsequent release of NO• and HNO_2 forms Cell—CHO and Cell—$CH(OH)_2$ intermediates, respectively. Following an attack of NO_2• may lead to a hydrogen abstraction reaction from the Cell—CHO and subsequent hydrolysis of the addition product, to yield the Cell–COOH. In the case of Cell—$CH(OH)_2$, it is likely to undergo an initial hydrogen abstraction reaction followed by an attack by NO_2• and subsequent elimination of HNO_2, resulting in the Cell—COOH formation of monocarboxy cellulose.

3.2. Effects of reaction time and sodium nitrite concentration on the oxidation of bamboo pulp fibers

The rate of carboxyl group generation in bamboo pulp cellulose by the oxidation from 0.7% and 1.4% sodium nitrite in combination with HNO_3 and H_3PO_4 is shown in Fig. 1a. The oxidized bamboo pulp fibers exhibited increase in carboxyl content ranging from 0.95% to 10.38% with the increase of oxidation time and concentration of $NaNO_2$. During the initial 60 min, the values of carboxyl group content in fibers oxidized by HNO_3/H_3PO_4–$NaNO_2$ mixture using different concentrations of $NaNO_2$ are very similar, and the reaction rate is fast. Subsequently increasing the reaction time, from 60 to 360 min, the HNO_3/H_3PO_4–$NaNO_2$ oxidized bamboo pulp fibers had higher carboxyl content compared to the fibers oxidized in the first stage, and the bamboo pulp fibers oxidized with 1.4% $NaNO_2$ presented higher carboxyl content than the fibers oxidized with 0.7% $NaNO_2$. Finally extending the oxidation time up to 480 min, caused only a small increase in the carboxyl content. The oxidation rate gradually decreased and the carboxyl content of bamboo pulp fibers oxidized with 0.7% and 1.4% $NaNO_2$ became closer.

During the HNO_3/H_3PO_4–$NaNO_2$ reaction, bamboo pulp cellulose chain-molecules would undergo scission with the production of soluble fragments due to side reactions of oxidation. The weight loss of oxidized bamboo pulp fibers may reflect not only the formation of soluble fragments but also the oxidative extent of the fibers oxidized by HNO_3/H_3PO_4–$NaNO_2$, as it is shown in Fig. 1b. The loss in weight of oxidized bamboo pulp fibers increased with the extended oxidation time, especially pronounced when the time of oxidation was over 60 min. Furthermore, the weight loss with values up to ~25.26% of the fibers oxidized by higher sodium nitrite charge (1.4% $NaNO_2$) combining with HNO_3 and H_3PO_4 is more noticeable than that (ranging in 3.48–15.72%) of the cellulose fibers

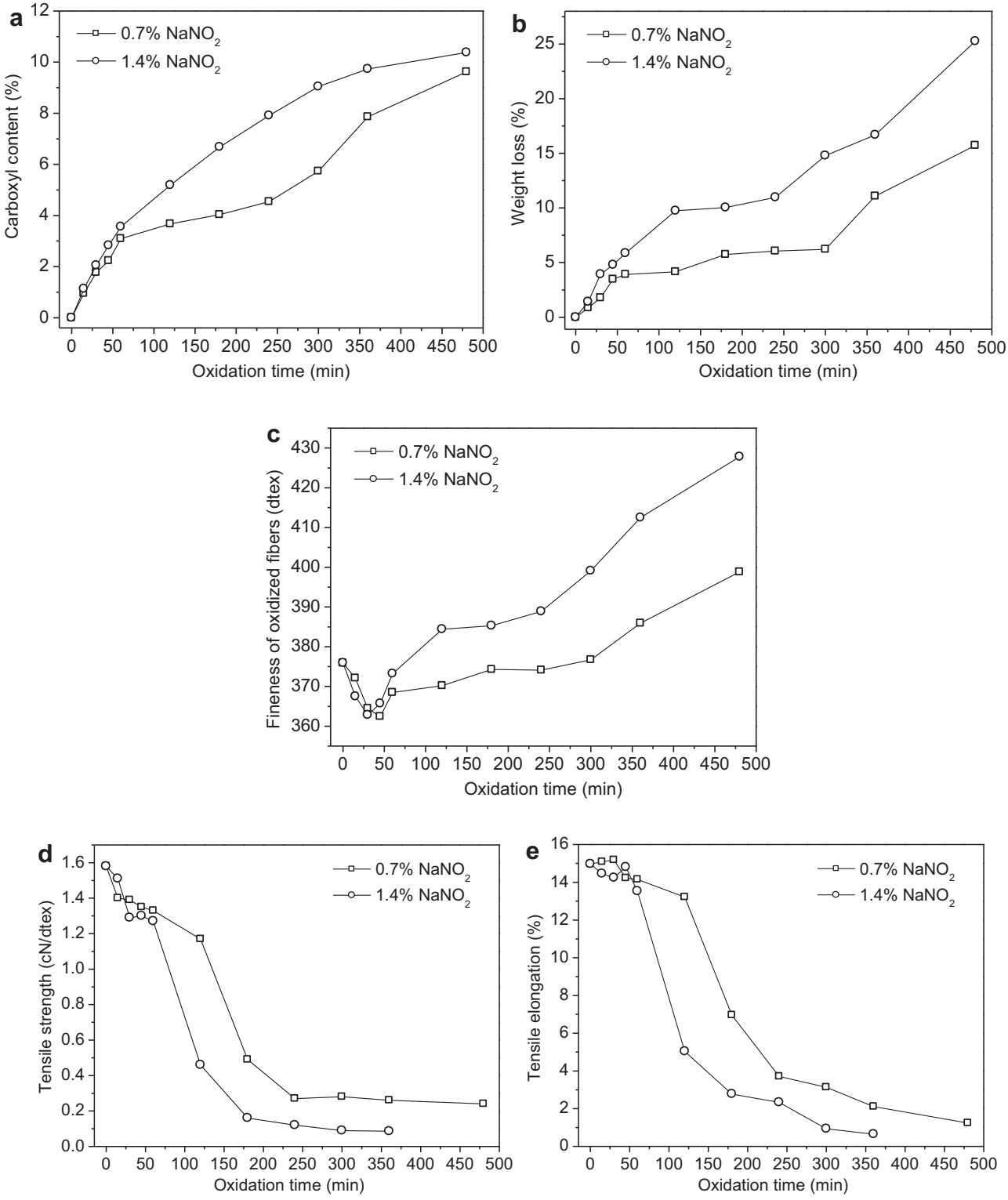


Fig. 1. Relationship between the carboxyl group content (a), weight loss (b), fiber fineness (c), breaking strength (d) and breaking elongation (e) of the oxidized bamboo pulp fibers and the oxidation time and the concentration of $NaNO_2$ used for the oxidation.

oxidized with low sodium nitrite charge. In addition, the bamboo pulp fibers contraction phenomenon can be observed in the oxidation process of HNO_3/H_3PO_4–$NaNO_2$ mixture. Fig. 1c clarifies that the fineness of oxidized bamboo pulp fibers basically increased with higher $NaNO_2$ concentration and increasing reaction time, and the value of the oxidized fibers fineness was enhanced up to 13.81%, namely from 37.59 tex for starting (non-oxidized) fibers to 42.78 tex for the fibers oxidized by 1.4% $NaNO_2$ during 480 min.

Theoretically, increasing oxidation time may increase the carboxyl content of the oxidized bamboo pulp fibers during the HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation process, and high carboxyl content may subsequently enhance the ability of further chemical modification for the oxidized fibers. However, the

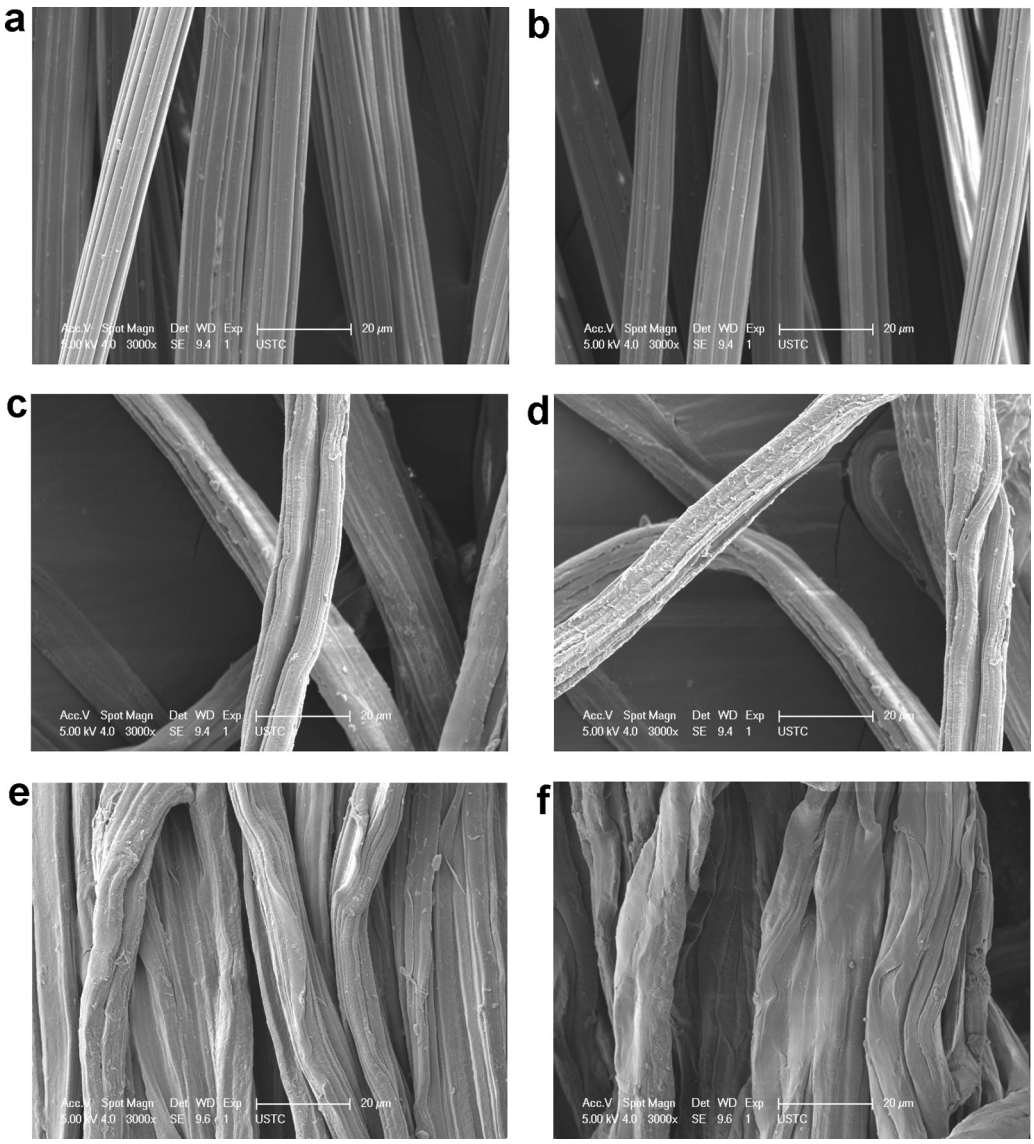


Fig. 2. SEM micrographs of: (a) non-oxidized bamboo pulp fiber, (b) fiber oxidized for 15 min, (c) fiber oxidized for 60 min, (d) fiber oxidized for 180 min, (e) fiber oxidized for 300 min, and (f) fiber oxidized for 360 min.

oxidation can break to some extent the crystal structure in the original cellulose (Saito & Isogai, 2004). Fig. 1d and e shows the effect of the oxidation time on the mechanical properties of the oxidized fibers. In contrast with the starting bamboo pulp fibers, the breaking strength and elongation of oxidized fibers decreased with prolonging time. The tensile strength and elongation of the oxidized fibers did not change remarkably for the oxidation time in the range of 0–60 min, whereas it dramatically decreased when the oxidation time was over 60 min. The bamboo pulp fibers oxidized by 1.4% $NaNO_2$ had much lower tensile strength and elongation than the fibers oxidized by 0.7% $NaNO_2$ during the severe oxidation degree, and the fibers oxidized with higher sodium nitrite concentration (1.4% $NaNO_2$) and longer oxidation time (480 min) became so rigid and crisp that their tensile strength and elongation could not be surveyed, consequently, no data are shown in Fig. 1d and e. From these results it is clear that slight oxidation of HNO_3/H_3PO_4–$NaNO_2$ for 60 min with a ratio of 2:1 (v/v) of nitric acid and phosphoric acid containing 1.4% (w/v) of sodium nitrite yields adequate carboxyl content in the oxidized cellulose to ensure larger reaction activity for the oxidized fibers when applied in more potential chemical modification. Meanwhile, the tensile properties of the bamboo pulp fibers with slight oxidation had no significant change, which are suitable for dry goods and medical textile applications.

3.3. Morphology analysis of oxidized bamboo pulp fibers

These micrographs obtained accordingly from the starting bamboo pulp fiber, the oxidized fibers with different oxidation time are shown in Fig. 2. It can be seen from Fig. 2a that the non-oxidized bamboo pulp fiber consists of fibrils which is basically arranged along the length of the fiber. There are full of grooves between fibrils in the longitudinal fiber surface and apertures along the length of the fibrils, and its morphology is straight stripes with a sleek shape. Fig. 2b and c shows that bamboo pulp fibers were suffered from mild corrosion of oxidant in the oxidation process of short time, some grooves on longitudinal surface of the oxidized fiber became deeper and wider, but the whole surface morphology is almost similar to the original fiber.

Further extending the oxidation time, the HNO_3/H_3PO_4–$NaNO_2$ system oxidized fibers have a great different longitudinal morphology as shown in Fig. 2(d, e and f) in comparison with non-oxidized

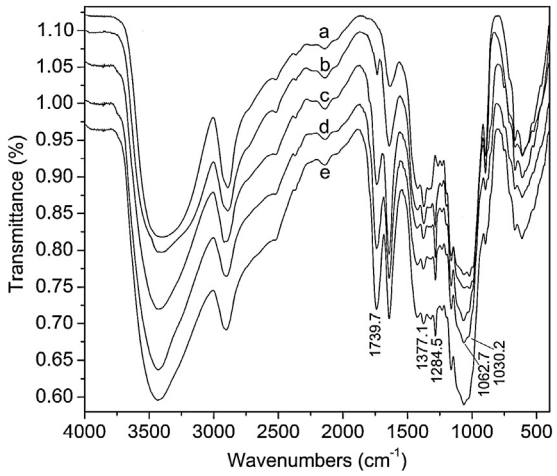


Fig. 3. FT-IR spectra of: (a) starting bamboo pulp fiber, (b) fiber oxidized for 60 min, (c) fiber oxidized for 180 min, (d) fiber oxidized for 300 min, and (e) fiber oxidized for 360 min.

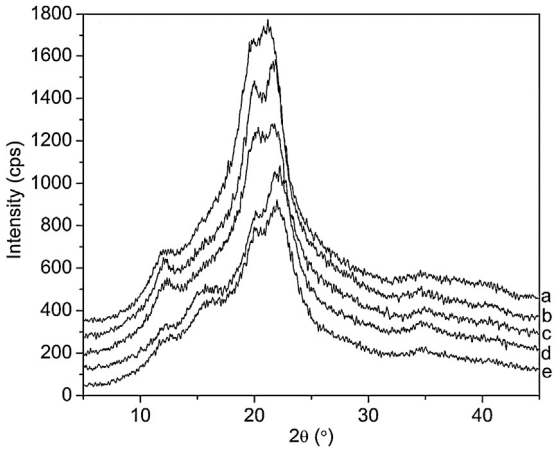


Fig. 4. X-ray diffraction patterns of bamboo pulp fibers oxidized with different oxidation time: (a) 0 min, (b) 60 min, (c) 180 min, (d) 300 min, and (e) 360 min.

ones. In Fig. 2d, the oxidized fiber surface is very rough, and many narrow lines and apertures affected by oxidation can be easily seen, some fibers start to generate slight convolution. The longitudinal surface of the bamboo pulp fiber with high oxidation degree of long time is tightly contracted and crimpled to some extent as shown in Fig. 2e. So it could be seen the grooves and fibril stripe outlines by spells. In the same way, Fig. 2f also represents the surface characteristics like in Fig. 2e, but there is an addition in large extent, and some small crevices and holes appear on the partial surface of the oxidized fiber. So there is nearly no sign of grooves between fibrils and the smooth and sleek straight stripes become illegible. This indicates that the acute oxidation of long time by HNO_3/H_3PO_4–$NaNO_2$ mixture may result in the increase of weakness on the fiber surface, that are responsible for a decrease in tensile properties of the oxidized bamboo pulp fibers.

3.4. FT-IR characterization

Fig. 3 shows FT-IR spectra of non-oxidized bamboo pulp fiber and oxidized fibers with different oxidation time. All of them had a broad peak corresponding to —OH group stretching of cellulose observed in the range 3100–3500 cm^{-1}. However, these absorption peaks of —OH stretching in oxidized fibers gradually became narrower and transferred to higher wavenumber position when increased the oxidation time. One possible reason for this could be that the hydrogen bonding between cellulose chains was weakened, loosening the crystalline structure of fibers due to deep oxidation for long time. For the bamboo pulp fibers oxidized for different oxidation time, a sharp band associated with —OH group in-plane bending of cellulose at 1377.1 cm^{-1}, a peak at around 1161.2 cm^{-1} due to C—O—C asymmetric stretching and a little peak at 1030.2 cm^{-1} due to C—O stretching totally decreased somewhat in the intensity. But another sharp band corresponding to —CH group bending of cellulose at about 1284.5 cm^{-1} was very stronger than that of original bamboo pulp fiber. Compared with non-oxidized bamboo pulp fiber, the infrared spectra of oxidized samples in Fig. 3(b–e) exhibit that a sharp characteristic absorption peak corresponding to C=O stretching vibration of carbonyl group clearly appeared at 1739.7 cm^{-1} or so, whose absorptivity enhanced with extending oxidation time, consistent with the increase of the carboxyl and ketone groups in oxidized fibers. This should be attributed to the formation of carboxyl and carbonyl groups in the bamboo pulp fibers with HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation.

3.5. X-ray diffraction analysis

Fig. 4 shows the X-ray diffraction spectra of bamboo pulp fiber samples treated with different oxidation time. The diffraction patterns of oxidized fibers are similitude with that of the non-oxidized bamboo pulp fiber. It is well known that the cellulose I structure of the native cellulose is changed to the cellulose II structure by cellulose regeneration. Bamboo pulp fiber was regenerated one, so it was the cellulose II structure (Yang, Xu, Ma, & Wang, 2008). The locations of the characteristic peaks of bamboo pulp cellulose were obtained by deconvoluting the XRD spectra with the Peakfit software. The diffractive peaks of oxidized bamboo pulp fibers at 2θ values of 12.4° and 20.2° were respectively attributed to the (1 1 0) and (0 0 2) planes of the typical cellulose II structure. Hence it can be deduced that the crystalline forms of the bamboo pulp fibers did not markedly change in the processing of HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation.

Additionally, the crystallinity and crystalline index were calculated by foregoing Eqs. (3) and (4) after the wide-angle X-ray diffraction (WAXD) patterns were deconvoluted by using the Gaussian deconvolution method and the diffraction peaks numerical fitting ratio achieved 99.99% through the PeakFit software, and the results were listed in Table 2. The data exhibited that the crystallinity and crystalline index of bamboo pulp fibers progressively decreased with increasing oxidation time. This reason may be that the oxidation reaction of HNO_3/H_3PO_4–$NaNO_2$ mixture destroyed hydrogen bonding between bamboo pulp cellulose chains in both crystal and amorphous regions during oxidizing in the range of our

Table 2
Characteristic peaks and crystalline parameters of bamboo pulp fibers oxidized with different oxidation time obtained from WAXD.

Sample no.	Location of characteristic peak, 2θ (°)					Crystallinity (%)	Crystalline index (%)
a	12.62	15.40	16.56	20.28	22.02	44.98	52.24
b	12.43	14.82	16.47	20.25	22.16	40.43	49.68
c	12.36	14.64	16.29	20.34	22.10	38.21	45.97
d	12.30	14.94	16.72	20.12	22.34	30.69	32.41
e	12.51	15.48	16.34	20.14	22.27	29.14	28.03

Table 3
Thermogravimetric data on the starting bamboo pulp fiber and oxidized bamboo pulp fiber samples.

Sample no.	Volatile content (%)	Initial weight loss		Final weight loss	
		Degradation temperature[a] (°C)	Weight loss (%)	Degradation temperature[a] (°C)	Weight loss (%)
Original bamboo pulp fiber	10.78	278.8	63.67	369.5	85.62
1 h-oxidation	13.22	236.7, 286.6	55.40	363.3	75.54
3 h-oxidation	14.58	216.3, 263.2	56.49	371.2	72.01
5 h-oxidation	16.76	194.4, 279.1	60.57	386.7	79.08
6 h-oxidation	17.31	190.2, 266.3	59.21	378.9	78.27

[a] Two or more temperatures indicate two or more stages of decomposition.

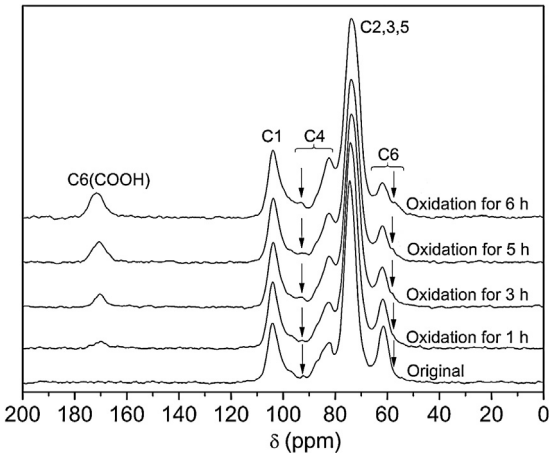


Fig. 5. Solid-state CP/MAS ^{13}C NMR spectra of the original bamboo pulp fiber and HNO_3/H_3PO_4–$NaNO_2$ oxidized bamboo pulp fibers under various conditions.

experiment conditions, which affects its physical properties, and that is consistent with the above results from mechanical properties analysis of oxidized bamboo pulp fibers.

3.6. Solid-state ^{13}C NMR analysis of HNO_3/H_3PO_4–$NaNO_2$ oxidized cellulose

In HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation of cellulose, the resonance signals of carbons in pyranose units of bamboo pulp cellulose can be monitored by the solid-state CP/MAS ^{13}C NMR method. It can be comprehended from Fig. 5 that the original and HNO_3/H_3PO_4–$NaNO_2$ oxidized bamboo pulp celluloses had broad C1, non-crystalline C4, crystalline C6 and C2,3,5 signals, while small signal due to crystalline C4 and non-crystalline C6 of cellulose II remained as well. The apparent C1 signal of the original bamboo pulp fiber at 102–108 ppm was basically unchanged. The overlapped signals due to C2, C3 and C5 appeared at 69–81 ppm. The chemical shift and intensities of C2, C3 and C5 signals somewhat changed by the oxidation. The signals for crystalline and non-crystalline C4 carbons were located at 87–92 and 81–87 ppm, respectively (Isogai, Usuda, Kato, Uryu, & Atalla, 1989). The shape and ratio of crystalline and non-crystalline C4 signals of the original bamboo pulp cellulose were roughly unchanged even after the HNO_3/H_3PO_4–$NaNO_2$ oxidation for 6 h. These results show that the HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation of bamboo pulp fibers has nearly no influences on the chemical shift and the patterns of C1 and C4 in solid-state ^{13}C NMR spectra. On the other hand, the C6 resonance signal in bamboo pulp cellulose appeared at 60–69 ppm, and the signal tops for crystalline and non-crystalline C6 carbons were respectively located at 64 and 61 ppm (Kumar & Kothari, 1999), the crystalline C6 signal gradually decreased with increasing the HNO_3/H_3PO_4–$NaNO_2$ oxidation time, while the shoulder signal due to non-crystalline C6 carbons at 61 ppm enhanced to some extent. Meanwhile, the signals due to carboxyl carbons in the oxidized fibers appeared at around 175 ppm, and their intensities increased with extended oxidation time. Probably the carboxyl groups formed in the HNO_3/H_3PO_4–$NaNO_2$ oxidized bamboo pulp celluloses are mostly present at the C6 position, and the HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation at the C6 position primary hydroxyls are progressed in the non-crystalline region and crystal zone of cellulose II of bamboo pulp fibers, in coincidence with those from XRD analysis.

3.7. Thermal analysis

Fig. 6 shows the TG (a) and DTG (b) curves of the original bamboo pulp fiber and oxidized bamboo pulp fibers, and the temperatures at which the major weight losses are also exhibited in Table 3. It was observed that all bamboo pulp fiber samples showed a weight loss from 45 °C to 125 °C due to the moisture content vaporization, and the moisture content in these celluloses increased with adding oxidation extent (seen in Table 3). This is

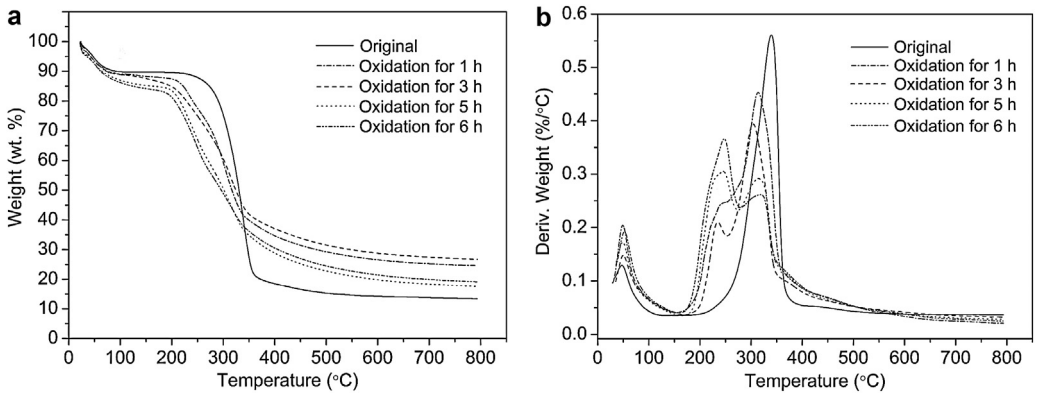


Fig. 6. TG (a) and DTG (b) curves of the starting bamboo pulp fiber and a series of oxidized bamboo pulp fibers.

because the bamboo pulp fibers with higher carboxyl content had the stronger affinity for water molecules. In the initial stage of weight loss (180–380 °C), almost all oxidized fiber samples started to decompose at lower temperatures than the starting bamboo pulp cellulose, and the fastest thermo-decomposition temperature for the original fiber was 340 °C, while they decreased to 235–318 °C for the oxidized products, again reflecting their lower crystallinity compared with the original cellulose. Furthermore, the decomposition patterns became more complex with extending oxidation degree, and two-stage decompositions occurred for all oxidized bamboo pulp materials during initial weight losses (up to about 380 °C). The final stage was that the crystal region of the fibers had been completely destructed and the cellulose decomposed totally from 380 °C to the termination of 800 °C. The final weight loss of all oxidized fiber samples was in the 72–79% range, while for the starting bamboo pulp fiber the value was 86%. Although the TG curves of the original bamboo pulp fiber and the oxidized fiber series are similar in some way, the temperatures of the oxidized bamboo pulp fibers at the beginning degradation and maximal thermo-decomposition rate are lower than those of the starting bamboo pulp fiber, so the thermal stability of these oxidized bamboo pulp fibers decreased with enhancing oxidation extent.

4. Conclusions

The results presented in this study show that the HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation of bamboo pulp fibers with different sodium nitrite concentrations and reaction time can obtain oxidized fiber products with high yield and various carboxyl content. It is manifested that the different ratios of HNO_3 and H_3PO_4 used in the oxidation reaction did not significantly influence the weight loss and carboxyl content of oxidized bamboo pulp fibers. Since the carboxyl content and weight loss of the oxidized fiber increased with adding oxidation time, we can easily acquire the oxidized bamboo pulp fiber with expectant yield and carboxyl content by controlling the oxidation time of HNO_3/H_3PO_4–$NaNO_2$ mixture. With increasing reaction time, the fiber fineness increased and mechanical properties of the oxidized bamboo pulp fiber reduced on the whole.

From the analysis of structure, it can be deduced that the crystallinity of the oxidized bamboo pulp cellulose decreased gradually with increasing oxidation extent, but the typical cellulose II structure was not changed. The results from TG and DTG show that the oxidized fiber materials had a lower thermal stability than the original bamboo pulp fiber. Solid-state ^{13}C NMR and X-ray diffraction analyses revealed that the carboxyl and carbonyl groups introduced into the HNO_3/H_3PO_4–$NaNO_2$ oxidized celluloses were mostly present at the C6 position of amorphous and crystalline regions in bamboo pulp fibers. In addition, the tensile properties of oxidized fibers were not changed very much, and the oxidized fiber materials containing 1.13–3.56% of carboxyl content and with 94–98% of high yields can be obtained in the range of oxidation time from 15 to 60 min. It can be implied that the resultant oxidized bamboo pulp fibers possess more potential for still more chemical modification due to their greater active carboxyl and carbonyl groups and may find extensive applications in textile and medical industries.

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