Improved Reactivity of Bamboo Dissolving Pulp for the Viscose Process: Post-Treatment with Beating

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Chemical and enzymatic modifications intended to improve the reactivity of dissolving pulp rapidly decrease its yield. In this study, a beating post-treatment intended to increase the reactivity of bamboo dissolving pulp was investigated. Beating post-treatment can create microfibrils on the surface of fibers. The reactivity of unrefined bamboo dissolving pulp prepared *via* pre-hydrolysis and a subsequent kraft cooking and Op-H-P (oxygen delignification enhanced with H_2O_2 and sodium hypochlorite) bleaching process was very low. The reactivity increased drastically as the Canadian standard freeness (CSF) of the bamboo dissolving pulp was decreased (*i.e.*, the degree of beating increased). The CSF decreased to 236 mL from its original, higher freeness. The average fiber width was larger and the curling and kink indexes were lower in the pulp of CSF 236 mL compared to those of pulps with greater freeness. However, there was little impact of beating on the crystallinity index of bamboo dissolving pulp.

Keywords: Bamboo dissolving pulp; Reactivity; Beating; Canadian standard freeness

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INTRODUCTION

Dissolving pulp is a chemically refined, bleached pulp composed of more than 90% pure cellulose. The end uses of dissolving pulp include cellophane and rayon, cellulose esters, cellulose ethers, and grafted and cross-linked cellulose derivatives. With a desire to make dissolving pulp, researchers have begun developing technologies for the use of new raw materials, such as cotton linter, jute stem, bagasse, aspen wood, masson pine, and bamboo (Abad *et al.* 2000; Chen and Yang 2011; Helmy and State 1991; Jahan 2009; Li and Ma 2009; Xu and Jiang 2005) as dissolving pulp production feedstocks. Traditionally, there are two methods for producing dissolving pulp. These are extended-time acidic bisulfite cooking and prehydrolysis-sulfate (kraft) cooking. The basic idea behind both processes is to remove as much hemicellulose as possible from cellulose fibers, while simultaneously delignifying them, to obtain a high content of alpha-cellulose. This is essential because the various end uses of dissolving pulp cannot tolerate short-chained hemicellulose molecules, as they have a randomly grafted molecular structure that can drastically decrease the reactivity of the dissolving pulp.

Reactivity is often considered the most important parameter of dissolving pulp. It is mainly related to the accessibility of chemicals to the cellulose. Novel approaches to form dissolving-grade pulp from paper grade pulp, such as the post-alkaline extraction of hemicellulose, have yielded pulps with limited reactivity, owing to poor chemical accessibility. Scientific attention has shifted toward the enzymatic modification of cellulose to increase its accessibility to chemicals. Gehmayr *et al.* (2011) studied the feasibility of enzyme treatments on *Eucalyptus globulus* dissolving pulp bound for viscose-related applications. The addition of an endoglucanase can further increase the amount of both soluble xylan and mannan removed from softwood sulfite dissolving pulps (Gubitz *et al.* 1997). The degree of pentosan removal has been found to be dependent on the time and enzyme charge of the treatment (Christov and Prior 1993; 1995; Christov *et al.* 1999). Endoglucanase activity can lead to swelling of the cell wall, resulting in increased exposure of the dissolving pulp cellulose to solvents and reagents (Henriksson *et al.* 2005). Some chemical methods for increasing the reactivity of dissolving pulps have also been tested, such as the impregnation-rapid-steam treatment (Ye *et al.* 2005), high-heat washing during the pulping process (Fischer *et al.* 1990), and hot water or nitren extraction treatment (which can readily dissolve xylan and cellulose) (Borrega *et al.* 2013; Janzon *et al.* 2008).

Bamboo, an abundant renewable resource in China, can be used to make dissolving pulp (Ma *et al.* 2011). However, bamboo dissolving pulps cannot be used to prepare high-quality viscose products due to their low reactivities. Although chemical and enzymatic treatments can improve the reactivity of dissolving pulp, these methods drastically increase yield loss. Some researchers have studied the potential of physical treatment to enhance the reactivity of dissolving pulp. Liu and Xue (2013) studied the influence of beating on the reactivity of cotton linter dissolving pulp. Beating is one of the most important unit operations undertaken when preparing papermaking fibers for the production of high-quality papers or paperboards. Traditionally, the goal of beating is to improve the bonding ability of fibers by creating many microfibrils on their surface so that they form a strong, smooth sheet with good print receptivity. In this study, the effects of beating post-treatment on the reactivity and morphology of bamboo dissolving pulps were examined.

EXPERIMENTAL

Samples and Preparation Conditions

Bamboo chips were obtained from a local pulp and papermaking group. Before pulping, the raw material (containing 19.64% pentosan) was hydrolyzed in water in a 15-L stainless steel digester rotating at 1 rpm. The optimal acid hydrolysis conditions were a liquor-to-bamboo ratio of 8:1, a sulfuric acid concentration of 1.0% (Zhou *et al.* 2012), a heating rate of 8 °C/10 min, a cooking time of 120 min, and a cooking temperature of 160 °C. After pre-hydrolysis, the hydrolyzed bamboo was kraft-pulped and bleached with an Op-H-P sequence. The optimized cooking conditions were a liquor-to-hydrolyzed bamboo ratio of 5:1, an alkali charge of 27% (as NaOH), a sulifidity of 5%, a heating rate of 6 °C/10 min, a cooking time of 120 min, and a cooking temperature of 165 °C.

The cooked pulps were bleached by Op-H-P bleaching sequences. Oxygen delignification enhanced with H_2O_2 (Op) was carried out at a pressure of 0.6 MPa, at 10% consistency, with chemical charges of 1.0% H_2O_2 and 3.0% NaOH, at 105 °C, for 60 min. Sodium hypochlorite treatment (H) was carried out at 10% consistency, with 3.0% active chlorine at 40 °C, for 90 min. Peroxide bleaching (P) was carried out with 2.0% Na_2SiO_3, 0.5% NaOH, 0.5% $MgSO_4$, 0.2% diethylenetriaminepentaacetic acid (DTPA), and 2.0% H_2O_2 at 10% consistency and 90 °C for 120 min.

Analytical Methods

The Kappa number of pulp samples was tested according to ISO 302-2004, and the brightness of pulp was determined according to ISO 3688/2470. Pentosan and α-cellulose contents were tested according to TAPPI Standards T223 and T203, respectively. The degree of polymerization was determined and calculated from the intrinsic viscosity, which was measured in a cupriethylene-diamine solution according to TAPPI Standard T206. The X-ray diffraction (XRD) patterns of the pulp were recorded with an X'Pert diffraction instrument (D8-ADVANCE) using Cu radiation ($\lambda = 0.15406$ nm). Data were collected in the 5 to 50º range of 2θ with a 0.05º step every 1.5 s. The crystallinity index of the pulp was calculated using the method introduced by Segal *et al.* (1959). Bamboo dissolving pulp samples (at 10% consistency) were refined in a laboratory PFI (KRK 8604082) refiner running at various revolutions. The degree of beating was determined by a Canadian standard freeness (CSF) tester (TMI) according to TAPPI Standard T227. The lower the CSF (mL) was, the higher was the degree of beating applied to the dissolving pulp.

Reactivity Measurements

The reactivity of the bamboo dissolving pulp was determined *via* a two-step process, according to the national standard FZ/T 50010.13-2011 in China.

The first step was the preparation of viscose from bamboo dissolving pulp. First, 14.4-g (bone dry) dry pulp samples were mixed with 361 mL of 13.7% NaOH in a 500-mL, brown, wide-necked bottle. The samples were stirred at 3000 rpm for 5 min at a temperature of 20 ± 1 °C. A constant volume of CS_2 (11 mL for non-wood dissolving pulp) was added to the brown, wide-necked bottle. The viscose was prepared by vibrating the samples on a KS oscillator for 15 min before reacting them for 4 h in the xanthator (rotating at 15 ± 1 rpm).

The reactivity was measured in the second step of the process. Viscose samples were added to a stainless cylinder with an inner diameter of 32 mm. A stainless-steel wire with 10,000 holes per square centimeter was located under the cylinder. Viscose samples filtered through the wire were collected in a 250-mL graduated cylinder. The average of the times taken for the cylinder to fill from 25 to 50 mL and from 125 to 150 mL was defined as the reactivity. The less time that was taken, the greater was the reactivity of the dissolving pulp.

RESULTS AND DISCUSSION

Preparation of Bamboo Dissolving Pulp

The bamboo dissolving pulp was prepared with pre-hydrolysis and subsequent kraft cooking and Op-H-P bleaching. The chemical composition and characteristics of the raw material and pulp are listed in Table 1. The results showed that prehydrolysis can remove more than 65% of the pentosan from the pulp. The subsequent extraction of hemicellulose occurred primarily in the kraft cooking stage, whereas the decrease in degree of polymerization occurred in all stages, and especially in the (H) bleaching stage. The brightness gains of the pulp were substantial during the (Op) stage, during which most of the lignin was removed. As bleaching proceeded, the alpha-cellulose content increased due to the purification of the fiber. Bamboo dissolving pulp with a pentosan content of 3.42%, an α-cellulose content of 96.5%, a degree of polymerization of 502, and a brightness of 85.6% ISO was obtained from the above process.

Table 1. Chemical Composition and Characteristics of Raw Material and Pulp

	Hydrolyzed bamboo	Cooked pulp	Op-bleached pulp	H-bleached pulp	P-bleached pulp
Final yield (%)	78.70	34.86	31.53	31.08	29.06
Pentosan content (%)	6.26	5.42	4.92	4.32	3.42
Kappa Number	-	14.55	2.38	1.15	0.86
α-cellulose content (%)	-	-	-	92.0	96.5
Brightness (% ISO)	-	34.5	64.2	78.4	85.6
Degree of polymerization	-	1331	898	543	502

The Effect of Beating Post-treatment on Reactivity

Although the initial α-cellulose content of the bamboo dissolving pulp was relatively high, its initial reactivity (Table 2) was very low. To achieve high reactivity levels comparable to those of wood dissolving pulp (more than 94.5% α-cellulose content for viscose fiber) or linter dissolving pulp (more than 92% α-cellulose content for viscose fiber), bamboo dissolving pulps must be treated or activated. In the present study, the bamboo dissolving pulps were subjected to a beating post-treatment before they are made pulp board. The degree of beating and the reactivity of unbeaten bamboo dissolving pulp were analyzed as the references for the experiment. The results indicate that the reactivity of bamboo dissolving pulp increases with decreasing pulp freeness. However, the reactivity rapidly decreased when the pulp CSF decreased from 236 mL to 174 mL, likely due to rapid decreases in the degree of polymerization and in α-cellulose content. Brightness changes were only moderate.

Table 2. Change in Reactivity at Different Degrees of Beating

Revolution of PFI mill refiner	0	1500	3000	4500	6000	7500
CSF (mL)	710	600	515	340	236	174
α-cellulose content (%)	96.5	96.8	97.0	96.4	96.0	93.2
Brightness (%ISO)	85.6	86.3	85.7	86.4	86.2	85.7
Degree of polymerization	502	498	485	472	468	398
Reactivity (s)	240.9	236.7	223.5	188.2	128.0	250.0

The Effect of Beating Post-treatment on the Morphology of Pulp Fibers

Beaten bamboo dissolving pulp fiber was observed with an optical microscope (BK3300) to investigate any morphology changes. Images (Fig. 1) show brooming of the bamboo dissolving pulp, a phenomenon which became increasingly obvious as the pulp CSF decreased. More beating led to the emergence microfibrils on the surfaces of fibers, causing an increase in their total surface area.

The crystal form of cellulose Ⅰ (between 2θ values of 22 and 23°) did not change after beating (Fig. 2). The crystallinity index (70.26%) of beaten pulp (of 236 mL CSF) was slightly lower than that (71.16%) of unbeaten pulp (of 710 mL CSF). These results show that the impact of beating on the crystallinity index of bamboo dissolving pulp is small.

(a) Original sample (b) CSF 600 mL (c) CSF 515 mL

(d) CSF 340 mL (e) CSF 236 mL (f) CSF 174 mL

Fig. 1. Electron micrographs of dissolving bamboo pulp fibers of different freenesses

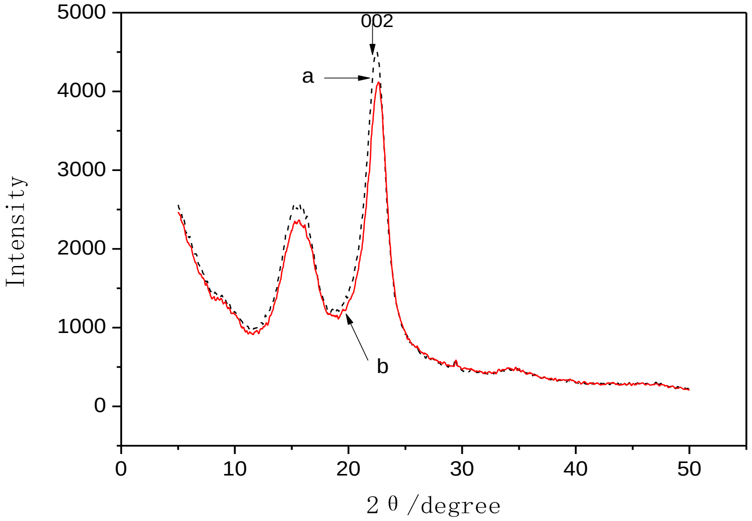

Fig. 2. X-ray diffractograms of bamboo dissolving pulps (a - CSF 710 mL, and b - CSF 236 mL)

The Effect of Beating Post-treatment on Pulp Fiber Quality

The average fiber length, fines content (defined to have size under 0.20 mm), curling index, and kink index of pulps at different freenesses were determined using a fiber quality analyzer (Optest) operating on a scale of 0 to 7.2 mm. Fiber breakage and shortening occurred due to shear forces.

The percentage of fines in the fibers increased drastically due to beating (Table 3). The average fiber width was larger, and the curling and kink indexes were lower, in the pulp with CSF 236 mL compared to those of the pulps of other freenesses. Therefore, these changes of pulp fiber quality after beating may result in the increase of reactivity of bamboo dissolving pulp.

Table 3. Change in Fiber Quality at Different Degrees of Beating

CSF (mL)	Fines content (%)	Average fiber length (mm)	Average fiber width (µm)	Curling index	Kink index
710	40.55	0.94	15.60	0.26	2.86
600	42.46	0.71	16.10	0.29	3.22
515	52.60	0.59	15.80	0.34	2.93
340	49.20	0.55	16.30	0.22	2.88
236	50.17	0.53	20.60	0.20	2.70
174	50.96	0.49	16.40	0.25	3.15

CONCLUSIONS

1. It is well-known that in a heterogeneous reaction, such as the mercerization of dissolving pulp, the degree of conversion and the reaction rate depend strongly on the availability of hydroxyl groups. The beating process helped in the brooming of the fiber surface, which can increase the number of the hydroxyl groups available. Some parameters (average fiber width and the fines content, *etc.*) in dissolving pulp also change with decreases in the pulp's CSF. This yields an increase in the accessibility of chemicals to the cellulose, thus increasing the reactivity of the dissolving pulp.

2. The improvement in reactivity yielded by post-treatment beating is important to viscose production process, as the preparation of high-quality bamboo dissolving pulp is only possible following post-treatment beating.

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