The Effects of NaOH-Urea Aqueous Solution on the Strength and Softness Properties of Bamboo Ligno-cellulosic Fibers

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APMP (alkaline peroxide mechanical pulp) of bamboo was treated in NaOH-urea aqueous solution to modify the fiber properties. The effects of soaking time, fiber concentration, alkali dosage, freezing temperature, and freezing time were evaluated by single-factor experiments. The optimal conditions were determined as a soaking time of 10 min, a fiber concentration of 15%, an alkali dosage of 6%, a freezing temperature of -7 °C, and a freezing time of 40 min. Compared with the properties of untreated APMP, the tensile index of the treated APMP was increased by 64%, and the burst index was increased by 82%. The bulk was reduced by 15%, and the softness was increased by 18%. There was no obvious variation on the folding strength. According to the instrumental analysis, there were no significant effects on the structure in terms of functional groups, the crystalline region, or the fiber surface morphology; however, the variation on the fiber quality was more significant.

Keywords: NaOH-urea aqueous solution; Ligno-cellulose fiber; Fiber property; APMP

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INTRODUCTION

To address concerns about low pulping yield and heavy pollution, the replacement of chemical pulp (CP) using chemi-mechanical pulp (CMP) has been examined in recent years (Hunt *et al*. 2004). The yield of CMP (85%) is much higher than that of chemical pulp (50%), while the pollution and the consumption of chemical reagents or energy is much lower. The use ratio of raw materials is also higher (Sundholm 1999). Therefore, the application of CMP has been widely extended.

Because the shortage of wood materials is also a global problem, some non-wood materials, especially bamboo, have been used due to their advantages of a short growing period and abundant supply (Khristova *et al*. 2006; Kenealy *et al*. 2007; Lei *et al*. 2010). The preparation of bamboo chemical pulp or chemi-mechanical pulp has attracted much recent attention. However, with high content of lignin in the fibers, the strength, softness, and toughness of paper made from CMP fibers are much lower than those of chemical pulp, which limits the applications of CMP (Berrocal *et al*. 2004).

Physical, chemical, and biological methods can be used to increase the strength potential of CMP (Hunt *et al*. 2004). A beating process with low fiber concentration (Laivins and Scallan 1996) is usually applied to modify paper strength, by increasing the fines content and fiber toughness. Strengthening agents (*e.g.*, starch, polyacrylamide) are also used, but they are lost easily during paper forming process (He 2010). Paper strength can be modified by the addition of NaOH during the CMP bleaching process in order to increase the fiber swelling degree (Zhan 2010). When pine wood chips are treated in aqueous oxalic acid solution for the preparation of thermal mechanical pulp (TMP), the strength is greater than that of untreated chips (Klungness *et al*. 2003). White-rot fungi can be used to treat chemi-thermo-mechanical pulp, leading to significant increases in the tensile and burst indices (Yang *et al*. 2008).

The beating process can also be applied to increase the paper softness made from CMP in paper-making industries. However, the effect is not obvious. The fibers of CMP are difficult to swell because of the lignin content (He 2010). Paper softness agents can be used to modify the softness of paper made from cellulose fibers (*e.g.*, bleached kraft pulp fibers, cotton fibers) (Kaunisto *et al*. 2002), but the effect on the paper made from ligno-cellulose fibers (*e.g.*, TMP, CTMP) is not obvious, for the agents are not absorbed by the fibers with a high content of lignin on the fiber surface (Dahlman *et al*. 2003). Moreover, paper strength made from cellulose fibers can decrease significantly with the addition of paper softness agents (Burrell *et al.* 2004). Therefore, new softness agents or fiber treating methods should be developed.

Regenerated cellulose or microcrystalline cellulose can be obtained using NaOH aqueous solution (Kamide *et al.* 1984; Yamashiki *et al.* 1992). Regenerated cellulose fibers can be prepared in the NaOH-urea aqueous solution (Zhang *et al.* 2001), and regenerated cellulose membranes or films can be prepared from cellulose using various coagulants (Zhou *et al.* 2002; Mao *et al.* 2006). Compared with those of NaOH aqueous solution, NaOH-urea aqueous solution has the advantages of a rapid dissolution rate and excellent product properties.

There have been few reports on the strength or softness modification of bamboo APMP with the NaOH-urea aqueous solution. Some lignin in APMP can be degraded by NaOH, thereby modifying the softness or toughness (Xu and Zhou 2005; Zhan 2010) of APMP fibers; lignin can contribute to stiffness of fibers, thereby reducing the softness or toughness. The removal of lignin might promote damage on the fiber surface so that more hydroxyl groups (-OH) could be exposed, leading to increased fiber bonding strength. The amorphous region of ligno-cellulose fiber can be swelled by NaOH, then urea could soak into the crystalline region of fibers (Jin *et al*. 2007), both of which are beneficial for increasing fiber toughness (Yang 2008). During the treatment with this solution, the fines content in the treated APMP could be increased, leading to improved bonding strength. In this work, the reaction conditions were mild (*e.g.*, low temperature and alkali dosage), so small losses in lignin, hemicellulose, or cellulose have little effect on the yield (93% under the optimal conditions). The goal of this work was to determine whether such a mild treatment increases the strength and softness of paper made from bamboo APMP.

EXPERIMENTAL

Preparation of Material and Treatment Solution

APMP board of bamboo (Chengdu, China) was soaked in water at room temperature for 4 h and defibrillated with a laboratory Hollander beater (fiber concentration of 2%). All fibers were collected and dewatered with a centrifugal hydroextractor (SS450, Mudan Centrifuge Manufacture, Suzhou, China). The moisture was balanced for 48 h, and the solid content was measured.

NaOH and urea were dissolved in deionized water at a mass ratio of 7.5:11:81.5 (NaOH: urea: H_2O) as described previously (Mao *et al.* 2006). The concentration was stabilized at room temperature for 96 h.

Experimental Procedure

APMP was added in the NaOH-urea aqueous solution, and the fiber concentration was regulated. The corresponding mixture was thoroughly mixed at room temperature and then frozen (Zhou *et al.* 2002). The treated APMP was washed and dewatered, and the moisture content was measured. The fibers were beaten to a beating degree of 30° SR, and then diluted to a concentration of 3% with hot water (90 °C) to remove the latency using electric stirring equipment at this temperature for 30 min. Paper was made at a basis weight of 60 g/m^2 for the measurement of bulk, softness, and tensile and burst indices. As a control, the processes were repeated for untreated APMP.

The untreated and treated APMP (under the optimal conditions found in this work) were freeze-dried (Heto Power Dry PL6000, Thermo Scientific, Norwood, MA, USA) for 48 h at -30 °C and an applied vacuum of -0.1 MPa.

Fiber morphology was observed using a scanning electron microscope (SEM; FEI Quanta-200, FEI, Hillsboro, OR, USA) at a magnification of 1000X. Fiber attributes were quantified with a fiber quality analysis (FQA) system (Morfi, Techpap, Grenoble, France) with a fiber consistency of 40 mg/L. The fibers were then broken apart with a fiber mill, and the powders were screened to obtain the components passing through the 100 mesh. The powders were analyzed by Fourier transform infrared (FT-IR; Nicolet 380, Nicolet, Madison, WI, USA), X-ray diffraction (XRD; Bruker D8 Advance, Karlsruhe, Germany), and elemental analysis (EA; Vario EL cube, Elementar, Langsenselbold, Germany) for the contents of C, H, O, and N elements. The scanning range of wave numbers in FT-IR was from 500 cm^{-1} to 4000 cm^{-1}. The scanning angle range of XRD was from 5° to 40°. The temperature of EA was 600 °C (O_2 atmosphere).

Some details on the experimental procedure were as shown below:

(1) Paper was made automatically with a sheet-making apparatus (RK-2A, PTI, Vorchdorf, Austria). According to the International Standard (ISO 5270-2012), to measure the physical properties of the paper with low basis weight or grammage prepared by the conventional sheet former, the paper basis weight should be controlled in the range from 58 g/m^2 to 62 g/m^2 (ISO 5270-2012). Besides, the efficiency of the applied laboratory sheet former in this work was the highest (*e.g.*, best paper evenness and moisture) when the paper grammage ranged from 50 g/m^2 to 70 g/m^2 according to our previous tests. Therefore, the basis weight was chosen to be 60 g/m^2 in this work.

(2) The moisture of the untreated and treated APMP, and the tensile or burst indices, bulk, and softness of the paper were measured by instruments according to the respective national standards (GB/T 741 (1989), GB/T 453 (1989), GB/T 454 (1989), GB/T 451.3 (1989), and GB/T 8942 (1988)).

(3) The bulk of paper could not be measured directly. According to the above-mentioned national standards, the paper thickness should be measured first, and then the bulk can be calculated as follows:

$$\text{Bulk (cm}^3\text{/g)} = T/W \quad (1)$$

where T is the paper thickness (mm), and W is the paper basis weight (60 g/m^2, a fixed value in this paper).

(4) The APMP fibers were respectively prepared according to the operating instructions before the FQA, FT-IR, XRD, EA, and SEM analyses.

(5) APMP fibers should be treated for the removal of latency to measure the paper strength accurately. However, in order to show the original fiber qualities (fiber length and width, the contents of kinked and curled fibers and fines) or the surface morphology of the untreated and treated APMP, this process was not applied before the FQA and SEM processes.

(6) The crystallinity of APMP fiber was determined by XRD analysis, and the value was calculated automatically by the instrument as shown in Eq. 2,

$$\text{Crystallinity} = CI / (AI + CI) \quad (2)$$

where AI is the absorption intensity of the amorphous region of APMP fibers, and CI is the absorption intensity of the crystalline region of APMP fibers.

RESULTS AND DISCUSSIONS

Effects of Alkali Dosage and Fiber Concentration

Table 1 shows the fiber properties at different alkali dosages (fiber concentration of 15%, soaking time of 10 min, freezing temperature of -8 °C, and freezing time of 50 min). With increased alkali dosage, the tensile and burst indices and softness were increased, and the bulk was decreased. However, when the alkali dosage was higher than 6%, the tensile and burst indices were decreased, the bulk was increased (the variation could be ignored), and there was no significant variation in softness. With high lignin content in the treated fiber, the folding strength was not affected during the treatment. The tensile index of 15.64 N·m/g, burst index of 0.98 kPa·m^2/g, bulk of 2.13 cm^3/g, and softness of 672 mN were determined as the optimal results at an alkali dosage of 6%.

Table 1. Effect of Alkali Dosage

Alkali Dosage (%)	Lignin Content (%)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Folding Strength (time)	Bulk (cm^3/g)	Softness (mN)	Beating Degree (°SR)
2	19.2	10.86	0.65	3	2.47	807	31
4	18.7	12.72	0.79	3	2.29	755	32
6	18.1	15.64	0.98	4	2.13	672	32
8	17.3	14.55	0.93	4	2.14	660	32
10	16.2	13.36	0.82	4	2.16	644	30

Table 2 shows the fiber properties at different fiber concentrations (alkali dosage of 6%, soaking time of 10 min, freezing temperature of -8 °C, and freezing time of 50 min). With increased fiber concentration, the tensile and burst indices and softness were increased, and the bulk was decreased. However, when the fiber concentration was higher than 15%, the tensile and burst indices were decreased, the bulk was increased (the variation could still be ignored), and there was also no significant variation in softness. With high lignin content in the treated fiber, the folding strength was also not affected. The tensile index of 15.69 N·m/g, burst index of 0.99 kPa·m^2/g, bulk of 2.14 cm^3/g, and softness of 682 mN were determined as the optimal results at a fiber concentration of 15%.

Table 2. Effect of Fiber Concentration

Fiber Concentration (%)	Lignin Content (%)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Folding Strength (time)	Bulk (cm^3/g)	Softness (mN)	Beating Degree (°SR)
10	18.8	12.95	0.71	3	2.27	815	32
15	18.3	15.69	0.99	4	2.14	682	30
20	17.9	15.22	0.95	4	2.15	669	30
25	17.5	14.75	0.88	4	2.17	652	31

With the increase of alkali dosage or fiber concentration, the alkali concentration in the mixture was increased. Under such conditions more lignin would be removed, more hydroxyl groups could be exposed on the fiber surface. With the decrease of lignin content, the strength of a single fiber and the fiber softness or toughness would be modified, and with more exposed –OH on the fiber surface, fiber bonding strength would be increased, both of which are helpful for the increase of paper strength. With the modified fiber softness, the paper softness was increased, and with the increased fiber bonding strength, the bulk was decreased correspondingly. Although the fiber softness and toughness could be modified, the content of lignin in treated fiber and the fiber stiffness were still much higher than those of CP, for the conditions were much milder than those in the cooking process (Zhan 2010). Therefore, there was no significant variation in folding strength.

However, with higher alkali dosage or fiber concentration, the mass ratios of C=O, -NH$_2$ (urea), Na$^+$, and OH$^-$ (NaOH) species in solution were also increased. With the increased NaOH content, the fiber swelling degree would be increased, leading to disruption of hydrogen bonding within the material. Besides, the C=O and –NH$_2$ groups of the urea would be expected to associate with the –OH groups in cellulose (Cai and Zhang 2006) and hemicellulose, leading to decreased original fiber bonding points and bonding strength. With the increase in lignin removal at higher alkali dosage or at fiber concentration, more polysaccharides are exposed and degraded more easily by NaOH, especially hemicellulose, as its reactivity is much higher than that of cellulose. The –OH content in the treated APMP fibers is decreased correspondingly, also leading to decreased fiber bonding points and bonding strength.

With the increase of alkali concentration, the fiber swelling degree and toughness was modified, and the strength of single fiber was increased. However, with high lignin content (stiffness contribution) in treated fibers, there would not be significant variation in the fiber softness. Therefore, the variation in the paper strength, bulk, and softness at higher alkali concentration was not obvious. An alkali dosage of 6% and a fiber concentration of 15% were chosen as the optimal conditions.

Effects of Soaking Time

Table 3 shows the fiber properties at different soaking times (alkali dosage of 6%, fiber concentration of 15%, freezing temperature of -8 °C, and freezing time of 45 min). With increased soaking time, the tensile and burst indices and softness were increased, and the bulk was decreased. However, when the soaking time was longer than 10 min, the tensile and burst indices were decreased, the bulk was increased (the variation could still be ignored), and there was no significant variation in softness. With high lignin content in the treated fiber, the folding strength was not affected during the treatment. The tensile index of 15.75 N·m/g, burst index of 0.96 kPa·m^2/g, bulk of 2.16 cm^3/g, and softness of 685 mN were determined as the optimal results at a soaking time of 10 min.

During the soaking process, the NaOH-urea aqueous solution is absorbed by fibers gradually. With increased soaking time, the absorption process was more efficient, which was beneficial to the freezing treatment. However, the process was balanced at the soaking time of 10 min. Then with increased soaking time, the total treating time of fibers in alkaline aqueous solution was longer, which was harmful to fiber bonding strength (similar to the effects of alkali dosage or fiber concentration). There were also no significant effects on the paper bulk or softness with longer soaking time. Thus, a soaking time of 10 min was chosen as the optimal condition in this work.

Table 3. Effect of Soaking Time

Soaking Time (min)	Lignin Content (%)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Folding Strength (time)	Bulk (cm^3/g)	Softness (mN)	Beating Degree (°SR)
5	18.9	13.64	0.77	3	2.21	722	30
10	18.2	15.75	0.96	4	2.16	685	31
15	17.8	15.58	0.93	4	2.16	676	32
20	17.6	15.36	0.89	4	2.18	663	31

Effects of Freezing Temperature

Table 4 shows the fiber properties at different freezing temperatures (alkali dosage of 6%, soaking time of 10 min, fiber concentration of 15%, and freezing time of 45 min). With decreased freezing temperature, the tensile and burst indices and softness were increased, and the bulk was decreased. However, when the freezing temperature was lower than -7 °C, the tensile and burst indices were decreased, the bulk was increased (the variation could still be ignored), and there was no significant variation in softness. With the high lignin content in the treated fiber, the folding strength was not affected. The tensile index of 15.82 N·m/g, burst index of 1.01 kPa·m^2/g, bulk of 2.15 cm^3/g, and softness of 690 mN were the optimal results at a freezing temperature of -7 °C.

As described in previous reports, when the NaOH-urea aqueous solution was used to dissolve cellulose fibers, low temperature was applied (cellulose will not be dissolved when the temperatures was higher than 0 °C in this solution), for the swelling, softening, and dissolving processes of fibers are exothermic processes, and fibers can be protected under the condition of low temperature (cellulose would not be degraded or hydrolyzed, and there is almost no variation on the degree of polymerization). Besides, urea might be decomposed or hydrolyzed at high temperature, leading to the decreased efficiency of the solution. Moreover, some of cellulose might be dissolved in NaOH-urea aqueous solution. According to the analysis mentioned above, low temperature is more suitable for the treatment of cellulose fibers in NaOH-urea aqueous solution, and the freezing process was used in this work.

APMP fibers were treated more completely with decreased freezing temperature, and the strength, softness, and bulk properties were modified effectively. However, when the freezing temperature was lower than -7 °C, the fiber bonding strength might be decreased by the solution. During the dissolving process of cellulose with NaOH-urea aqueous solution, the bonding strength was reduced by –C=O, $-NH_2$, and -OH interactions, and then it would be dissolved (Zhang *et al.* 2001; Zhou *et al.* 2002; Mao *et al.* 2006). Thus, the paper strength was decreased. There were no substantial effects on the bulk and softness properties at lower temperature. A freezing temperature of -7 °C was chosen as the optimal condition.

Table 4. Effect of Freezing Temperature

Freezing Temperature (°C)	Lignin Content (%)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Folding Strength (time)	Bulk (cm^3/g)	Softness (mN)	Beating Degree (°SR)
-3	19.1	11.43	0.58	3	2.32	855	33
-5	18.8	13.27	0.77	3	2.24	772	30
-7	18.3	15.82	1.01	4	2.15	685	32
-9	17.7	15.39	0.99	4	2.17	672	31
-11	17.2	14.65	0.94	4	2.16	659	33

Effects of Freezing Time

Table 5 shows the fiber properties at different freezing times (alkali dosage of 6%, fiber concentration of 15%, soaking time of 10 min, and freezing temperature of -7 °C). With increased freezing time, the tensile and burst indices and softness were increased, and the bulk was decreased. However, when the freezing time was longer than 40 min, the tensile and burst indices were decreased, the bulk was increased (the variation could still be ignored), and there was no significant variation in softness. With high lignin content in the treated fiber, the folding strength was not affected. The tensile index of 15.98 N·m/g, burst index of 1.02 kPa·m^2/g, bulk of 2.17 cm^3/g, and softness of 690 mN were determined as the optimal results at a freezing time of 40 min.

With short freezing times, the temperature of the mixture was relatively high. With short treating times at low temperature, it was beneficial to the modification on fiber strength, bulk, and softness. Therefore, the paper strength and softness of treated APMP were increased, and the bulk was decreased. However, the mixture temperature was lower with longer freezing times, then the total treating time was increased, and the bonding strength might be decreased by –C=O, $-NH_2$ and OH^-, leading to decreased paper strength. A freezing time of 40 min was chosen as the optimal condition.

Table 5. Effect of Freezing Time

Freezing Time (min)	Lignin Content (%)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Folding Strength (time)	Bulk (cm^3/g)	Softness (mN)	Beating Degree (°SR)
20	19.2	12.56	0.64	3	2.33	866	32
30	18.8	13.87	0.81	4	2.26	784	31
40	18.5	15.98	1.02	4	2.17	690	32
50	17.9	15.32	0.98	4	2.19	676	32
60	17.1	14.74	0.91	4	2.20	662	31

Paper Properties and Fiber Qualities Analysis

Table 6 shows the paper properties and fiber qualities of the untreated and treated APMP. Compared with those of the untreated APMP, the tensile index of the treated APMP was increased by 64%, the burst index was increased by 82% with similar beating degree, the bulk was decreased by 15%, and the softness was increased by 18%. However, there was no significant variation in the folding strength. The fiber length and the contents of kinked or curled fibers of treated APMP were lower than those of untreated APMP, and the fiber width was higher. However, these variations were not obvious. The content of fines was increased remarkably.

Table 6. Analysis of Paper Properties and Fiber Qualities

	Untreated APMP	Treated APMP
Lignin Content (%)	19.5	18.5
Beating Degree (°SR)	32	31
Tensile Index (N·m/g)	9.75	15.98
Burst Index (kPa·m^2/g)	0.56	1.02
Folding Strength (time)	5	4
Bulk (kPa·m^2/g)	2.55	2.17
Softness (mN)	841	690
Fiber Length (mm)	0.725	0.712
Fiber Width (mm)	32.7	33.9
Kinked Fibers (%)	21.8	21.2
Curled Fibers (%)	10.6	10.2
Fines (%)	25.8	33.5

With the degradation of lignin, the contents of the exposed alcoholic hydroxyl groups (*e.g.*, -CHOH, -CH_2OH, mainly supplied by cellulose and hemicellulose) on the fiber surface and the fines in the treated APMP fibers were increased compared with those in the untreated APMP, leading to the increase in fibers bonding strength and the decrease in the bulk. Besides, with the removal of lignin and the increased swelling degree, the fiber softness and toughness and the strength of single fiber were modified. Moreover, with the modification on the fiber bonding strength and single fiber strength, the paper strength was increased effectively. Some detailed explanations on these observations are shown below:

(1) The effect of fiber bonding strength on paper strength was remarkable, and the number of alcoholic hydroxyl groups on the fiber surface as well as the bonding strength of these functional groups could affect the fiber bonding strength. With other conditions being similar, the bonding strength of the functional groups will increase leading to the increase in fiber bonding strength or paper strength.

(2) During the preparation process of bleached chemical pulp (BCP), the lignin in the materials is almost completely removed by chemical agents, so the main components in BCP are cellulose and hemicellulose. However, during the preparation of APMP, the removal ratio of lignin is much lower than that of BCP, so APMP fibers are mainly comprised of lignin and polysaccharides. Besides, some cellulose and hemicellulose will also be wrapped by the lignin present on the surface of APMP fibers. Therefore, the

contents of the alcoholic hydroxyl groups on APMP fiber surface and the fiber bonding strength of APMP are much lower than those of BCP.

(3) Paper strength could also be affected obviously by the strength of single fiber. According to the previous reports (He 2010), with other conditions being similar, the stiffness of fibers will increase and the softness or toughness will reduce with the increase in lignin content, leading to the decreased single fiber strength. Thus, with higher lignin content, the single fiber strength of APMP is much lower than that of BCP.

(4) In this work, while treated under the optimal conditions, some of the lignin in APMP fibers was removed by NaOH (removal ratio of 12%), resulting in the increased exposure of alcoholic hydroxyl on the fiber surface and the effective increase in fiber bonding strength. Besides, the softness and toughness of APMP fibers could be modified with the decrease in the lignin content. On the other hand, fibers can be swelled in NaOH-urea aqueous solution, and with the increase in swelling degree, fibers could also be softened, and the softness or toughness will thereby be increased. Accordingly, with the decreased the lignin content and the increased fiber softness or toughness, the single fiber strength of APMP will be increased, and with the increase in the fiber bonding strength and single fiber strength, the paper strength of the treated APMP was higher than that of the untreated APMP.

(5) While other properties are similar, with the increase in the exposed alcoholic hydroxyl content and the fiber bonding strength, the paper's apparent density (tightness) will be increased, leading to the decreased paper bulk (the reciprocal of apparent density). Thus, the bulk of the treated APMP was lower than that of the untreated APMP.

Although the fiber softness or toughness was modified, the lignin content in treated APMP and the fiber stiffness were much higher than those of CP (Zhai and Lee 1989). Therefore, in this work, there was no major variation in the folding strength compared with that of untreated APMP under the optimal conditions.

Some lignin and hemicellulose were removed by NaOH (Liu *et al*. 2012), and with the loss of fiber components, the fiber length was decreased. NaOH swells fibers, and the fiber width was increased with increased swelling degree. However, the alkali dosage or treatment temperature were much lower than those in the cooking process, and the removal ratio or the increase of swelling degree were also much lower, thus, the variations in the fiber length or width were not very obvious. Some detailed explanations on this paragraph are shown as below:

(1) Under suitable cooking conditions (*e.g*. cooking temperature of 165 °C, cooking pressure of 0.6 MPa, alkali dosage of 20%), there was no significant variation in the fiber length of the pulp compared with that of the raw materials (*e.g*. natural grass, hardwood, and softwood). However, with the degradation or dissolving of lignin and hemicellulose, the fiber length could still decrease by a small range (low decrease ratio, could be ignored).

(2) According to previous tests by the authors, under drastic conditions in bamboo kraft cooking process (*e.g*., cooking temperature of 175 °C, pressure of 1.0 MPa, alkali dosage of 25%, sulfidity of 28%), cellulose will be hydrolyzed by NaOH much more easily, and the polymerization degree and the length of the main chain in cellulose molecule will be decreased remarkably, leading to the reduction of fiber length (The length of the untreated bamboo fiber was 0.743 mm, the length of the bamboo kraft pulp prepared under the suitable conditions was 0.722 mm, but the length of the bamboo kraft pulp fiber prepared under the drastic conditions mentioned above was 0.596 mm with high cellulose removal ratio.). Therefore, it is proposed that with a high degree of removal of lignin, in addition to reactions involving the polysaccharide components, there may be a

corresponding decrease in fiber length. Besides, fibers can be swelled in alkaline aqueous solution, and the fiber swelling degree or fiber width will be increased obviously at high alkali dosage. As is known, the reactivity of pulp fibers is higher than that of raw material fibers that have not been pulped or separated into individual fibers. Thus it can be concluded that the variations in the fiber length and width of bamboo APMP would be much more remarkable than those of bamboo materials under the above treatment conditions.

(3) In this work, bamboo APMP fibers were treated under milder conditions (low alkali dosage (6%), low temperature (-7 °C), and low treating pressure (0.1 MPa)) compared with those in the cooking process, therefore, the removal ratios of lignin (about 12%) and hemicellulose (about 16%) were also much lower, and cellulose could not be degraded. Besides, the increase in the swelling degree of fibers was not obvious at low alkali dosage. As a result, the variations in the fiber length and width were not noticeable under the optimal conditions.

Through the actions of refiners, the contents of kinked or curled fibers in APMP are usually higher than those in chemical pulp. In this work, this kind of fiber morphology was not altered by NaOH-urea aqueous solution, as it involves lower loss ratio of chemical components. Therefore, there were no noticeable variations in the contents of kinked and curled fibers in the treated APMP. Some detailed explanations are presented below:

(1) During the high yield pulp (HYP; *e.g.*, APMP, BCTMP) preparation process, the raw materials (*e.g.*, wood, bamboo) are defibrated by the action of the disks (one fixed disk and one rotatable disk) in the refiner. The friction between fibers and disks is quite high at high rotational speed (3600 rpm); therefore, the fibers will be deformed, and with the rotation action, lots of fibers might be kinked or curled. However, During the CP (*e.g.*, kraft pulp) preparation process, the materials are defibrated by the degradation and dissolution of lignin with the chemical treatment of NaOH, Na_2S, Na_2SO_3 or other agents, indicating that there are no mechanical actions in this process. Thus, the contents of the kinked or curled fibers in chemical pulp are usually much lower than those in HYP.

(2) The paper strength is decreased with the increasing contents of kinked or curled fibers, which is also one of the reasons why the paper strength of HYP is much lower than that of chemical pulp. Therefore, before the paper-making process, HYP should be soaked or stirred in hot water (*e.g.* 70 °C) at low fiber concentration (*e.g.* 4%) to decrease the contents of kinked or curled fibers as much as possible and increase the paper strength, which is called the removal of latency. During this process, fibers can be expanded and stretched fully (thermal expansion), lots of the kinked or curled fibers might become much straighter, and the contents of these fibers were decreased.

(3) Besides, according to the previous reports, the contents of the kinked and curled fibers could also be reduced under more drastic chemical treatment conditions or at higher removal ratios of lignin and hemicellulose (Zhai and Lee 1989; Yang 2008; Zhan 2010). For example, the contents of these fibers in semi-chemical pulp are much lower than those in chemi-mechanical pulp.

(4) Under the optimal conditions in this work, APMP fibers were treated in the NaOH-urea aqueous solution at low temperature (-7 °C) and high fiber concentration (15%). Under these condition, lignin or hemicellulose could not be degraded noticeably (removal ratios of 12% and 16% respectively), and there was no variation in the cellulose polymerization degree. Therefore, the variations in the contents of the kinked or curled fibers in the treated APMP were not remarkable compared with those in the untreated APMP.

The variation in the fines content was much more remarkable compared with that of the fiber qualities as mentioned above. Some lignin and hemicellulose had been degraded or dissolved by NaOH during the treatment. Therefore, with the removal of these two polymers, some fiber fragments might be generated on the surface or the outer sphere of the primary or secondary wall of fibers (Bhardwaj *et al.* 1995). As the fiber length and width of these fiber fragments were analogous to those of the ordinary fines, such fragments were named as secondary fines.

With the increase in the fines content, the fiber bonding strength or paper strength was increased with other fiber qualities being similar (Sain and Li 2002; He 2010). With larger specific surface area, fines can be easily absorbed by longer fibers and exist in the gaps; thus the bonding strength of the adjacent ordinary fibers can be modified due to the hydrogen bonding of fines (Retulainen 1992), illustrating that the increased fines content can be beneficial to the modification of the fiber strength property.

Elemental Analysis

Table 7 shows the elemental analysis of the untreated and treated APMP. There were no remarkable variations in the content of C, H, and O contents, indicating that the removal ratios of lignin, cellulose, and hemicellulose in the treatment were similar, for the contents of C, H, and O are quite different in these polymers. The degradation ratios were also much lower than those in cooking process.

However, the variation in the N content was more remarkable, indicating that the removal ratio of organic extracts in APMP fibers was higher, for most N exists in organic extracts rather than in lignin, cellulose, or hemicellulose. Organic extracts are harmful to the paper-making process. They react with chemical agents, forming “stickies” that are harmful to the preparation of paper materials (He 2010).

According to our test, the total content of lignin, cellulose, and hemicellulose in the APMP fibers used in this paper was about 96%, the content of organic extracts was about 3%, and the content of ash was about 1%. As is known, lignin, cellulose and hemicellulose are comprised of C, H, and O. Organic extracts are comprised of C, H, O, and N, and these chemical compounds can combust under the measurement condition of elemental analysis (applied to show the variation in the content of the organic chemical compounds in APMP fiber in this work). Therefore, the total percentage of C, H, O, and N in Table 7 was about 99% (96% + 3%).

The ash (mainly comprised by SiO_2 and inorganic salt) cannot combust or decompose under this condition, and the content could not be shown in elemental analysis of organic compounds. SiO_2 can react with NaOH, leading to the increased consumption of NaOH-urea aqueous solution. However, the contents of SiO_2 in bamboo material or bamboo pulp were much lower than those in wheat straw, rice straw, or the corresponding pulps. Thus, the effect was not obvious, and the APMP fibers could still be treated effectively.

The cooking characteristics of raw materials with high content of ash (non-wood raw material) is much less favorable than those with low content of ash (wood raw material), for the viscosity of black liquor is quite high and it is difficult for the black liquor to be evaporated and combusted. As the ash content in bamboo is usually much lower than that of other non-wood raw materials, the growing period of bamboo (1 year) is shorter than that of wood (at least 4 years), and the fiber properties of bamboo and hardwood are similar, lots of attention has been paid on the pulping and paper-making properties of bamboo fibers in recent years.

Table 7. Elemental Analysis

	Untreated APMP	Treated APMP
C (%)	47.22	47.43
H (%)	6.15	6.27
O (%)	44.48	44.71
N (%)	1.43	0.54

FT-IR Analysis

Figure 1 shows the FT-IR spectra of the untreated and treated APMP. In this work, FT-IR analysis revealed the variations in the structures of functional groups or the formation of derivatives during the treatment process. According to the FT-IR analysis, there was no noticeable variation in the position of absorption peaks in the spectra, indicating that the structure of functional groups were not destroyed and there were no new derivatives were generated in NaOH-urea aqueous solution.

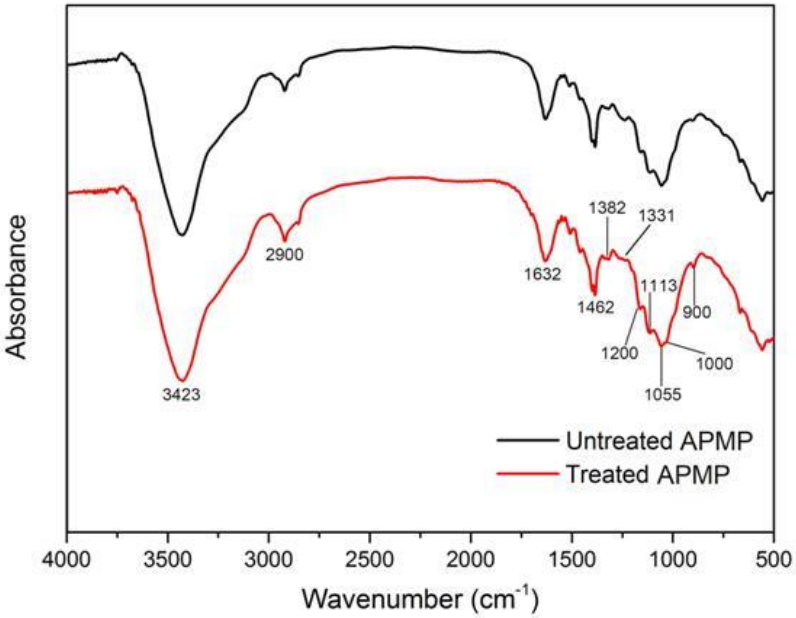

Fig. 1. FT-IR spectra of untreated and treated APMP

The peaks at the wave number of 3423 cm^{-1} and 1113 cm^{-1} indicated the stretching and associated absorptions of –OH group in cellulose and hemicellulose, respectively. The stretching, deformation, and asymmetric absorption peaks of -C-H in methylene (–CH_2) (lignin, cellulose, and hemicellulose) and methyl (–CH_3) (lignin and hemicellulose) groups were found at 2900 cm^{-1},1462 cm^{-1}, and 1382 cm^{-1}, respectively. The peak at 1331 cm^{-1} was attributed to the skeletal vibrations of C-C and C-O groups in lignin, cellulose, and hemicellulose. The overlapped vibrations of benzene ring accompanied with the stretching vibrations of -C-OH group on the side chain of benzene ring (lignin) were found at the wave bands between 1200 cm^{-1} and 1000 cm^{-1}. The stretching absorption peak of -C-C and -C-O group at C-3 (lignin, cellulose, and hemicellulose) was at the wave number of 1055

cm^{-1} (a strong signal). The peak at the wave number of 900 cm^{-1} was due to the absorption of the glucosidic bond in cellulose and hemicellulose (Sang and Dong 2005; Li *et al.* 2010).

The FT-IR results can be used to show the variation of the functional groups and the generation of cellulose derivatives (chemical reaction). During the treatment of NaOH-urea aqueous solution in this work, under drastic conditions (*e.g.* high alkali dosage, long freezing time), more –OH might be combined with –C=O or $-NH_2$, which might damage the fiber bonding strength and paper strength. However, according to the previous studies on cellulose dissolving in NaOH-urea aqueous solution, the above fiber bonding was hydrogen bonding (physical bonding, not covalent bonding), which meant that there would be no generation of new derivatives, and in the washing process, NaOH and urea could be removed and replaced by water, indicating that the physical bonding would be damaged and transferred to the hydrogen bonding between the –OH in fiber and the –OH in water (no residual treatment solution in the washed fiber). Therefore, the variations in the whole structure of the functional group in treated cellulose fibers and the FT-IR spectrum were not remarkable compared with those of the untreated fibers.

APMP fibers are mainly comprised of lignin, cellulose, and hemicelluloses. According to the previous reports on the pulping principle, some of the lignin and hemicellulose could react with NaOH at low temperature, and then these two polymers will be degraded or dissolved (much lower removal ratios than those in cooking process); however, no derivatives were generated in this process. Besides, as mentioned above, cellulose in APMP fibers could still not be derived, and the structure of the functional group would not be changed. As a result, the variation in the FT-IR spectrum of the treated APMP was not noticeable compared with that of the untreated APMP.

XRD Analysis

Figure 2 shows the XRD spectra of the untreated and treated APMP. The variation on the spectra was not obvious. The crystallinity of the treated APMP was 0.643, about 0.018 higher than that of the untreated APMP, indicating that the crystalline structure of APMP was not greatly affected by NaOH-urea aqueous solution under the optimal conditions in the present work.

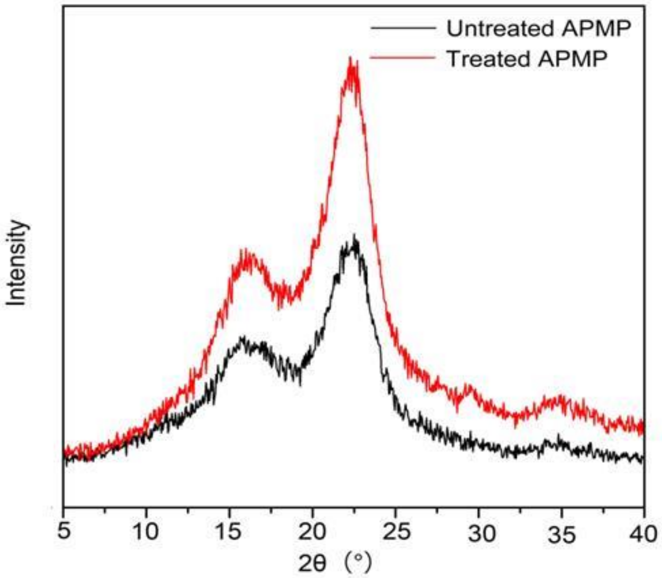

Fig. 2. XRD spectra of untreated and treated APMP

The crystallinity of the treated APMP was 0.643, about 0.018 higher than that of the untreated APMP, indicating that the crystalline structure of APMP was not greatly affected by NaOH-urea aqueous solution under the optimal conditions in the present work.

The crystalline region of cellulose fibers was affected when the alkali concentration is higher than 12.5% (Zhou *et al*. 2002; Yang 2008). In this work, the optimal alkali dosage used was 6%, and the alkali concentration was about 1% through calculation. Besides, some NaOH was consumed during the degradation of lignin and hemicellulose, and consequently the crystalline region of APMP was not affected under the optimal conditions.

During the dissolving process of cellulose fibers with NaOH-urea aqueous solution, the alkali concentration was 7.5%, and the alkali dosage was 150%. Under these conditions, fibers could be fully swelled, the swelling degree would increase remarkably, the crystalline structure of cellulose fibers would be damaged, and the XRD spectrum (applied to show the variation of the crystalline structure, not to show the variation in the structure of functional group) would be different from that of original fibers according to the previous reports.

However, in this work, NaOH-urea aqueous solution was used to treat APMP (ligno-cellulose fiber), and the contents of lignin and hemicellulose in APMP fibers were much higher than those in cellulose fibers. Besides, the alkali dosage was 6%, the alkali concentration was about 1% under the optimal conditions by our calculation, and some of the lignin or hemicellulose can be degraded by NaOH, which meant that the content of NaOH consumed in the fiber swelling process was much lower than that in the cellulose dissolving process. Therefore, the increased swelling degree of APMP fiber was much lower, and the variations in the crystalline structure or XRD spectrum were not obvious under the optimal conditions in this work.

SEM Analysis

Figure 3 shows the fiber surface morphology of the untreated and treated APMP, as investigated by SEM. Figure 3a shows the surface morphology of the untreated APMP, and Fig. 3b shows that of the treated APMP.

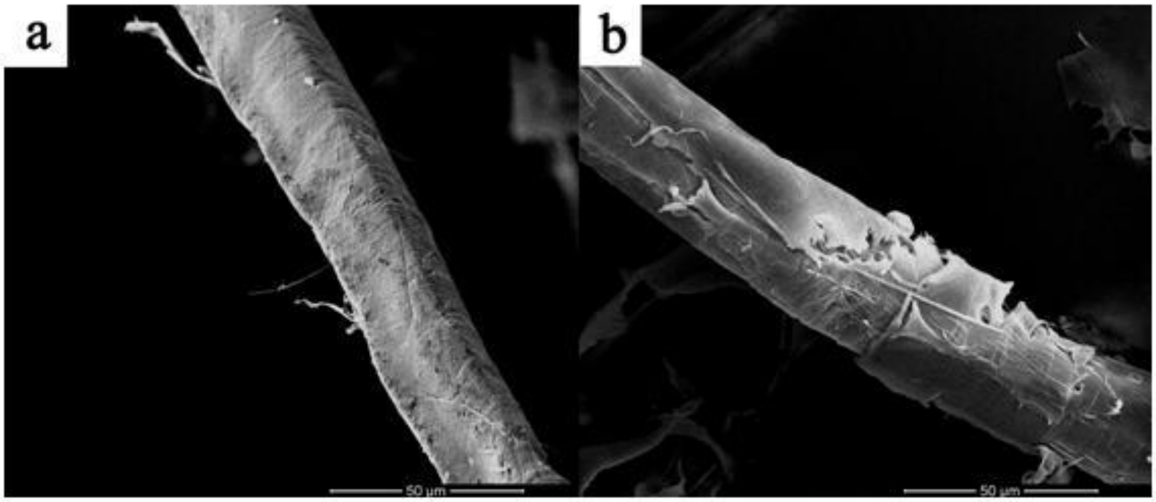

Fig. 3. SEM images of untreated and treated APMP

Compared with that of the untreated APMP, there was more damage on the fiber surface of the treated APMP, leading to increased content of –OH exposed on the fiber surface and fiber bonding strength. However, there were no obvious variations in the whole fiber structure. The fiber treatment of NaOH-urea aqueous solution was mainly on the fiber surface, and there was little effect on the interior of APMP fibers under the optimal conditions employed in this work.

Proposed Mechanism

Under the optimal conditions, the strength and softness properties of the paper made from APMP were modified by NaOH-urea aqueous solution. The following effects were observed:

(1) Lignin was degraded by NaOH. The paper strength of the fibers with high lignin content is usually lower than that with low lignin content. With the removal of lignin, the fiber stiffness was decreased, and the softness and toughness were increased, which was beneficial for the increase of single fiber strength. However, the removal ratio of lignin under the optimal conditions in this work was much lower than that in cooking process, and the stiffness of treated APMP was still much higher than that of chemical pulp. Therefore, there was no significant variation in the folding strength compared with that of untreated APMP.

(2) With lignin degradation, there was damage on the fiber surface. More –OH in cellulose and hemicellulose was exposed, which increased the fiber bonding strength (He 2010). The fines content in the treated APMP was increased. Usually, the specific surface area of fines is larger than that of longer fibers, and it is easy for the fines to be absorbed and exist in the gaps between longer fibers. The bonding strength of adjacent fibers is increased due to the hydrogen bonding of fines (Retulainen 1992).

(3) The increase in the fiber swelling degree at low alkali dosage was much lower than that at high alkali dosage. As is known, high swelling degree is harmful to hydrogen bonding strength with larger fiber distance, indicating that the fiber bonding strength would not be decreased noticeably by the increased fiber swelling degree under the optimal conditions in this work. However, fibers could still be softened by the –C=O and $–NH_2$ in urea, leading to the increased fiber softness and toughness (the main advantage and difference of NaOH-urea aqueous solution compared with that of NaOH aqueous solution as reported previously).

According to the analysis mentioned above, after the NaOH-urea treatment, both the single fiber strength and fiber bonding strength of treated APMP was increased. Because paper strength is mainly based on the factors mentioned above, the strength of the treated APMP was increased. Besides, with the modification of fiber softness and toughness properties, the paper softness was also increased. The bulk is usually decreased with the increase of fiber bonding strength or paper strength as mentioned above, therefore, the bulk of treated APMP was lower than that of untreated APMP.

With high alkali dosage, long treating time, or other drastic conditions, the paper strength was decreased, as described below using alkali dosage as an example:

(1) Lignin was degraded by NaOH, and its removal was increased by an increased alkali dosage. Thus, more hemicellulose was removed, for more hemicellulose might be exposed on fiber surface that could also be degraded by NaOH. The NaOH-urea aqueous solution was a cellulose solvent. Though in this work, cellulose in APMP fibers could not be dissolved completely, some cellulose might be removed with higher alkali dosage or concentration. The cellulose content in treated APMP was 66% under the optimal

conditions in this work, and the content was reduced to 61% when the alkali dosage was increased to 12%. The increase of cellulose and hemicellulose loss ratio greatly reduces the –OH content in fibers and fiber bonding strength (*i.e.*, the number of fiber bonding points was decreased).

(2) Cellulose and ligno-cellulose fibers can be swelled by NaOH (Na^+ and OH^-). At low alkali dosage, the fiber swelling degree was lower than that at high alkali dosage. With lower swelling degree, the fiber softness and toughness would be affected by the functional groups (C=O and $–NH_2$), which increased paper strength. However, at high alkali dosage, the fiber swelling degree will be increased remarkably, leading to more disruption of the original hydrogen bonding in the material. Besides, with higher swelling degree and urea content, more C=O and $–NH_2$ could combine with –OH in fibers, and the original fiber bonding points and bonding strength would be reduced.

CONCLUSIONS

1. The optimal conditions for treatment of bamboo alkaline peroxide mechanical pulp (APMP) were determined as an alkali dosage of 6%, a fiber concentration of 15%, a soaking time of 10 min, a freezing temperature of -7 °C, and a freezing time of 40 min.
2. Some lignin in APMP fibers was removed by NaOH-urea aqueous solution. The content of –OH functional groups exposed on fiber surface or the fines in the fibers was increased. The fiber toughness might be modified effectively with the degradation of lignin and the swelling or softening actions of the solution, leading to the increase of paper strength or softness and the decrease of bulk for APMP.
3. Under the optimal conditions determined in this work, the structure of the functional groups and the crystalline region of ligno-cellulose fibers were not altered. However, there was some damage on the fiber surface.

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