Improvement to the Solubility and Reactivity of Purified Bamboo Fibers Using a Combined Chemi-mechanical Process

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Bamboo fibers exhibit poor solubility and reactivity because of the aggregational structure of cellulose macro-molecules in fiber cell walls. It has been shown that more free hydroxyl groups on cellulose molecules can be exposed *via* fibrillation of the fiber walls during a PFI beating process. The changes in fiber characteristics, such as the fibrillation degree, water retention value (WRV), and crystallinity, were analyzed. The results showed that the fiber fibrillation increased from 0.781% to 1.072%, and the WRV increased from 112.8% to 213.6% during the beating process, indicating that a fibrillation effect was present in the bamboo fiber walls that corresponded to an incremental change in the degree of mechanical pretreatment. The saturated solubility value of the treated fibers in an alkali/urea solvent system at low temperature increased from 0.22 wt.% to 2.69 wt.% with an incremental change in the degree of mechanical pretreatment. After high-revolution PFI beating, the cellulose crystallinity index of the samples decreased from 66.4% to 50.0%, but the intrinsic viscosity changed only slightly. The oxidation degree of the cellulose in the treated samples increased from 0.85 mol/AGU to 1.03 mol/AGU, which suggested that the reagent accessibility and chemical reaction performance of the bamboo fibers were both improved.

Keywords: Bamboo fibers; PFI beating; Solubility; Reaction performance

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INTRODUCTION

As the energy economy shifts towards being based on biomass, chemical production in the future will also increasingly depend on biomass, particularly plant biomass. The utilization of biomass-based sustainable materials as alternatives to conventional chemical materials has been previously considered an economic opportunity. The development of biomass-based chemical production processes can create comparable energy values to that of the current fuel industry, but require less base stock, as shown over the past few years (Smith 2009; FitzPatrick *et al.* 2010). Twelve chemicals derived from biomass were identified by the U.S. Department of Energy in 2004 as having the potential to be used in a biomass-based economy (Werpy *et al.* 2004).

Cellulose, the most abundant and an almost inexhaustible biomass resource (Klemm *et al.* 2005), is regarded as an important raw material to meet the increasing demand for environmentally friendly and biocompatible products. In recent years, cellulose and its derivatives have been widely studied, with the focus being placed on their biological, chemical, and mechanical properties. Materials produced from cellulose and its derivatives have wide applications, such as in the food, pharmaceuticals, paper and board production, and biofuels industries (Zheng 2014). Purified, highly reactive, and soluble cellulose is in high demand for use with the synthesis of many other cellulose derivatives, such as rayon, esters, ethers, and other new cellulose-based products (Duan *et al.* 2016).

However, natural cellulosic macromolecules show some special chemi-physical properties, such as a lower reagent accessibility and poorer dissolubility, because of the presence of many intra- and intermolecular hydrogen bonds, the aggregation structure, and crystallization, which may be enhanced by the removal of lignin and hemicellulose during pulping and bleaching processes (Duchesne *et al.* 2001). Before the utilization of raw cellulose material, different pretreatments, such as chemical (Agbor *et al.* 2011; Silveira *et al.* 2015), hydrothermal (Ximenes *et al.* 2013), mechanical refining, biological (Alvira *et al.* 2010), and combination methods (Xu and Zhou 2007), are performed to improve the fiber reaction and dissolution performance. A successful pretreatment method must lead to partial or total separation of the lignocellulosic components, increasing the accessibility of cellulose to the reagents with the least inhibitory compounds being released for subsequent steps. Each pretreatment technology has a different specificity against both carbohydrates and lignin and may or may not be efficient for different types of biomasses. Mechanical refining, which includes shredding, grinding, and milling, can improve the accessibility of cellulosic fibers by increasing the available specific surface area, and directly improve the reactivity of cellulose (Tian *et al.* 2014). One of the most common mechanical pretreatments, PFI milling, was developed for laboratory-scaled pulp fiber treatment and can provide enough compression and shear force to achieve internal and external fibrillation of treated fibers (Chen *et al.* 2013). The multilayered structure of fiber walls is loosened by crushing and kneading, and thus the fibrillation of fiber walls could effectively expose more free hydroxyl groups of the cellulosic molecular matrix. However, very few researchers have studied the effect of characteristic changes on the dissolution and reactivity performances of cellulose fibers after PFI beating.

In this paper, PFI milling with different extents of beating was applied to bamboo fibers. The changes to the characteristics of the fibers were determined by using an advanced fiber quality analyzer. The swelling and dissolution of the fiber in an alkaline solution were observed. Also, an oxidation reaction of cellulose was used to investigate the effects PFI mechanical treatment had on the reactivity performance of bamboo fibers.

EXPERIMENTAL

Materials Preparation

Bleached kraft pulp from bamboo chips (*Neosinocalamus affinis*) was bought from Chitianhua Holdings Co., (Guizhou, China). Sodium periodate ($NaIO_4$) was supplied by the China National Medicine Group chemical reagent co., LTD (Shanghai,China). All of the other chemicals were guaranteed reagents and used without further purification. Distilled water was used in all of the experiments.

Methods

Purification

The residual lignin in the pulp samples were further removed using a two-stage bleaching sequence referred to as DP. The chlorine dioxide bleaching (D) stage involved 0.7 wt.% chlorine dioxide, and hydrogen peroxide bleaching (P) stage used 5 wt.% hydrogen peroxide. This was followed by alkali extraction (3 wt.%) to obtain the purified bamboo fiber.

Beating with a PFI mill

Approximately 30 g of purified bamboo fiber were beaten in a PFI mill under the following beating conditions: beating consistency of 10 wt.%; revolution speed of 1400 rpm; beating gap of 0.24 mm; and beating pressure of 33.3 N/cm. Fiber samples were named according to the number of beating revolutions, which included 0 *r*, 10000 *r*, 30000 *r*, 50000 *r*, and 80000 *r*.

Characterization

The change in morphology and properties of the bamboo fibers during the PFI beating process were measured with a fiber quality analyzer (Morfi Compact: ISO/FDIS 16065-2, Techpap Co., Rennes, France) and observed with an electron microscope. The intrinsic viscosity of all of the samples was measured using a copper ethylenediamine (CED) solvent solution, according to the method in a previous report (Duan *et al*. 2016).

The water retention value (WRV) was measured using a laboratory centrifuge with a 3000 g centrifugal acceleration for 30 min. The samples were dried at 105 °C until reaching a constant weight. The results were calculated by the amount of water held in the samples upon centrifugation relative to the oven dry weight.

Schopper Riegler Freeness Schopper Riegler (°SR) is a traditional and most frequently used method for evaluating the refining result. The samples in this method have lower concentrations, and a reverse scale is used for measuring of the water drainage.

The X-ray diffraction patterns and crystallinity index of the samples were determined using a Bruker D8 Discover X-ray diffractometer (Bruker, German) with Cu Kα1 radiation at room temperature. The samples were scanned at 30 kV and 20 mA over a 2θ range of 10° to 40° at a rate of 8.0°/min. The Segal crystallinity index (Segal *CrI*) was calculated with Eq. 1 (Nelson and O'Connor 1964; Nam *et al.* 2016):

$$\text{Segal } CrI = [(I_{\text{total}} - I_{\text{am}}) / I_{\text{total}}] \times 100 \qquad (1)$$

where I_{am} corresponds to the intensity of the minimum peak between the major (20.0°) and secondary peaks (12.0°) for cellulose II, and I_{total} is the intensity of the major peaks (22.5° for cellulose Iβ, and a doublet at 20.0° and 22.1° for cellulose II).

The Fiber Quality Analyzer (FQA), with good reproducibility and stable data, is usually used to detect fiber parameters, such as fiber length, fiber width, broken fiber content, fine fiber content, fiber bundle content, and other indicators. To ensure the accuracy of the measurement results during the process, the number of measured fiber should not be less than 5000, and the determination interval of fiber is from 0.07 mm to 10 mm.

Dissolution in the NaOH/urea solvent system

A solvent with 7% NaOH and 11% urea-water was precooled at -12 °C for 2 h and used to dissolve the cellulose. A desired amount of cellulose was immersed in the solvent and stirred at 1200 rpm for 1 h. The dissolution temperature was controlled at 5 °C. The resultant cellulose solution was centrifuged at 8000 rpm for 10 min. The undissolved fractions were obtained and washed using water and acetone, and then vacuum dried at 60 °C for 24 h. Thus, the saturated solubility ($C_{\max}$, wt.%) of the bamboo cellulose was calculated by:

$$C_{\max} = (M_0 - M_i) / (100 + M_0 - M_i) \tag{2}$$

where M_0 is the weight of the original cellulose (g), and M_i is the weight of the undissolved fraction (g).

The morphological changes to the cellulose in the precooled NaOH/urea aqueous solution were observed. The cellulose solutions were taken out at the same time during dissolution, and placed on glass slides. Then, they were pressed by a cover glass for observation under an electron microscope at ambient temperature. One hundred fibers were selected randomly to measure the average swelling size, and the fiber swelling rate (S, %) was calculated by,

$$S = (W_i - W_0) / W_0 \times 100\% \tag{3}$$

where W_0 is the average width of the non-beaten bamboo fiber (μm), and W_i is the width of the swollen fiber for different extents of beating (μm).

Oxidation reaction

The oxidation reaction of the fiber was used to determine the effects of PFI beating on the bamboo fiber. As was previously reported, the hydroxyl groups on the C2 and C3 of the cellulose molecules are oxidized by sodium periodate ($NaIO_4$) to generate dialdehyde cellulose without the generation of by-products during the oxidation process (Tang and Liang 2010). As a result, the cellulose oxidation degree (D_o: moles of sodium periodate that have been consumed by one mole of anhydroglucose unit, mol/AGU) can be calculated by the amount of reacted sodium periodate.

Two grams of bamboo fiber beaten at different numbers of revolutions of the PFI mill were added to 0.18 mol/L sodium periodate solution and reacted in the dark at 60 ℃ for 4 h. Then, the concentration of the residual sodium periodate solution was measured by using an ultraviolet spectrophotometer (T6, PuXi instrument co. LTD, Beijing, China) to calculate the amount of reacted sodium periodate. The average is taken after parallel experiments. The D_o was calculated with the following equation:

$$D_o = n_i / n_{\mathrm{AGU}} \tag{4}$$

where n_i is the mole fraction of the reacted sodium periodate, and n_{AGU} is the mole fraction of the glucose unit.

RESULTS AND DISCUSSION

Purification of Cellulose

The residual lignin and other impurities in the pulp samples were further removed by using the two-stage DP bleaching sequence. The percent of α-cellulose increased from

88.06% to 98.15%. Additionally, the pentosan, intrinsic viscosity [*η*], and degree of polymerization (DP) were all reduced by the purification process (Table 1).

Table 1. Chemical Composition and Physical Properties of the Bamboo Fiber

	α-Cellulose (%)	Pentosan (%)	[η]	DP
Kraft bamboo pulp	88.06	19.50	819.54	1206
Depth-delignification bamboo fibers	98.15	4.30	446.67	616

Fiber Structural Properties

Table 2. Effects of the Beating Extents on the Morphological Properties of the Bamboo Fibers

Fiber Sample	Fiber Length (mm)			Fiber Width (μm)	Fiber Curl Index (%)	Broken Fiber Content (%)	Fine Content (%)	Macro Fibrillation Index (%)
	L_n	L_l	L_w					
B0	0.62	0.78	1.12	19.4	25.5	32.9	16.5	0.781
B10000	0.57	0.76	1.10	18.3	24.6	33.5	16.8	0.826
B30000	0.53	0.71	0.93	18.2	23.9	33.7	20.2	0.946
B50000	0.48	0.61	0.78	17.2	19.8	34.3	32.8	0.951
B80000	0.47	0.60	0.77	17.1	19.2	35.9	34.2	1.072

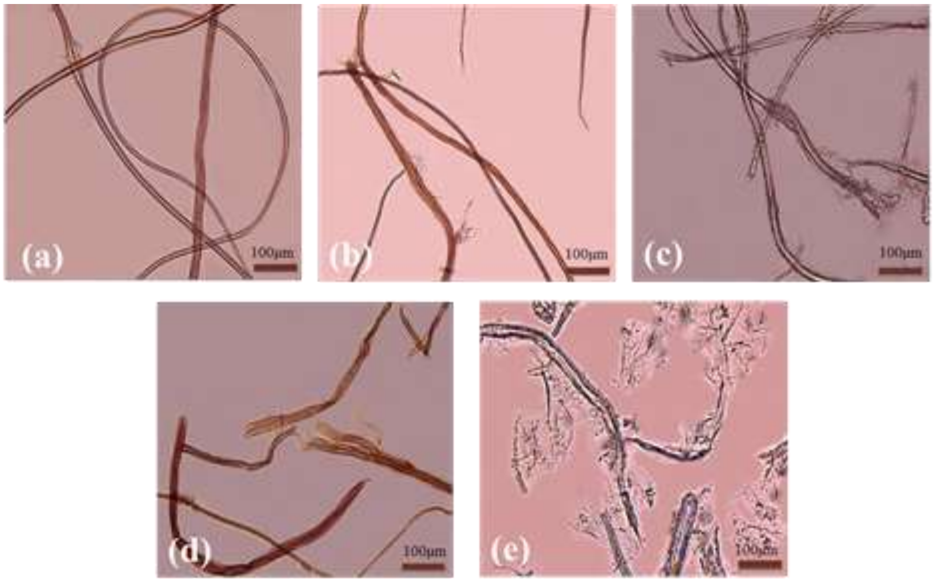

Fig. 1. Fiber morphology of the non-beaten fiber (a) and fiber beaten at extents of 10000 *r* (b), 30000 *r* (c), 50000 *r* (d), and 80000 *r* (e) (**Note:** All magnification of the microscope photos is 400 times)

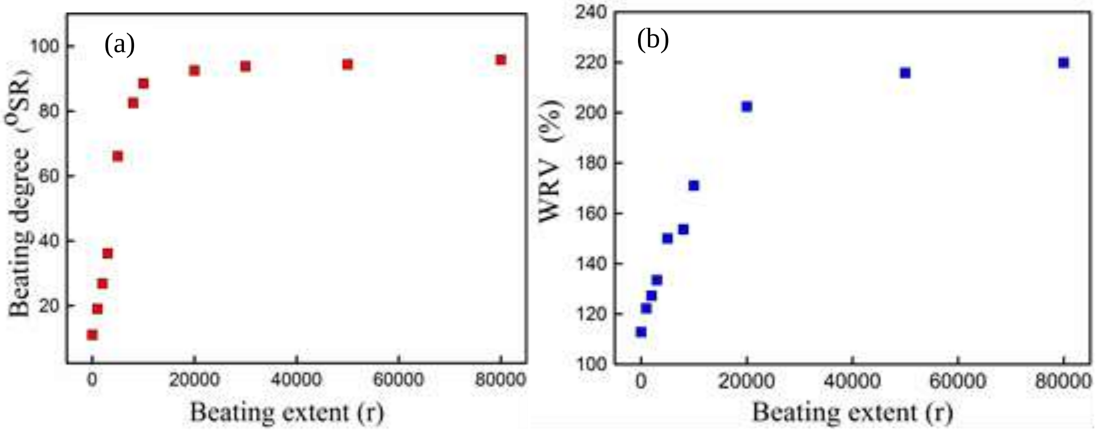

Fig. 2. Effect of the PFI beating extent on the beating degree (a) and WRV (b)

An improvement in the accessibility of the bamboo fibers after the PFI refining treatment was expected because of the change to the fiber morphology properties and disruption of the compact cellulose structures. Accordingly, the changes to the structure and properties of the bamboo fiber, such as fiber swelling, fiber shortening, and internal and external fibrillation, during the PFI beating process were determined in this study. Aggregated fiber bundles were separated into fibrils, and some fibrils were torn into small fines, large fragments, or curled fibers because of external shear forces that caused the fiber length, width, and curl index to decrease (Yasumura *et al.* 2008; Lecourt *et al.* 2010). This was observed from the decrease in the fiber length, width, and curl index as the beating extent increased, as shown in Table 2. After the PFI mill beating at 50000 *r*, the fiber length (L_n), width, and curl index decreased to 0.48 mm, 17.2 μm, and 19.8% from those of the non-treated fiber, which were 0.62 mm, 19.4 μm, and 25.5%, respectively. In contrast, the broken fiber content, fine content, and fibrillation of the bamboo fiber increased because the PFI beating affected the pulp fibers by fibrillation. The fine content and fibrillation of the fiber increased by 99% and 22%, respectively, as shown in Table 2, after PFI beating at 50000 *r*. However, at a beating extent above 50000 *r*, the characteristics of the bamboo fibers changed only slightly.

The images from the electron microscopy observation show that the surface of the non-beaten fiber (Fig. 1a) was smooth, and no fibrillation or curl phenomenon existed, which was consistent with previous findings (Hoeger *et al.* 2013). Small fines and a rough fiber surface were observed after a PFI beating at 10000 *r*. Curled fibers were observed on the fiber surface, as well as cracked fibers, which resulted in the formation of large fragments above a beating extent of 50000 *r*. Continuing the PFI beating, some hydrophilic compounds from the cell wall were released, which produced gel-like layers (Fig. 1e). These gelatinous layers improve fiber–fiber bonding, which can appear as a film after drying (Mou *et al.* 2013).

Fiber fibrillation change and fiber swelling were also seen with an increase in the beating degree and WRV (Fig. 2). Figure 2a shows that the beating degree increased with the increasing extent of beating. Also, fiber fines and fragments were produced by fiber fibrillation. The WRV, related to the fibril surface area, internal pores, and reagent accessibility (Luo and Zhu 2011), also increased with the increasing extent of beating (Fig. 2b). Below a beating extent of 20000 *r*, the beating degree and WRV increased sharply, and the WRV increased from 112.8% to 202.4% as the beating degree increased from 13.5 °SR to 92.5 °SR. This was because there was an increase in water-accessible surface on the fiber with the increase in the fibrillation degree (Gao *et al.* 2015). Consequently, the accessibility of cellulose to chemical reagents was improved after PFI beating, which promoted the dissolution and reactivity performances of the fibers. Continuing the PFI beating, the beating degree and WRV increased at a much smaller rate, which suggested that higher beating extents were not able to provide more water-accessible surface on the fiber.

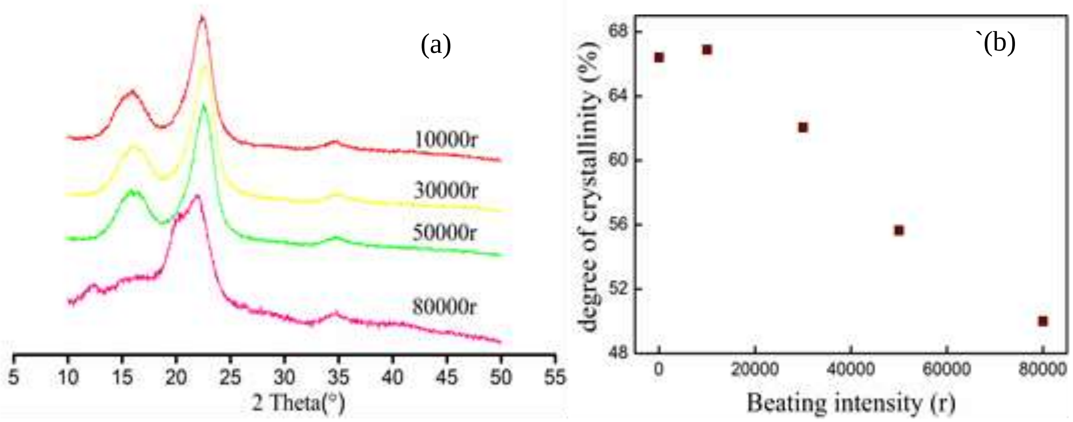

Fig. 3. XRD patterns (a) and crystallinity (b) of treated bamboo fibers with different beating extent

The XRD patterns and crystallinity of treated bamboo fibers with different extents of beating are illustrated in Fig. 3. The XRD results (Fig.3a) showed that crystalline structure of fiber was not changed, when the beating revolutions is less than 50000 *r*. However, after a high extent of beating (80000 *r*), the cellulose was converted from cellulose I to cellulose II. A slight increase in the crystallinity for the lower extents of PFI refining was observed in Fig. 3b, and then it decreased as the beating level further increased, which was consistent with a previous study by Liu *et al.* (2016). As previously reported, the forces of PFI refining mainly affected the amorphous regions of cellulose first, which resulted in the increase in crystallinity. As the beating extent increased, the crystalline regions of the cellulose were attracted by the force, and therefore the crystallinity decreased (Ibrahem *et al.* 1989). However, cellulose fiber with a low degree of crystallinity and high degree of fibrillation are good at attacking reagents during dissolution and chemical reaction.

Fiber Dissolution Performance Analysis

Table 3. Effect of the PFI Beating Extent on the Alkali Swelling

Number of Revolutions (*r*)	0	10000	30000	50000	80000
Average width of the swelled alkali fiber (μm)	24.81	38.42	61.98	65.60	67.95
S (%)	53.15	137.60	282.59	304.94	319.44
C_{max} (wt.%)	0.22	0.85	1.23	2.56	2.69

There were two steps involved in the cellulose dissolution process in the precooled NaOH/urea aqueous solution: (1) cellulose was immersed in the precooled solvent to disperse cellulose chains by mechanical stirring; and (2) the dispersed cellulose chains were attracted by NaOH hydrates to form new hydrogen-bonded networks at low temperatures, and then the NaOH hydrogen-bonded cellulose surrounded the urea hydrates to prevent the cellulose chains from aggregating. The specific surface area of the fibrils increased because external fibrillation occurred during the beating process (Nugroho 2012). Mechanical refining by PFI milling can result in an increase in the total pore volume of the pulp and also improve the mean pore diameter (Duan *et al.* 2016). The shorter fibers obtained under the mechanical force and the fiber longitudinal direction simultaneously resulted in splitting. Meanwhile, PFI beating can cause the internal fibrillation of fibers by replacing intra-fiber hydrogen bonds with fiber-water hydrogen bonds. External fibrillation of fibers can be achieved through high external forces. The fibrillation of the cellulose fibers can loosen the fiber bundle into fiber fines and increase the specific surface area of fibrils, which promotes a high dispersion of cellulose in the solvent. Additionally, the crystalline regions of the bamboo fiber have also been destroyed during the PFI beating process (Fig. 3). The swelling of fiber was affected by the crystallinity because the water and other chemical reagents were limited to penetrating into the crystalline region. In other words, the absorption of the NaOH/urea aqueous solution by the cell wall was increased by a decrease in the crystallinity, which facilitated the dissolution of the bamboo fiber. The images in Fig. 4 indicate that the non-beaten bamboo fiber only swelled in the NaOH/urea aqueous solution, and the average swelling diameter, *S*, and C_{max} were 24.81 μm, 53.15%, and 0.22 wt.%, respectively (Table 3).

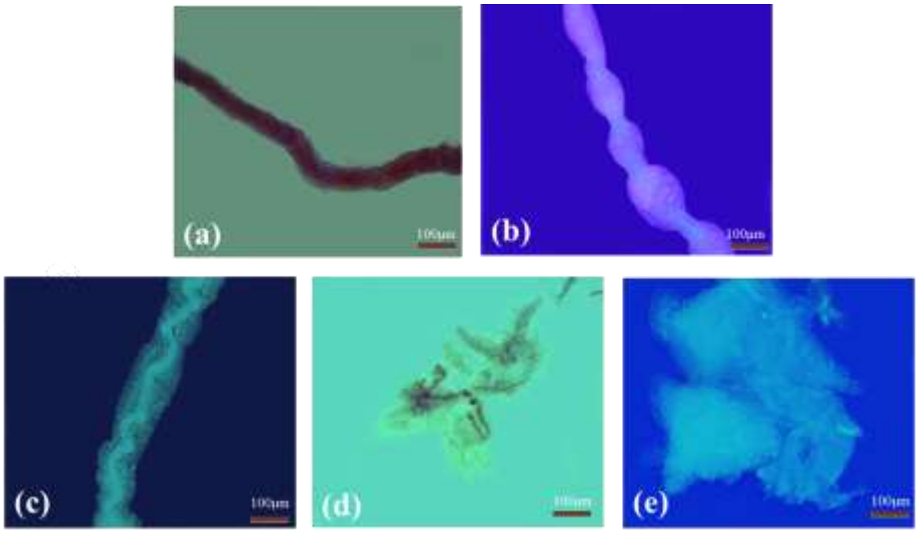

Fig. 4. Microscope images of the fiber dissolving in the NaOH/urea aqueous solution for different PFI revolutions: (a) 0 *r*, (b) 10000 *r*, (c) 30000 *r*, (d) 50000 *r*, and (e) 80000 *r* (**Note:** All magnification of the microscope photos is 400 times)

As the number of PFI beating revolutions increased, the fiber swelling diameter increased from 24.81 μm to 67.95 μm and *S* increased from 53.15% to 319.44%. When the beating extent was above 50000 *r*, the swollen bamboo fiber converted from a rod-like shape to a flaky fiber (Fig. 4d and e), which led to more bamboo fiber being dissolved in the NaOH/urea aqueous solution. The $C_{\max}$ increased from 0.22 wt.% to 2.69 wt.%, which indicated that the solubility was remarkably improved after PFI beating.

Oxidation Reaction Analysis

The fibrillation of the pulp fibers in the beating process can provide more fibrils, and thus the surface area accessible to reagents is increased, which was expected to improve the reactivity. However, inter- and intra-fibril/fiber hydrogen bonding inevitably forms during the drying process of the treated fibers (Larsson *et al.* 2013), which results in a negative effect on the amount of accessible surface. To study the real influence of PFI refining on the improvement to the reactivity of the bamboo fibers, ethanol-water, acetone-ethanol, and trichloromethane-acetone solutions with different percentages (0%, 20%, 40%, 60%, 80%, and 100%) were used in turn to replace the water in the fiber step by step instead of drying with direct heat. Then, the "dried" fiber was reacted with sodium periodate. The reaction equation is shown below as Fig. 5.

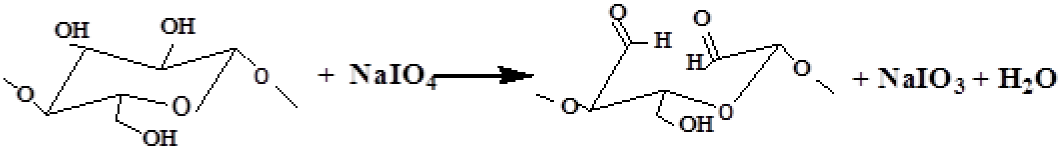

Fig. 5. Reaction equation for cellulose oxidation

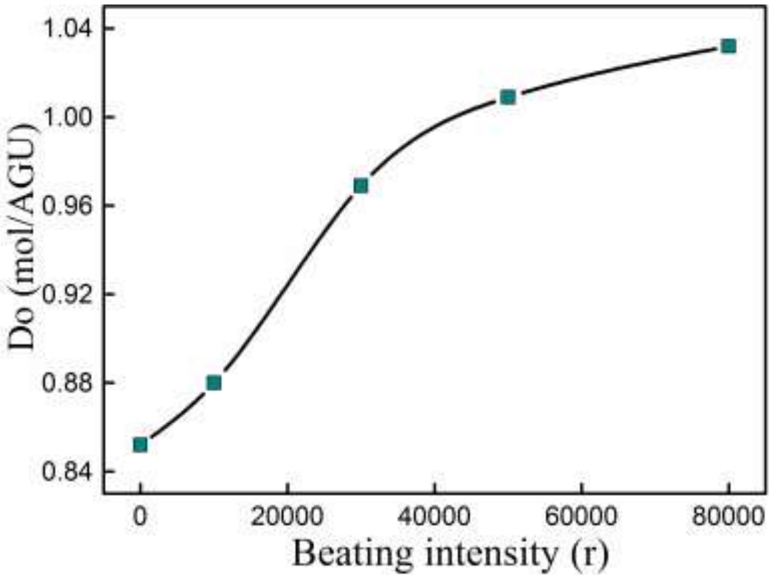

Fig. 6. Reaction performance of PFI-treated bamboo fibers as a function of the extent of beating

An improvement to the reactivity during the oxidation reaction was observed after PFI refining, which was proven by the increased $NaIO_4$ consumption during the oxidation reaction (Table 4).

Previous studies have reported that the ultraviolet visible absorbency of periodate has a good linear relationship with the solution concentration at 290 nm over a wide range (Maekawa and Koshijima 1984).

Table 4. Properties of the Cellulose Oxidized by Sodium Periodate

Number of Revolutions (*r*)	0	10000	30000	50000	80000
Intrinsic Viscosity (mL/g)	447	438	422	414	398
$NaIO_4$ Consumption (mmol/100 g of cellulose)	526	543	598	623	637

A standard curve for the sodium periodate aqueous solution, shown by Eq. 5, was obtained in this study to calculate the amount of reacted $NaIO_4$,

$$A = 0.2203 + 0.0053C \tag{5}$$

where the R^2 was 0.9999.

Compared with the non-beaten bamboo fiber, the $NaIO_4$ consumption increased from 526 mmol/100 g of cellulose to 637 mmol/100 g of cellulose and the D_o increased from 0.85 mol/AGU to 1.03 mol/AGU (Fig. 6), which meant that approximately 52% of the hydroxyl groups on the C2 and C3 of the cellulose molecules could be oxidized to form aldehyde. This was 23.5% higher compared with the untreated fiber. Many other treatments have been used to improve the cellulose reactivity. For example, enzymes have often been used to enhance the reactivity of fiber. However, this usually results in a more severe viscosity loss (Mao *et al.* 2014), which leads to a poor physical strength for the final fiber products. Ultrasound has also been used to pretreat fibers in many previous reports (Bussemaker and Zhang 2013; Luo *et al*. 2014). However, the individual effect of ultrasound was not remarkable (Alivu and Hepher 2000), and so a combination with other techniques was needed, which led to the development of a costly and complex operation. For economic and efficiency reasons, PFI refining might be a suitable option for the mechanical treatment of bamboo fiber, which can change the fiber morphology properties and disrupt the compact cellulose structures to increase the accessible surface on the fiber and consequently improve the reactivity.

CONCLUSIONS

1. A high PFI beating extent can lead to major changes in the characteristics of bamboo fiber. The fibrillation of fiber increased from 0.781% to 1.072%. An increase in water-accessible surface on the fiber was obtained with the increase in the fibrillation degree. The WRV was increased from 112.8% to 202.4%, and the beating degree increased from 13.5 °SR to 92.5 °SR. However, the characteristics of the bamboo fibers changed only slightly when extent of beating was over 50000 *r*.
2. The solubility of the bamboo fiber was improved noticeably, which resulted in an increased specific surface area and decreased the crystalline regions in the fibrils during the PFI beating process. The best result obtained was an increase in the $C_{\max}$ from 0.22 wt.% to 2.69 wt.% in the NaOH/urea aqueous solution.
3. An improvement to the accessibility of the bamboo fibers after the PFI refining treatment was demonstrated by the cellulose oxidation reaction conducted in this work. The cellulose oxidation degree increased from 0.85 mol/AGU to 1.03 mol/AGU. Also, 52% of hydroxyl groups on the C2 and C3 of the cellulose molecules could be oxidized to form aldehyde, which was 23.5% higher compared with the untreated fiber.

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