NaOH-Thiourea Aqueous Solution Treatment of Cellulose Fiber and its Effects on Bulk and Softness

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Bleached kraft pulp of hardwood was pretreated in a NaOH-thiourea aqueous solution to modify the bulk and softness of the cellulose fibers with minimal reduction in paper strength. The effects of soaking time, fiber concentration, alkali dosage, and freezing time were evaluated through single factor experiments. The optimal conditions were determined to be a soaking time of 15 min, fiber concentration of 15%, alkali dosage of 9%, and freezing time of 75 min. Under the optimal conditions, the bulk and softness of the treated cellulose fibers were increased by 28.7% and 21.6%, respectively, compared with those of untreated cellulose fibers. The tensile and burst indices were only reduced by 1.2% and 5.1%, respectively, under these conditions. Also, there were almost no effects on the polymerization degree, the thermostability, and the structure of the functional groups or crystalline regions.

Keywords: Cellulose fiber; Bulk; Softness; NaOH-thiourea aqueous solution; Jellification

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INTRODUCTION

To the best of our knowledge, strength is one of the crucial properties of paper, and it is usually controlled strictly during the preparing processes of almost all papery products. However, paper with higher bulk usually exhibits higher stiffness, ink-absorption, and opacity properties, and it could also be used as an important papery material. Therefore, it is believed that paper's bulk (the reciprocal of its apparent density) is also critical in preparing process of paper, alongside of its strength properties (Ma *et al.* 2011). Recently, more attention has been given to the bulk properties of fibers, and many methods have been applied to increase paper's bulk, such as the increase of high yield pulp (HYP) dosage, the usage of bulk-enhancing reagents, and the lowering of linear pressure during the pressing process. Among these methods, the former two have attracted growing attention.

Paper's bulk can be increased with the increase of HYP content in the paper stock during the paper-making process (Sundholm 1999; Pan 2001; Morsy and Sherbiny 2004; Andreson *et al.* 2006). Fiber bonding strength is decreased by the increase in lignin content in the fibers (He 2010), which can improve the bulk. Also, in the preparation of HYP, the efficiency of utilization of fibrous materials can be improved and the pulping pollution can be reduced substantially as compared with a chemical pulping process (Zhan 2010). However, paper strength is usually greatly reduced with the increase in HYP dosage.

Bulk-enhancing reagents can also be applied to increase paper bulk (Kang and Shen 2008; Takashi 2009). The effect of inorganic bulk-enhancing reagents is not

obvious due to their poor retention ratio in the paper-making process. Thus, organic bulk-enhancing reagents have been used to increase the bulk, and the effects were much more noticeable than those of inorganic reagents. Typically, organic bulk reagents are toxic and reduce paper strength (Liu 2007). Therefore, bulk-enhancing reagents with relatively lower toxicity and fewer negative effects on paper strength have been sought in recent years.

Though fibers can be softened by beating, the effect of beating on the softness of fibers is usually not effective. The fiber or paper softness properties can be modified effectively using paper softening reagents (*e.g*., cationic or anionic surface-active reagents). However, fiber bonding strength and paper strength are reduced by the addition of softening reagents (Kaunisto *et al*. 2002; Burrell *et al*. 2004).

According to previous studies, cellulose products can be obtained using NaOH aqueous solution (Kamide *et al*. 1984; Yamashiki *et al*. 1992). Regenerated cellulose membranes can be prepared from cellulose in a NaOH-urea aqueous solution using various coagulants (Zhou *et al*. 2002; Mao *et al*. 2006), and novel microporous membranes can be prepared from cellulose in a NaOH-thiourea aqueous solution with an ammonium sulfate aqueous solution (Ruan *et al*. 2004; Weng *et al*. 2004). Compared with NaOH aqueous solutions and NaOH-urea aqueous solutions, NaOH-thiourea aqueous solutions have the advantages of high solubility, rapid dissolution rate, and excellent product properties.

Little is known about the modification on the paper bulk or softness of bleached hardwood kraft pulp (BHKP or HKP, and it was called "HKP" for short in this paper) treated with NaOH-thiourea aqueous solution. Fiber bonding strength is decreased by alkali, thereby reducing paper strength and increasing paper bulk (Fengel and Wegener 1984; Weng *et al*. 2004; Yang 2008). Also, fibers swelling degree and the toughness or softness of the fibers can be increased by NaOH and thiourea. Moreover, some fibers in the solution are jellified with a lower alkali dosage or higher fiber concentration, thus increasing the fiber bonding strength and softness (Zhang *et al*. 2001; Zhang *et al*. 2002). The information mentioned above is beneficial for the improvement of paper bulk and softness and to compensate for the paper's strength loss (He 2010). In this study, the reaction conditions were mild (*e.g*., low temperature and alkali dosage), so there would be relatively little effect on fiber yield (about 90% under the optimal conditions). The goal of the present work was to determine whether such a mild treatment could be used to increase the paper bulk and softness of cellulose fibers with a relatively low reduction in paper strength.

EXPERIMENTAL

Preparation of Materials and Treatment Solution

Bleached kraft pulp board of hardwood (Gold East Paper Mill, Zhen Jiang, China) was soaked in water at room temperature for 4 h and then defibrillated with a laboratory Hollander beater (fiber concentration of 2%). The fibers were then collected and dewatered with a centrifugal hydroextractor (SS450, Mudan Centrifuge Manufacture, Suzhou, China). The moisture was balanced for 72 h, and the solid content was then measured.

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NaOH and thiourea were dissolved in deionized water at a mass ratio of 9.5:4.5:86 (NaOH: thiourea: H_2O) as described previously (Ruan *et al.* 2004). The solution concentration was stabilized at room temperature for 72 h.

Experimental Procedure

The HKP was added to the NaOH-thiourea aqueous solution, and the fiber concentration was regulated. The corresponding mixture was thoroughly mixed at room temperature and then frozen at -8 °C (Weng *et al.* 2004). The treated HKP was washed and dewatered, and the moisture content was measured. Finally, 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 process was repeated for untreated HKP.

The untreated and treated HKP (under the optimal conditions found in this work) were dried in a freeze dryer (Heto Power Dry PL6000, Thermo Scientific, Norwood, USA) for 48 h at a temperature of -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, USA) at a magnification of 1000X. Fiber attributes were quantified with a Fiber Quality Analysis 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 screen. The powders were then analyzed by FT-IR (Nicolet 380, Nicolet, Madison, USA), X-ray diffraction (Bruker D8 Avance XRD device, Bruker, Karlsruhe, Germany), thermogravimetric analysis (Q600, DSC-TGA, TA, New Castle, USA), and MAS ^{13}C-NMR (Avance III, 400MHz, Bruker, Karlsruhe, Germany). The scanning range of the FT-IR analysis was from 0 to 4000 cm^{-1}. The scanning angle range of the XRD was from 5° to 50°. The temperature range of the thermogravimetric analysis (TGA) spectrum was from 30 °C to 800 °C (air atmosphere).

Some details on the experimental procedure were as shown below:

(1) According to previous studies, the softening, gelling, and dissolving processes of cellulose fibers are all based on the swelling of fibers. During the swelling process in NaOH-thiourea aqueous solution, fibers could be softened gradually, and then jellified or dissolved. To our best knowledge, the swelling, gelling, and dissolving process of cellulose fibers are exothermic processes, and thiourea can be oxidized by oxygen easily at higher temperature, and the generated chemicals (*e.g.*, sulphur oxides) are toxic and harmful to the environment, especially in alkali aqueous solution. On the other hand, the original fibers bonding strength can be decreased by OH^-, C=S, or –NH, which is also beneficial to the softening of fibers, and this reaction is an exothermic process as well, and then cellulose fibers could be dissolved or jellified in this solution according to our tests. According to the analysis mentioned above, lower temperature is more suitable for the treatment of cellulose fibers with NaOH-thiourea aqueous solution, and freezing process was used in all the single factor experiments in this work (During the dissolving process of cellulose fibers in this solution, freezing treatment was also applied in the previous studies). Therefore, the treating temperature was chosen as -8 °C (Weng *et al.* 2004), and the authors had also verified the effect of temperature and determined that -8 °C was the optimal condition (This analysis is shown in Table 5).

(2) Fibers might be kinked or curled during the treatment of NaOH-thiourea aqueous solution, and the contents of kinked or curled fibers in treated HKP were higher than those in untreated HKP; therefore, the fibers of the treated HKP was stirred in an electronic blender for 30 min (rotational speed of 800rpm, fiber concentration of 3%,

temperature of 90 °C) before paper-making process to reduce the contents of kinked or curled fibers (similar to the latency removal process of high yield pulp), for the paper strength would be decreased with the increase of kinked or curled fibers contents. As a control, the stirring process mentioned above was repeated for the untreated HKP to accurately evaluate the effects of NaOH-thiourea aqueous solution.

(3) Paper was made with an automatic sheet-making apparatus (RK-2A, PTI, Vorchdorf, Austria).

(4) The moisture, tensile or burst indices, bulk and softness were measured according to GB/T 741-1989, GB/T 453-1989, GB/T 454-1989, GB/T 451.3-1989, GB/T 8942-1998 respectively (Chinese National Standard). All of the measurements of paper properties were automatic in the instruments.

(5) Bulk (cm^3/g) = T/M, where T is the thickness of the paper (g), and M is the basis weight of paper (60 g/m^2).

(6) The methods of preparation of cellulose fibers before Fiber Quality Analysis, FT-IR, XRD, TGA, NMR and SEM analysis were applied according to the instrument operating introductions, and all these instrumental analyses were also automatic.

(7) The crystallinity of cellulose fibers was directly shown in the X-ray diffraction. The crystallinity calculation of this kind of fiber sample in the XRD analysis equipment was calculated as shown below,

$$Crystallinity = I_2 / (I_1 + I_2) \tag{1}$$

where I_1 is the absorption intensity of the amorphous region of pulp, the absorption intensity at a horizontal ordinate of 15° in Fig. 2 in this paper, and I_2 is the absorption intensity of the crystalline region of pulp, the absorption intensity at a horizontal ordinate of 22.5° in Fig. 2 in this paper.

(8) The water used to dissolving NaOH and thiourea and was deionized water, and in other experiments (e.g. defibrillating, washing), the water was tap water.

RESULTS AND DISCUSSIONS

Effect of Soaking Time

Table 1 lists the paper properties at different soaking times (fiber concentration of 15%, alkali dosage of 10%, and freezing time of 90 min). The results indicated that the tensile and burst indices decreased and the bulk and softness increased with increasing soaking time. The tensile and burst indices, bulk, and softness were 21.77 N·m/g, 1.52 kPa·m²/g, 2.32 cm^3/g, and 612 mN, respectively, at a soaking time of 15 min, reaching optimal values. However, the variations in paper properties were much more noticeable with longer soaking time.

During the soaking process, the solution was absorbed gradually by the fibers. The fibers were swelled, and the bonding strength decreased. Some of the fibers were jellified by the solution, and thus the bulk and softness increased during the freezing process. With the increase in soaking time, the absorption gradually reached equilibrium. Fibers were likely damaged by NaOH-thiourea aqueous solution at longer soaking time after equilibrium, leading to noticeable variations in paper properties. Considering the paper properties, a soaking time of 15 min was chosen as the optimal soaking time.

The paper softness is usually represented by the friction force between paper and the detection probe of the detector. According to the softness instrument, the friction

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force increases with increasing hardness of the fiber or paper; the friction force decreases with increasing of softness of the fiber or paper. Therefore, in the present work, the softness of cellulose fibers increased with the decrease of the testing result.

Table 1. Effect of Soaking Time on Paper Properties

Soaking Time (min)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Bulk (cm^3/g)	Softness (mN)	Beating Degree (°SR)
5	22.08	1.67	2.07	691	15
10	21.96	1.60	2.18	645	15
15	21.77	1.52	2.32	612	16
20	20.84	1.41	2.50	569	16
25	20.12	1.25	2.69	508	17

Effect of Freezing Time

Table 2 lists the paper properties at different freezing times (fiber concentration of 15%, alkali dosage of 10%, and soaking time of 15 min). The results indicated that the tensile and burst indices decreased and the bulk and softness increased with increasing freezing time. The tensile and burst indices, bulk, and softness were 21.88 N·m/g, 1.59 kPa·m^2/g, 2.39 cm^3/g, and 608 mN, respectively, at a freezing time of 75 min, reaching optimal values. Just as with the longer soaking time, the variations in paper properties were greater with longer freezing time.

Fiber bonding strength was reduced by NaOH and thiourea during the freezing process. Also, some fibers were jellified and then removed during the washing and paper-making process, reducing the paper strength and increasing the paper bulk and softness. With shorter freezing time, the loss of paper strength could be compensated by the effect of the jellified fibers and the increase in fibers toughness, leading to minimal effects on paper strength. However, with longer freezing time, the damages to the fibers were much more noticeable than those with shorter freezing time, causing the reduction in fiber bonding strength and paper strength. Therefore, the freezing time of 75 min was chosen as the optimal condition.

Table 2. Effect of Freezing Time on Paper Properties

Freezing Time (min)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Bulk (cm^3/g)	Softness (mN)	Beating Degree (°SR)
15	22.21	1.71	1.98	765	16
30	22.13	1.69	2.04	721	17
45	22.02	1.66	2.15	680	17
60	21.96	1.64	2.23	643	16
75	21.88	1.59	2.39	608	17
90	21.17	1.40	2.56	533	18
105	20.26	1.12	2.77	449	17

Effect of Fiber Concentration and Alkali Dosage

Table 3 lists the paper properties at different fiber concentrations (alkali dosage of 10%, soaking time of 15 min, and freezing time of 75 min), and Table 4 lists the paper properties at different alkali dosages ((oven-dried weight mass ratio of NaOH and HKP fibers, fiber concentration of 15%, soaking time of 15 min, and freezing time of 75 min).

The results indicated that the tensile and burst indices decreased and the bulk and softness increased with the increase in fiber concentration and alkali dosage. In Table 3, the optimal tensile and burst indices, bulk, and softness were determined as 21.75 N·m/g, 1.63 kPa·m^2/g, 2.39 cm^3/g, and 615 mN, respectively, at a fiber concentration of 15%. The optimal tensile and burst indices, bulk, and softness were 21.98 N·m/g, 1.67 kPa·m^2/g, 2.34 cm^3/g, and 624 mN, respectively, at an alkali dosage of 9% (Table 4). However, the variations in paper properties for the tested conditions were much more obvious with the higher fiber concentration and alkali dosage.

The NaOH-thiourea aqueous solution concentration increased with increasing fiber concentration or alkali dosage. At the higher NaOH-thiourea aqueous solution concentration, the solution was absorbed by the fibers more effectively and the treatment in the freezing process was more efficient (*e.g.*, the swelling of fibers, the reduction in fiber bonding strength, the improvement of fiber toughness, and the jellification of cellulose fibers). However, at the high fiber concentration or alkali dosage, the fibers were likely damaged by the NaOH-thiourea aqueous solution, thus reducing the fiber bonding strength and paper strength. Therefore, a fiber concentration of 15% and an alkali dosage of 9% were determined as the optimal conditions.

According to the tests, cellulose fibers were swelled in NaOH-thiourea aqueous solution, and the swelling degree, softness, or toughness of fibers increased. With lower swelling degree, fiber toughness increased with increasing fiber softness, and bonding strength was modified at the same time (without the loss of fiber). However, with higher swelling degree, fiber toughness or bonding strength decreased with increased softness.

These results showed that fiber softness increased with increasing swelling degree or treatment time. Fiber toughness increased at lower swelling degree or shorter treatment time and decreased at higher swelling degree or longer treatment time. The goal of this work is to modify the bulk and softness of fiber with lower effects on fiber bonding strength or paper strength; therefore, the most suitable fiber softness should be found during the treatment.

Table 3. Effect of Fiber Concentration on Paper Properties

Fiber Concentration (%)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Bulk (cm^3/g)	Softness (mN)	Beating Degree (°SR)
10	22.02	1.72	2.18	702	16
15	21.75	1.63	2.39	615	18
20	21.14	1.44	2.65	511	18
25	20.26	1.17	2.84	405	18

Table 4. Effect of Alkali Dosage on Paper Properties

Alkali Dosage (%)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Bulk (cm^3/g)	Softness (mN)	Beating Degree (°SR)
3	22.21	1.74	2.18	718	15
6	22.10	1.71	2.24	669	16
9	21.98	1.67	2.34	624	16
12	20.62	1.51	2.52	530	18
15	18.75	1.24	2.74	422	17
18	16.24	0.88	3.03	306	18

The term "fiber damage" refers to a noticeable reduction in fiber bonding strength and paper strength under drastic conditions. Some detailed explanations include:

(1) Reduction of fiber bonding strength in NaOH-thiourea aqueous solution. Cellulose fibers were swelled by the alkali (NaOH, OH$^-$). The internal cohesion of fibers decreased during the swelling process, and the XRD spectrum changed when the alkali concentration was higher than 12.5%, indicating that the crystalline region was affected (Fengel and Wegener 1984; Yang 2008). Bonding in the amorphous region of cotton fibers can be reduced by NaOH, and the bonding in the crystal region might be decreased by thiourea (C=S, -NH) under a high alkali dosage or concentration (Jin *et al*. 2007).

(2) Jellification reaction of the cellulose fibers in the NaOH-thiourea aqueous solution. Cellulose can be dissolved by the solution, which has been used for dissolving cotton fibers to prepare cellulose materials (Ruan *et al*. 2004; Weng *et al*. 2004). Under the drastic conditions (*e.g*., high alkali dosage or fiber concentration) in this work, though the cellulose fibers were not dissolved by the solution, the ratio of jellified fibers was much higher than under the optimal conditions, leading to the increase in fiber loss ratio during washing and the paper-making process and thus the reduction in fiber bonding strength and paper strength.

Effect Verification of Treatment Temperature

The temperature (-8 °C) was applied in the cellulose dissolving process with NaOH-thiourea aqueous solution, and the selected temperature was the most suitable for the mass ratio of the solution (9.5:4.5:86) according to previous studies. Therefore, the values of these two factors were directly used for the bulk and softness modification of cellulose fibers in this paper. In order to verify the conclusion, the effects of temperature on the properties of fibers or paper were measured under the optimal conditions in this work, and the results were shown as below.

The ratio of jellified cellulose fibers was lower at higher temperature; therefore, the fibers bonding strength or paper strength could not be compensated effectively, and the strength was increased and the bulk or softness was reduced with the decrease of temperature. However, if the temperature was lower than -8 °C, the ratio of gelled fibers would be increased significantly, and the loss ratio of fibers would be increased during the washing process, leading to the significant decrease of the paper strength. According to these analysis, -8 °C was determined as the optimal temperature for the treatment (consistent with the results in previous reports).

Table 5. Effect Verification of Temperature on Paper Properties

Temperature (°C)	Tensile Index (N·m/g)	Burst Index (kPa·m^2/g)	Bulk (cm^3/g)	Softness (mN)	Beating Degree (°SR)
0	16.32	1.44	2.57	465	15
-2	17.13	1.49	2.51	521	16
-4	18.32	1.53	2.46	576	16
-6	19.96	1.58	2.41	603	15
-8	21.98	1.67	2.34	624	16
-10	19.25	1.51	2.48	542	17
-12	17.76	1.29	2.71	433	16

Analysis of Paper Properties and Fiber Qualities

Table 6 lists the paper properties and fiber qualities of the untreated and treated HKP. Compared with the paper properties of the untreated HKP, the tensile and burst indices of the treated HKP decreased by 1.2% and 5.1%, respectively, and the bulk and softness increased by 28.7% and 21.6%, respectively. The fiber length or the polymerization degree of the treated HKP was lower and the fiber width was higher compared with those of the untreated HKP. Also, the content of fines in the treated HKP was lower than that in the untreated HKP.

As fiber bonding strength was reduced by the NaOH-thiourea aqueous solution, the paper strength of the treated HKP decreased and the bulk increased. Also, the fibers were swelled and jellified by the solution, thus decreasing the fiber length and polymerization degree and increasing the width. However, the variations in fiber length, width, and polymerization degree were not obvious, for the cellulose was not noticeably degraded, hydrolyzed, or swelled under the optimal conditions.

During the treatment with alkali aqueous solution, the fines content increased due to the fiber fragments being peeled from the fiber surface by the solution. Usually, these types of fragments are called secondary fines that come from the outer layer of the primary fiber wall or the secondary fiber wall under suitable treatment conditions (Sain and Li 2002; He 2010). This action of alkali aqueous solution is similar to that of the beating process. However, because the specific surface and reaction activity of fines are much higher than those of longer fibers and NaOH-thiourea aqueous solution is a cellulose solvent, the fines were jellified or dissolved much more easily and removed during the treatment, leading to lower fines content in the treated HKP.

The contents of kinked fibers and curled fibers in the treated HKP were higher than those in the untreated HKP. This is due to the fact that the cellulose fibers were jellified in the NaOH-thiourea aqueous solution during the treatment, changing the surface morphology of the fibers. With the variation in fiber morphology, the softness of the fiber or paper increased, and detailed explanations are provided in the SEM analysis.

Table 6. Analysis of Paper Properties and Fiber Qualities

Property	Untreated HKP	Treated HKP
Beating Degree (°SR)	15	16
Tensile Index (N·m/g)	22.25	21.98
Burst Index (kPa·m^2/g)	1.76	1.67
Bulk (cm^3/g)	1.82	2.34
Softness (mN)	796	624
Degree of Polymerization	977	965
Fiber Length (mm)	0.976	0.964
Fiber Width (μm)	18.2	18.7
Kinked Fibers (%)	18.4	24.8
Curled Fibers (%)	7.5	10.2
Fines (%)	25.2	21.8

FT-IR Analysis

Figure 1 shows the FT-IR spectra of the untreated and treated HKP. The peaks were assigned from published data (Schmidt *et al*. 2002; Li *et al*. 2010). Both the untreated and treated fibers exhibited similar spectra, suggesting that the structure of the functional groups in the HKP were not greatly altered by the solution. Additionally, there was no evidence of cellulose derivatives generated under the optimal conditions.

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The absorption at 3423 cm^{-1} indicates the stretching of OH groups, and the peak at 2900 cm^{-1} is attributed to C-H stretching from the CH$_2$ groups in the cellulose. The peak at 1330 cm^{-1} is attributed to C-C and C-O skeletal vibrations. The bands between 1200 and 1000 cm^{-1} are dominated by ring vibrations overlapped with stretching vibrations of C-OH side groups. The peak at 1100 cm^{-1} is indicative of associated OH groups of cellulose. A strong signal at 1055 cm^{-1} is indicative of C-O and C-C stretching.
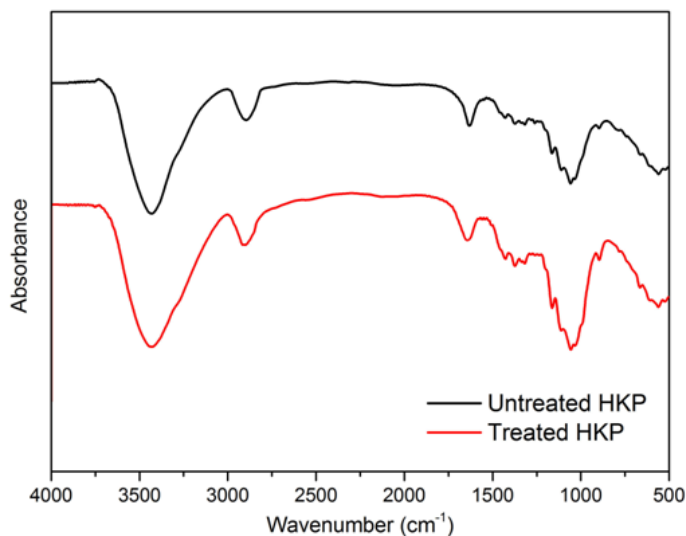
Fig. 1. FT-IR spectra of the untreated and treated HKP

XRD Analysis

Figure 2 shows the XRD spectra of the untreated and treated HKP. No major variation between the two spectra was observed. Through the automatic calculation of XRD instrument, the crystallinity of the treated HKP was found to be 0.64, about 0.04 lower than that of the untreated HKP. This indicated that the structure of the crystalline region was not altered substantially by the NaOH-thiourea aqueous solution under the optimal conditions.
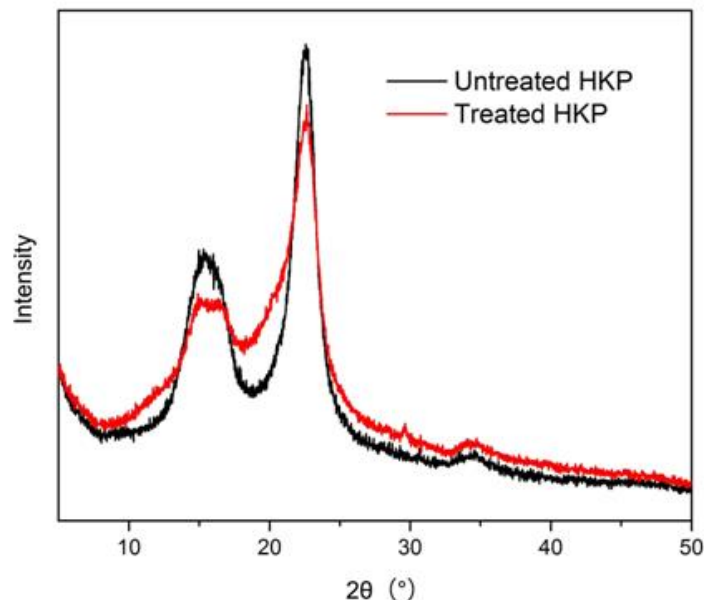
Fig. 2. XRD spectra of the untreated and treated HKP

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When the solution was used to dissolve cellulose, the alkali concentration was 9.5%, and the alkali dosage was 190% (oven-dried weight mass ratio of NaOH and cotton linter). Under these conditions, the crystalline region structure of the cellulose fibers was affected (Ruan *et al.* 2004 and Weng *et al.* 2004). However, the alkali concentration under the optimal conditions was about 3.2%, and the alkali dosage was 9%. Thus, the crystalline structure of the cellulose fiber was not affected by the NaOH-thiourea aqueous solution at a lower alkali dosage or concentration.

TGA Analysis

As shown in Figure 3, there was nearly no variation between the mass ratios of the untreated HKP and treated HKP. When the temperature increased from 30 °C to 250 °C, the weight decreased by 8% due to the loss of moisture. Thereafter, a large amount of the fiber was burnt as the temperature increased from 250 °C to 420 °C. There was a 90% loss in weight due to the formation of carbon dioxide and water vapor. The fibers were likely already completely combusted by 420 °C, and there was little variation in the mass ratio of the fibers as the temperature increased further. After the fiber combustion, only the incombustible and other stable components (*e.g*., the ash in the wood material or the salts generated in the pulping or bleaching processes) were left for TGA analysis. The results of the TGA analysis are in accordance with those of the XRD, considering that the thermostability of the cellulose fibers can be changed with the variation of the structure in the crystalline region.
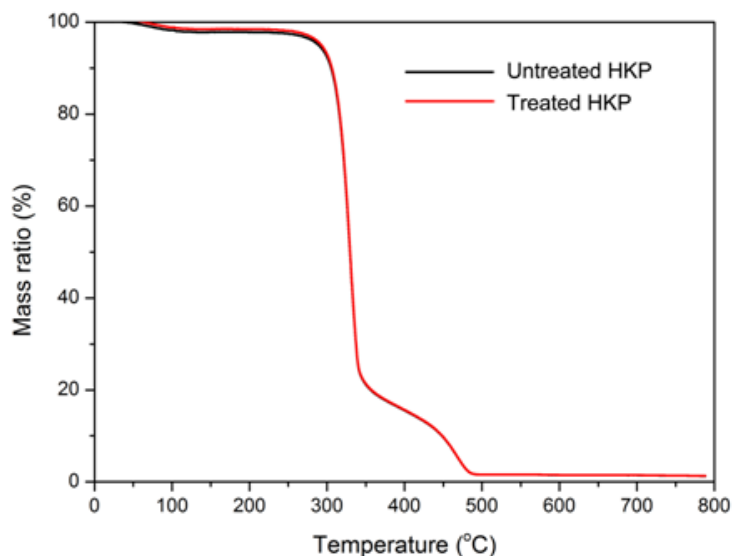

Fig. 3. TGA spectra of the untreated and treated HKP

MAS ^{13}C-NMR Analysis

Results of the NMR analysis are shown in Fig. 4. According to the previous reports (Jin *et al*, 2007), the absorption peak of C-1 (the aldehyde group in the monomer of cellulose molecule) is at the chemical shift of 105 ppm, and the absorption peaks of C-6 and C-4 are at the chemical shifts of 65 ppm and 90 ppm, respectively. The absorption peaks of C-2, C-3, C-5 are in the chemical shift from 72-78 ppm, for the chemical shifts of them are quite similar, and the peak width of MAS NMR is larger than that of liquid NMR, leading to the incomplete separation of the absorption peak.

From this analysis, it could be known that the NaOH-thiourea aqueous solution was not a derivatizing treatment reagent of cellulose fibers, indicating that there was no cellulose derivative generated or the variation on the crystal form during the treatment, which is in accordance with those of the analysis of FT-IR, XRD, and TGA.
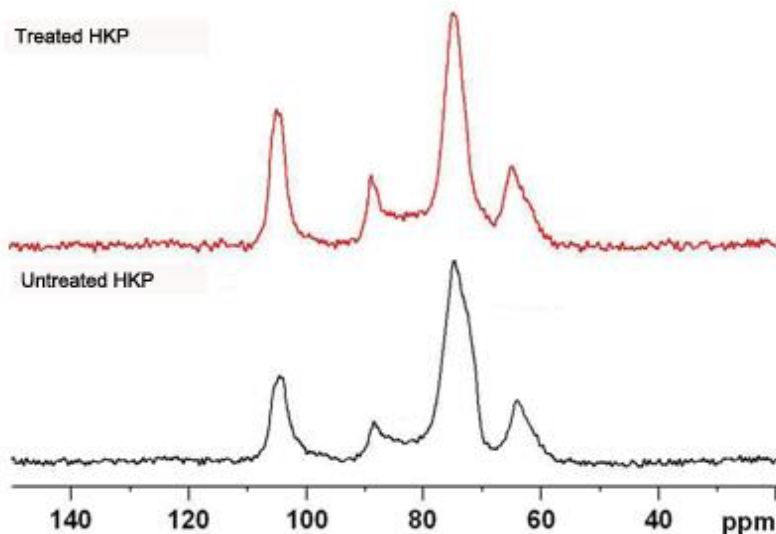

Fig. 4. MAS ^{13}C-NMR spectra of the untreated and treated HKP

SEM Analysis

The fiber surface morphology of fasciculus is shown in Fig. 5 (observed with SEM). Some of the fibers of the treated HKP were kinked, curled, or twined, and possible explanations for this are proposed below. Under the optimal conditions, the cellulose fibers could not be dissolved by the NaOH-thiourea aqueous solution. Some cellulose fibers, however, could be jellified in this solution. Gelled materials are known to have absorption properties. In this case, the gelled fibers could absorb onto the surfaces of the original fibers or other jellified fibers during treatment. This would cause the morphology of the treated cellulose fibers to drastically change compared with the untreated cellulose fibers, due to the different jellification or absorption positions of the single fiber.
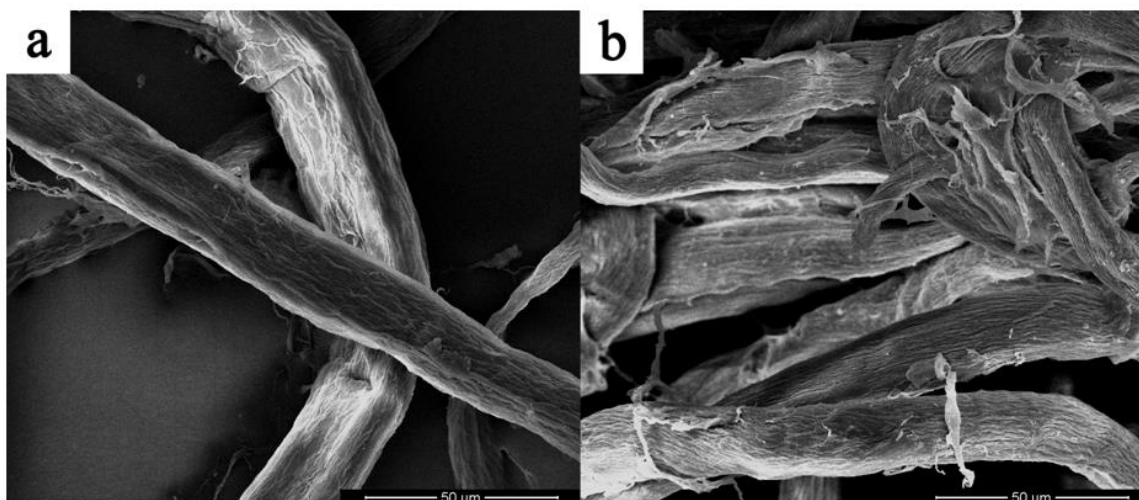

Fig. 5. SEM images of a) untreated HKP at 1000x and b) treated HKP at 1000x

The fiber morphology of the treated HKP was similar to that of mercerized fiber, which has much higher bulk and softness properties than the original cellulose fibers (Dahlman *et al.* 2003; Duarte *et al.* 2010). Therefore, the bulk and softness of the treated HKP were much higher than those of the untreated HKP, and the treated HKP could be used to prepare the cellulose-based paper materials with high bulk or softness properties and excellent strength properties.

The surface morphology of single fibers is shown in Fig. 6. After the treatment of NaOH-thiourea aqueous solution, some fibers of the treated HKP were kinked, curled, or twined, so it was quite difficult to obtain the surface morphology of the single fiber for the treated HKP. In order to solve this problem, the fiber refiner of high concentration was used to defibrillate the treated HKP, and the defibrillated fibers were then frozen in liquid nitrogen and dried in freezing dryer for SEM analysis.

There was no significant variation on the fiber structure of the treated HKP compared with that of the untreated HKP, however, there was some damage on the fiber surface of the treated HKP. Hemicellulose might be degraded or dissolved by NaOH, and cellulose might be jellified in this solution, therefore, some of the fiber components (hemicellulose and cellulose) in HKP would be removed during the treatment process, and the fiber surface would be damaged. However, the treatment yield (90% under optimal conditions in this work) was much higher than that of cooking or pulping process (usually less than 50%), indicating that the loss ratio of fiber components was much lower during the treatment, therefore, the variation on the fiber structure was not significant and the damages on the fiber surface were also not obvious.
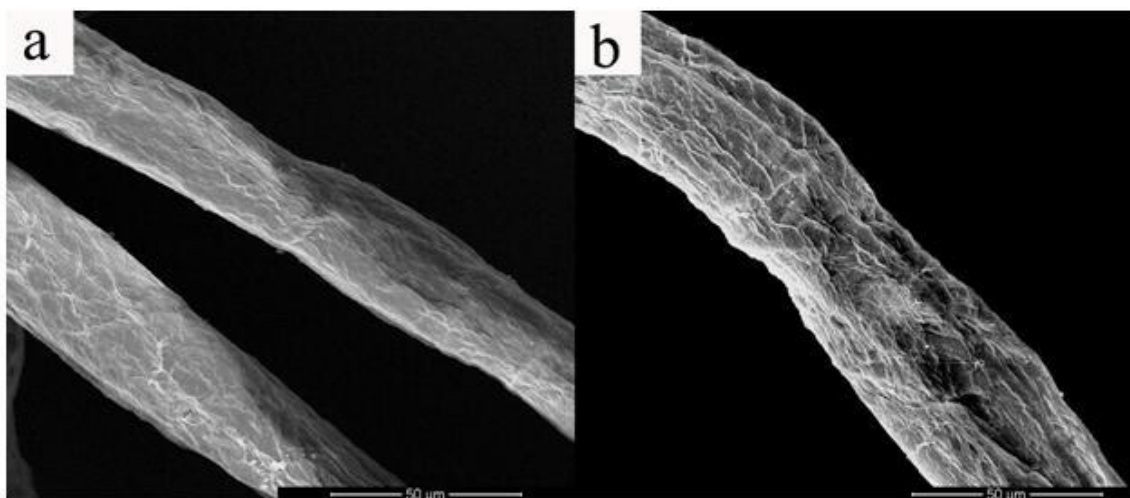

Fig. 6. SEM images of a) fibers of untreated HKP at 1200x and b) fibers of treated HKP at 1200x

The surface morphology of paper surface morphology is shown in Fig. 7. There was no variation on the surface morphology of the paper made from untreated and treated HKP. Fibers were defibrillated before paper-making process. Then the cumulus fibers could transform to single fiber during the defibrillating process, (defibrillating is also essential in paper-making industry), and finally the single fiber will be cross-linked again during forming process. With similar surface morphology of single fiber, the variation on the paper surface morphology was not obvious.
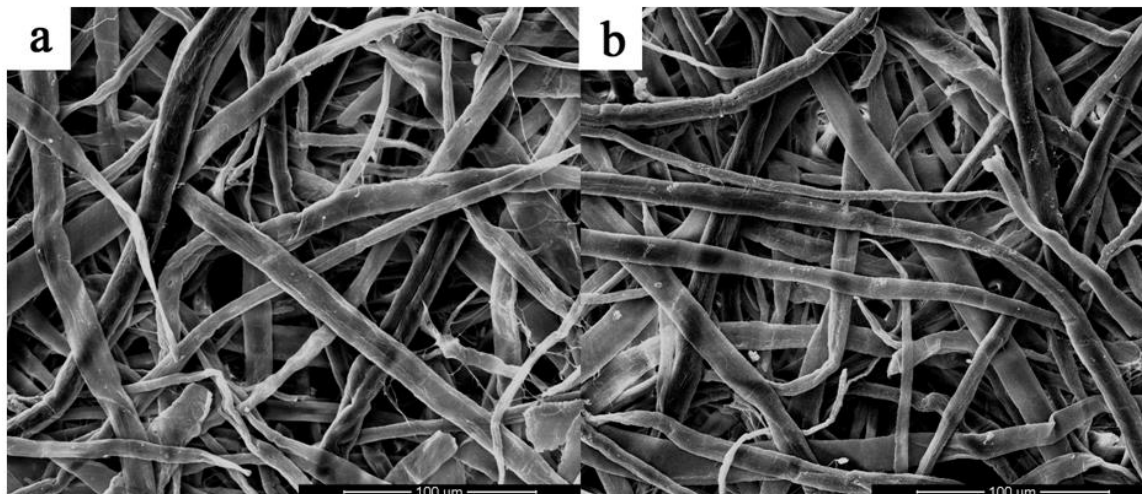
Fig. 7. SEM images of a) paper of untreated HKP at 500x and b) paper of treated HKP at 500x

The surface morphology of paper cross-section is shown in Fig. 8. It could be observed that the gap between the fiber layers of the paper made from the treated HKP was much more significant than that made from the untreated HKP with the decrease on the number of fibers bonding points in the treatment, leading to the obvious variation on the bulk property.
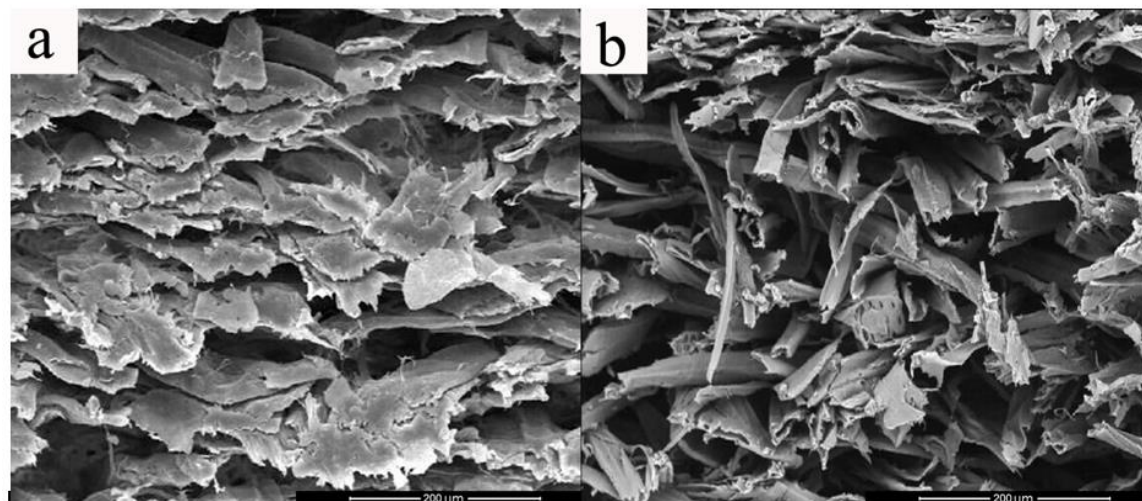

Fig. 8. SEM images of a) paper of untreated HKP at 400x and b) paper of treated HKP at 400x

Proposed Mechanism

The main theory and hypothesis of this paper was shown as below:

(1) The NaOH-thiourea aqueous solution was used to dissolve cellulose to prepare cellulose materials (e.g. cellulose membrane, regenerated cellulose, cellulose silk) in previous studies. The authors measured the paper properties of the regenerated cellulose fibers, and found that compared with those of the untreated HKP, the treated HKP exhibited higher bulk or softness and lower strength. During the dissolving process, the fibers bonding strength might be decreased significantly by the solution, and cellulose fibers could be thereby dissolved in this solution under drastic conditions (high alkali concentration or dosage). According to the results mentioned above, the authors

discussed whether there could be less effect on paper strength of treated cellulose fibers with mild conditions when the bulk and softness were still modified reasonably. By evaluating the effects of fiber concentration, alkali dosage, soaking time and freezing time on the properties of cellulose fibers (bleached kraft pulp), the feasibility of our assumption was explored in this work, and it was found that the bulk and softness properties of cellulose fibers could be increased effectively without significant effect on strength properties.

(2) During the dissolving process, the main action of NaOH was swelling the amorphous region of cellulose fibers and reducing the bonding strength in this region, and the main action of thiourea was soaking into the amorphous and crystal region and reducing the bonding strength of cellulose fibers. With the reduction of bonding strength, cellulose could be dissolved finally. In this paper, the main actions of NaOH and thiourea were similar to those mentioned above. However, according to our tests, under the optimal conditions, cellulose fibers could not be dissolved in the solution and they could only be jellified with high fiber concentration and low alkali concentration or dosage.

The proposed mechanism of the modification on the bulk and softness of cellulose fibers in this paper is described below:

(1) Fiber bonding strength was decreased by the solution. The C=S, -NH (thiourea), and OH$^-$ (NaOH) combined with the cellulose macromolecule and reduced the original hydrogen bonding strength of the cellulose fiber (Cai and Zhang 2006). Additionally, some of the fibers were transformed into jellified fibers, especially the original fines in the untreated HKP fibers, which were likely removed during the washing and paper-making process, thus reducing the number of fiber bonding points and the fiber bonding strength. All of the variations mentioned above decreased the paper strength and increased the paper bulk.

(2) During the treatment, the cellulose fibers were swelled by the solution, which increased the softness of the fibers. With the variation in surface morphology of the fibers, some of the fibers were kinked, curled, or twined. The morphology of the treated cellulose fibers was quite similar to that of mercerized fibers. Therefore, the softness of the treated HKP was also much higher than that of the untreated HKP.

(3) Under the optimal conditions found in this work, the swelling degree of the cellulose fibers and the concentration of the NaOH-thiourea aqueous solution were much lower than those under the drastic conditions (*e.g.*, high fiber concentration and alkali dosage). The loss ratio of the jellified fibers was also much lower than that under the drastic conditions, leading to the smaller effect on paper strength. As described previously (Zhang *et al.* 2001, 2002), the jellified fibers were beneficial for the fiber bonding strength (*e.g.*, the cellulose membrane strength made from the jellified cellulose fibers was much higher than that of the paper made from the original cellulose fibers). Thus, the fiber bonding strength was increased by the jellified fibers being absorbed by the original cellulose fibers. Some of the jellified fibers were removed during the washing and paper-making process, leading to a decrease in the number of fiber bonding points and paper strength. In contrast, some jellified fibers were likely absorbed by the original cellulose fibers and remained in the washed fibers and paper, leading to the increase in fiber bonding strength. The fiber strengthening effect of the jellified fibers is similar to that of fines. Although the number of fiber bonding points decreased, the bonding strength of the residual bonding points that remained from the jellified fibers increased, and the fiber bonding strength and paper strength of the treated cellulose fibers were compensated effectively. Therefore, under the optimal conditions, the bulk of the

cellulose fibers was modified, and there was no downside effect on fiber bonding strength or paper strength.

(4) However, at a higher solution concentration (high fiber concentration and alkali dosage), the concentrations of C=S, -NH, and OH⁻ were higher than those under the optimal conditions, which caused the original hydrogen bonding in the cellulose fibers to be decreased. Also, with the increase in solution concentration, the reaction activity of the cellulose fibers (Zhan 2010) was greatly increased during the swelling process (Sang and Dong 2005; Jin *et al.* 2007), and more cellulose fibers were jellified, which caused the loss ratio of the cellulose fibers to be increased during the washing and paper-making processes, and the number of fiber bonding points was decreased. The treatment yield under the optimal conditions was 90%. However, the yield decreased to 82% when the alkali dosage was increased to 12%, and the yield decreased further to 70% with an alkali dosage of 15%. Therefore, the fiber bonding strength and paper strength decreased much more noticeably with all the variations mentioned above, and paper bulk increased with the decrease in fiber bonding strength.

(5) With longer soaking time or freezing time, the treatment time of the cellulose fiber in the NaOH-thiourea aqueous solution was increased. According to previous studies (Zhang *et al.* 2001, 2002; Yang 2008), fibers bonding strength decreased with long treatment time in an alkaline aqueous solution, thus decreasing the paper strength of the treated cellulose fiber and increasing the bulk and softness.

CONCLUSIONS

1. In this work, the optimal conditions were determined to be a soaking time of 15 min, fiber concentration of 15%, alkali dosage of 9%, and freezing time of 75 min.

2. The cellulose fibers were swelled or jellified by the NaOH-thiourea aqueous solution. The fiber bonding strength and paper strength decreased, and the surface morphology of the fibers was greatly changed. Therefore, the paper bulk and softness were improved effectively, and the paper strength decreased. However, the loss of paper strength was compensated by the jellified fibers generated during the treatment under the optimal conditions in this work.

3. Under the optimal conditions determined in this work, the thermostability and the structure of the functional groups and the crystalline region of the cellulose fibers were not altered. The fiber surface and the paper cross-section morphology, however, were affected significantly.

4. During the treatment of NaOH-thiourea aqueous solution, the bulk of cellulose fibers or paper could be increased without significant effect on the fibers bonding strength or paper strength, as shown in this paper, and there were no toxic chemical reagents used or generated during the treatment of this solution, compared with those of the methods usually used to increase the bulk of fibers or paper.

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REFERENCES CITED

Andresen, M., Johansson, L., Tanem, B. S., and Stenius, P. (2006). "Properties and characterization of hydrophobized microfibrillated cellulose," *Cellulose* 13(6), 665-677. DOI: 10.1007/s10570-006-9072-1

Burrell, M. C., Butts, Matthew. D., Derr, D., Genovese, S., and Perry, R. J. (2004). "Angle-dependent XPS study of functional group orientation for aminosilicone polymers adsorbed onto cellulose surfaces," *Applied Surface Science* 227(1-4), 1-6. DOI: 10.1016/j.apsusc.2003.11.053

Cai, J., and Zhang, L. N. (2006). "Unique gelation behavior of cellulose in NaOH/urea aqueous solution," *Biomacromolecules* 7(1), 183-189. DOI: 10.1021/bm0505585

Dahlman, O., Jacobs, A., and Sjöberg, J. (2003). "Molecular properties of hemicelluloses located in the surface and inner layers of hardwood and softwood pulps," *Cellulose* 10(4), 325-334.

Duarte, G. V., Ramarao, B. V., and Amidon, T. E. (2010). "Polymer induced flocculation and separation of particulates from extracts of lignocellulosic materials," *Bioresource Technology* 101(22), 8526-8534

Fengel, D., and Wegener, G. (1984). *Wood Chemistry Ultrastructure Reactions*, Walter de Gruyter, Berlin, Germany.

He, B. H. (2010). *Paper-making Principles and Engineering*, China Light Industry Press, Beijing, China.

Jin, H. J., Zha, C. X., and Gu, L. X. (2007). "Direct dissolution of cellulose in NaOH/thiourea/urea aqueous solution," *Carbohydrate Research* 342(6), 851-858. DOI: 10.1016/j.carres.2006.12.023

Kamide, K., Okjima, K., Matsui, T., and Kowsak, K. (1984). "Study on the solubility of cellulose in aqueous alkali solution by deuteration IR and ^{13}C- NMR," *Polymer Journal* 16(12), 857- 866. DOI: 10.1295/polymj.16.857

Kang, Y. F., and Shen, Y. D. (2008). "Advances in research of stiffness agent for paper and paper board," *China Pulp & Paper Industry* 29(9), 58-61.

Kaunisto, M., Watson, H., and Rosenholm, J. B. (2002). "Adsorption of γ-UPS silane onto E-glass fibers from aqueous solutions," *Journal of Adhesion Science and Technology* 16(1), 59-80. DOI: 10.1163/15685610252771167

Li, M. F., Fan, Y. M., Xu, F., Sun, R. C., and Zhang, X. L. (2010). "Cold sodium hydroxide/urea based pretreatment of bamboo for bioethanol production: Characterization of the cellulose rich fraction," *Industrial Crops and Products* 32(3), 551-559. DOI: 10.1016/j.indcrop.2010.07.004

Liu, W. (2007). "The characteristic and application of bulking agents," *World Pulp and Paper* 26(6), 44-47.

Ma, L. (2011). "The improvement of bulk of paper and the influence on paper's printability," *East China Pulp & Paper Industry* 42(1), 31-35.

Mao, Y., Zhou, J. P., Cai, J., and Zhang, L. N. (2006). "Effects of coagulants on porous

structure of membranes prepared from cellulose in NaOH/urea aqueous solution," *Journal of Membrane Science* 279(1-2), 246-255. DOI: 10.1016/j.memsci.2005.07.048

Morsy, F. A., and Sherbiny, S. E. (2004). "Mechanical properties of coated paper: Influence of coating properties and pigment blends," *Journal of Materials Science* 39(24), 7327-7332. DOI: 10.1023/B:JMSC.0000048747.93113.6d

Pan, G. X. (2001). "An insight into the behavior of aspen CTMP in peroxide bleaching," *Pulp and Paper Canada* 102(11), 41-45.

Ruan, D., Zhang, L. N., Mao, Y., Zeng, M., and Li, X. B. (2004). "Microporous membranes prepared from cellulose in NaOH/thiourea aqueous solution," *Journal of Membrane Science* 241(2), 265-274. DOI: 10.1016/j.memsci.2004.05.019

Sain, M., and Li, H. J. (2002). "Enhancement of strength properties of mechanical pulp," *J. Wood Chemistry and Technology* 22(4), 187-197. DOI: 10.1081/WCT-120016257

Sang, Y. O., and Dong, I. Y. (2005). "FT-IR analysis of cellulose treated with sodium hydroxide and carbon dioxide," *Carbohydrate Research* 340(3), 417-428. DOI: 10.1016/j.carres.2004.11.027

Schmidt, A. S., Mallon, S., Thomsen, A. B., Hvilsted, S., and Lawther, J. M. (2002). "Comparison of the chemical properties of wheat straw and beech fibers following alkaline wet oxidation and laccase treatments," *Journal of Wood Chemistry and Technology* 22(1), 39-53. DOI: 10.1081/WCT-120004433

Sundholm, J. (1999). *Mechanical Pulping Papermaking Science and Technology Series*, Finnish Pulp and Paper Engineers Association and TAPPI, Helsinki, Finland.

Takashi, T. (2009). "Density-reducing agent for paper and method for producing low-density paper," Japan Patent No. 2009275304 (A).

Weng, L. H., Zhang, L. N., Ruan, D., Shi, L.H., and Xu, J. (2004). "Thermal gelation of cellulose in a NaOH/thiourea aqueous solution," *Langmuir* 20(6), 2086-2093. DOI: 10.1021/la035995o

Yamashiki, T., Matsui, T., Kowsaka, K., Saitoh, M., Okajima, K., and Kamide, K. (1992). "New class of cellulose fiber spun from the novel solution of cellulose by wet spinning method," *Journal of Applied Polymer Science* 44(40), 691-698. DOI: 10.1002/app.1992.070440416

Yang, S. H. (2008). *Plant Fiber Chemistry*, China Light Industry Press, Beijing, China.

Zhan, H. Y. (2010). *Pulping Principles and Engineering*, China Light Industry Press, Beijing, China.

Zhang, L. N., Ruan, D., and Gao, S. J. (2002). "Dissolution and regeneration of cellulose in NaOH/thiourea aqueous solution," *Journal of Polymer Science Part B: Polymer Physics* 40(14), 1521-1529. DOI: 10.1002/polb.10215

Zhang, L. N., Ruan, D., and Zhou, J. P. (2001). "Structure and properties of regenerated cellulose films prepared from cotton linters in NaOH/urea aqueous solution," *Industrial and Engineering Chemistry Research* 40(25), 5923-5928. DOI: 10.1021/ie0010417

Zhou, J. P., Zhang, L. N., Cai, J., and Shu, H. (2002). "Cellulose microporous membranes prepared from NaOH/urea aqueous solution," *Journal of Membrane Science* 210(1), 77-90. DOI: 10.1016/s0376-7388(02)00377-0