Enhanced Effect of NaOH/Thiourea/Urea Aqueous Solution on Paper Strength of High Yield Pulp

Rui Zhai* and Xiaofan Zhou

In this work, the thermomechanical pulp of *Pinus massoniana* was pretreated with a NaOH/thiourea/urea aqueous solution to promote fiber bonded area and to increase paper strength. The effects of pulp concentration, alkali dosage, dipping time, and freezing time were evaluated through single factor experiments. The optimum conditions were found to be 15% pulp consistency, 8% NaOH, a dipping time of 15 min, and a freezing time of 60 min. Under these conditions, the paper tensile and burst index of treated pulp increased nearly 100%, and the bulk also was reduced by 10%, but there were no significant effects on folding.

Keywords: NaOH/thiourea/urea aqueous solution; Paper strength; High yield pulp; Pinus massoniana; Thermomechanical pulp

*Contact information: Key Lab of Pulping and Paper Science and Technology, Nanjing Forestry University, Nanjing, P. R. China, 210037; *Corresponding author: zhairui860916@sina.com*

INTRODUCTION

Recently, high yield pulp (HYP) has been finding many new applications because of its high yield (80% to 90%), low pollution, high bulk (Sundholm 1999), and other advantages. However, because of limitations in bonding ability, its applications are limited. The presence of lignin on the fiber surface can lead to poor fiber flexibility and low fiber bonding strength. To the best of our knowledge, the strength of paper made by certain types of high-yield pulps, *e.g.* bleached chemithermomechanical pulp (BCTMP) and alkaline peroxide mechanical pulp (APMP), can approach that of chemical pulps such as kraft pulp. However, the paper properties for most kinds of HYP (*e.g.* refiner mechanical pulp (RMP), thermomechanical pulp (TMP), and stone groundwood (SGW) pulp) are much lower than those of chemical pulp. Thus, most types of HYP are not suitable for paper with high strength and surface property requirements. Such pulps are often used in paper board, newspaper, tissue, and so on. Recently, this problem has received significant attention.

Physical, chemical, and biological methods have been used in past research to solve the problem of poor bonding of HYP varieties. Chemithermomechanical pulp (CTMP) of spruce was treated with a dielectric barrier discharge, and it was found that the dry strength and wet tensile index were increased effectively (Van der Wielen *et al.* 2006). Additionally, paper strength was improved with low consistency refining, as the content of fine fibers increased in the refining process (Franzen 1986; Moss and Retulainen 1997). It was also found that adding more NaOH into the HYP bleaching process increased the paper strength (Zhou and Zou 2003). Birch chips have been pretreated with maleic and phthalic anhydride; the mixture was separated by polypropylene screen before refining, and it was found that the paper strength increased considerably (Marhberg *et al.* 2001). A dilute aqueous solution of oxalic acid has been used to treat pine chips for thermo-mechanical pulp (TMP), which could also increase the paper strength effectively (Klungness *et al.* 2003). Wheat straw has been treated with *Streptomyces cyaneus* to produce semi-chemical pulp, and the tear and burst indices were increased by 15% and 19%, respectively (Berrocal *et al.* 2004). Using white-rot fungi to pretreat wood CTMP, the tensile and burst indices were enhanced by 49% and 34%, respectively (Yang *et al.* 2008).

In recent years, a NaOH/thiourea/urea aqueous solution, as a new solvent system for cellulose (Jin *et al.* 2007), is enjoying growing attention due to its advantages of high solubility (8%), low cost, rapid dissolution, and environmental friendliness. Cellulose products have been obtained with a NaOH/H_2O system (Kamide *et al.* 1984 and Yamashiki *et al.* 1992). Regenerated cellulose membranes have been prepared from cellulose in a NaOH/urea aqueous solution using various coagulants (Mao *et al.* 2006 and Zhou *et al.* 2002). Novel microporous membranes have been prepared from cellulose in a NaOH/thiourea aqueous solution using an ammonium sulfate aqueous solution with different concentrations (Ruan *et al.* 2004). A NaOH/thiourea/urea aqueous solution, modified according to the three systems mentioned above, has also been used to generate cellulose membranes or other products.

However, the paper strength improvement of TMP has not been reported, to the best of our knowledge. It is known that NaOH can swell the amorphous regions of cellulose, and treatment with a lower alkali concentration can be sufficient to increase the toughness of paper (Yang 2008; Fengel and Wegener 1984). At the same time, a small amount of sodium hydroxide can degrade lignin, and lignin will contribute to stiffness of the fibers, thereby reducing paper strength (Zhan 2010; Sjoblom *et al*. 1998; He 2010). Urea or thiourea can be used to presoak in the crystalline region of swelled fibers, and could also modify the toughness of fibers after their formation into paper (Zhang *et al*. 2001, 2002). All of the reports above are beneficial to improving the paper strength. In the present work the reaction conditions are mild (*e.g.* low temperature and alkali dosage), so the ratio of degraded lignin, hemicellulose, or cellulose is small and there will be relatively little effect on yield (about 96% under the optimal conditions). Because of the low level of component losses, particularly the cellulose loss, so one can expect there to be little breakdown in the structural integrity of the fibers. The goal of the present work is to find out whether such a mild treatment has potential to increase the strength of paper made from HYP.

EXPERIMENTAL

Preparation of Material and Treatment Solution

TMP board of *Pinus massoniana* (DaDong paper mill, Zhen Jiang, China) was soaked in water at room temperature and defibrillated with a valley beater; then, all pulps were collected. The pulps were dewatered with a centrifugal hydroextractor, moisture was balanced in a refrigerator for 24 h, and the solid content was measured. Then the beating degree was measured (the beating degree was 13°SR).

NaOH, thiourea, and urea were dissolved in deionized water at the mass ratio of 8:6.5:8:77.5 (NaOH:thiourea:urea:H_2O; Zha *et al.* 2008); then, the concentration was stabilized at room temperature for 72 h.

Experimental Procedure

First, 20 g of oven-dried TMP was added to an aqueous solution of NaOH/ thiourea/urea. The pulp consistency was regulated, and the mixture was soaked at room temperature to fully mix the pulp with the solution. The corresponding mixture was frozen at -10 °C (Wang *et al.* 2008) and then washed, and the pulp was diluted to a concentration of 3% with hot water (90 °C) to remove latency using an electric mixer at this temperature for 30 min. Finally, the pulp was dewatered with a centrifugal hydro-extractor, and the moisture was balanced in a refrigerator for 24 h. Then paper was made at 60 g/m^2 to measure the fold strength and the bulk, tensile, and burst indices. As a control, the process was repeated for the untreated TMP to evaluate the effect of the solution.

Freeze-drying of the untreated and treated TMP (treated under the optimal conditions found in this paper) was carried out in a freeze dryer (Thermo Scientific Heto Power Dry PL6000) for 48 h. The temperature was -30℃ and the applied vacuum was -0.1 MPa**)**.

The fiber morphology was observed by scanning electron microscopy (SEM; FEI Quanta-200, USA). The magnification was 1000X. Fiber attributes were quantified with a Fiber Quality Analysis system, Morfi, France, with a pulp consistency of 40 mg/L used for the analysis. Then the sample was broken apart with a fiber mill, and the powder was screened to obtain the components passing through the screen of 100 mesh for analysis of FT-IR spectrum (Nicolet 380, USA) and X-ray diffraction. The scanning range, in wave numbers, was from 0 to 4000 cm^{-1}. X-ray diffraction data were obtained with a Bruker D8 Avance XRD device, Germany. The scanning angle was from 5°to 50°.

RESULTS AND DISCUSSIONS

Effects of Pulp Concentration and Alkali Dosage

Table 1 shows the paper qualities at different pulp concentrations (alkali dosage of 10%, soaking time of 30 min, and freezing time of 90 min), and Table 2 shows the paper qualities at different alkali dosages (pulp concentration of 15%, soaking time of 30 min, and freezing time of 90 min).

The data in these tables indicate that when the pulp concentration or alkali dosage began to be increased along with the beating degree, the tensile and burst indices increased, but the bulk decreased.

As can be seen in Table 1, the tensile and burst indices were 20.34 N·m/g and 1.119 $kPa \cdot m^2/g$, respectively, when the concentration of pulp was 15%, and in Table 2, when the dosage was 8%, the tensile and burst indices were 20.87 N·m/g and 1.186 $kPa \cdot m^2/g$, respectively, all reaching the maximum. However, with higher pulp concentration or alkali dosage, a decreasing trend for the tensile and burst indices was also observed and the variation of the bulk was not obvious.

Table 1. Effect of Pulp Concentration

Pulp concentration (%)	Tensile index (N·m/g)	Burst index (kPa·m^2/g)	Fold strength (time)	Bulk (cm^3/g)	Beating degree (°SR)
10	17.27	0.976	3	2.546	13
15	20.34	1.119	4	2.511	14
20	18.76	1.012	4	2.505	14
25	16.28	0.952	3	2.497	15

Table 2. Effect of Alkali Dosage

Alkali dosage (%)	Tensile index (N·m/g)	Burst index (kPa·m^2/g)	Fold strength (time)	Bulk (cm^3/g)	Beating degree (°SR)
4	18.77	1.006	3	2.658	15
6	19.34	1.109	3	2.602	14
8	20.87	1.186	4	2.522	14
10	20.12	1.045	4	2.513	15
12	18.65	0.987	3	2.505	16

The concentration of the solution was higher when the pulp concentration or alkali dosage increased, making it more suitable for the soaking and freezing treatment. During the process, damage to the fiber surface was more obvious, and more hydroxyl and other functional groups were exposed, promoting the bonding of fibers and resulting in a tighter combination. However, if the pulp concentration or dosage increased continuously, the concentration of alkali would be increased. So the solution might permeate more rapidly into the cell walls of fibers, thereby damaging the fibers. In such cases, the damage to the whole fiber will be much more obvious than the effect of more exposed hydroxyl groups, so the bonding of the fiber would be weaker, thus accounting for the observed decreases in the tensile and burst indexes. Also, because of the repulsive force between fibers, they were not able to conform to each other to a greater extent. Additionally, the variation of the bulk was not obvious. A fiber consistency of 15% and a NaOH dosage of 8% were therefore chosen as the optimized conditions in this experiment.

In the present work, “damage” means that the solution may soak into the internal part of the fibers and decrease fiber bonding or paper strength with high alkali concentration. Some detailed explanations are provided below:

(1) The bonding will be reduced by NaOH-thiourea-urea aqueous solution. Fibers can be swelled by alkali (NaOH). The internal cohesion will decrease during swelling process, and the XRD spectrum will be changed when alkali concentration is beyond 15% , which means that the crystalline region has be affected at this time (Yang 2008; Fengel and Wegener 1984). Another study indicated that the bonding of amorphous regions for cotton fibers could be reduced by NaOH treatment at low temperature and the bonding in crystal region will be decreased by urea and thiourea (Wang *et al*. 2008).

(2) The fiber degradation process is affected. Cellulose can be dissolved in NaOH-urea-thiourea aqueous solution, and it has been used in dissolving cotton fiber to produce cellulose material (Zha *et al*. 2008; Jin *et al*. 2007). Also, hemicellulose can be dissolved by alkali much more easily, and cellulose or hemicellulose are polysaccharides, both of which could provide hydroxyl or hydrogen bonding and promote bonding of fibers. With the conditions used in the present work, it is impossible to dissolve all of the polysaccharides; however, it is probable that some of the polysaccharides component, especially the hemicellulose, might be degraded (*e.g.* the content of hemicellulose in untreated TMP is about 17.8%, the hemicellulose content of treated TMP is about 16.0% and the extend of removal for cellulose is 13.7% in the present work; however, the ratio of removal for cellulose is only 2.2%), and some of the hydrogen bonding will be lost, both of which are harmful to paper strength. However, compared with the effect of reduction in bonding, the loss of paper strength associated with fiber degradation is much smaller.

Effect of Soaking Time

Table 3 lists the paper qualities at different soaking times (pulp concentration of 15%, alkali dosage of 8%, and freezing time of 90 min). The results indicate that the tensile and burst indices increased and the bulk decreased with increasing soaking time at the same beating degree. The tensile and burst indices were 21.14 N·m/g and 1.207 kPa·m^2/g at 15 min, respectively, reaching the maximum. However, with longer soaking time, a decreasing trend for the tensile and burst indexes were also observed, and the variation of the bulk was not obvious.

During the soaking process, the solution was absorbed by the pulp, and the absorption was more efficient with increasing soaking time. The more efficient the absorption is, the more suitable the pulp will be for the freezing treatment. Compared with the alkali dosage, the soaking time had a similar effect on the fiber surface. However, the absorption trend was balanced with increasing soaking time, and the internal damage of the fiber was serious. At this time, the bonding of the fiber was weaker and the tensile and burst indices decreased. The fibers cannot be further combined because of the repulsive force between fibers; additionally, the variation of the bulk is not obvious. It was therefore determined that a soaking time of 15 min was the optimal condition.

Table 3. Effect of Soaking Time

Soaking time (min)	Tensile index (N·m/g)	Burst index (kPa·m^2/g)	Fold strength (time)	Bulk (cm^3/g)	Beating degree (°SR)
10	20.27	1.174	4	2.536	15
15	21.14	1.207	4	2.525	15
20	21.05	1.201	4	2.518	16
25	20.92	1.195	4	2.513	15

Effect of Freezing Time

Table 4 lists the paper qualities at different freezing times (pulp concentration of 15%, alkali dosage of 8%, and soaking time of 15 min). The results indicate that the tensile and burst indices increased and the bulk decreased with increasing freezing time. When the freezing time was 60 min, the tensile and burst indices were 21.45 N·m/g and 1.217 kPa·m^2/g, respectively, reaching the maximum at the same beating degree. However, when the freezing time was longer than 60 min, a decreasing tendency was also observed and the variation of the bulk was not obvious. Also, as seen in all tables, there was almost no effect on the folding endurance.

The NaOH/thiourea/urea aqueous solution needed to be applied at low temperatures. During the freezing process, damage to the fiber surface was more obvious and more hydroxyl and other functional groups were exposed, promoting the bonding of fibers and resulting in a tighter combination. However, when the treatment time was increased, the fibers were damaged internally, not only on the surface. Under such conditions, the bonding of the fiber was weaker and the tensile and burst indices decreased. A freezing time of 60 min was therefore chosen as the optimized condition.

As is well known, high temperature is needed for dissolving or degradation of lignin, at least 100 ^{o}C for grass, and 160 to 170 ^{o}C is required for wood material (Zhai and Lee 1989; Barbe *et al.* 1990). Also, high alkali dosage (*e.g.* 20%) and pressure (0.4 to 0.8 MPa in the studies of authors) are necessary for this process (Norden and Teder 1979). In the present work, the temperature was -10 ^{o}C, the optimal alkali dosage was 8%, and it was applied at ambient pressure. With these conditions, only a little lignin was degraded or dissolved by this solution (lignin content of untreated TMP was 27.75% and that of treated TMP was 25.43%). Although the value was lower after treatment, the variation was not obvious enough, and the lignin content was still much higher than that of bleached chemical pulp; usually the content of lignin in bleached chemical pulp is lower than 5% (Zhan 2010; Casey 1980). For these reasons, the fibers of treated TMP were still stiff, due to their high lignin content, and the variation of paper fold strength was not obvious.

Table 4. Effect of Freezing Time

Freezing time (min)	Tensile index (N·m/g)	Burst index (kPa·m^2/g)	Fold strength (time)	Bulk (cm^3/g)	Beating degree (°SR)
30	20.07	1.182	3	2.575	15
45	20.64	1.195	3	2.543	15
60	21.45	1.217	4	2.511	16
75	20.92	1.201	4	2.498	15
90	20.17	1.191	4	2.481	16

Fiber Quality Analysis

Table 5 lists the qualities of two kinds of TMP. Compared with untreated TMP, the tensile and burst indices nearly doubled and the bulk was reduced by 10% due to the presence of more hydroxyl and other functional groups and tighter bonding of the treated fibers. Also, there was no variation of fold strength because of lignin on the fiber surface.

The solution could swell the fiber and degrade lignin, hemicellulose, and other components, so the fiber length was reduced and the width increased. It is more difficult for shorter fibers to become kinked or curled; however, the variation of length was small, so there were few differences in the number of kinked or curled fibers. With the degradation of the components, the fibers became smoother and the coarseness decreased after treatment.

The content of fines became higher, which contributed to the increase of HYP paper strength (Sain and Li 2002; Xu 2002). The fiber fragments peeled from the fiber surface by the solution make the fines content increase, and this result is similar to that of beating process. Thus it is appropriate to use the term secondary fines when referring to such released fragments. Usually, they come from the outer sphere of the primary wall or secondary wall of fiber under suitable treatment conditions (Bhardwaj *et al.* 1995; He 2010), not from the internal, so the structure of the whole fiber will not be damaged in the course of their generation.

Table 5. Analysis of Fiber Qualities

Sample	Untreated TMP	Treated TMP
Tensile index (N·m/g)	10.48	21.45
Burst index (kPa·m^2/g)	0.664	1.217
Fold strength (time)	4	4
Bulk (cm^3/g)	2.754	2.511
Beating degree (°SR)	13	15
Brightness(%)	64.75	62.87
Arithm in length (mm)	0.748	0.725
Weighed in length (mm)	1.262	1.233
Width (μm)	34.1	35.2
Coarseness (mg/m)	0.2395	0.1683
Kinked fiber (%)	22.6	22.4
Curled fiber (%)	8.0	7.8
Fines (% in length)	55.6	64.3

FTIR Analysis

To further understand the changes of the samples, FT-IR spectra were recorded to compare the samples. The spectra of untreated and treated TMP are shown in Fig. 1, and the peaks are assigned by comparing with the literature data (Schmidt *et al.* 2002; Li *et al.* 2010). As shown in Fig. 1, both samples exhibited similar spectra, which indicated that the solution did not change the chemical composition of the TMP. 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 in CH_2 and CH_3 groups from hemicelluloses, cellulose, and lignin.

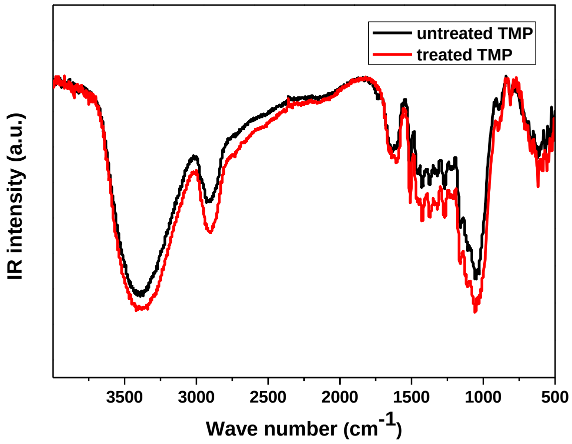

Fig. 1. FTIR spectra of treated and untreated TMP

The C-H deformation in CH_3 and CH_2 occurs at 1462 cm^{-1}, and the C-H asymmetric deformation appears at 1382 cm^{-1}. The peak at 1331 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 signal at 900 cm^{-1} is attributed to the dominant glycosidic linkages between sugar units. The peak at 1113 cm^{-1} is indicative of associated OH groups from cellulose and hemicelluloses. A strong signal at 1055 cm^{-1} is indicative of C-O stretching at C-3 and C-C stretching.

XRD Analysis

The XRD spectra of the treated and untreated samples are shown in Fig. 2. The variation of the spectra is not obvious. Through calculation, the crystallinity of the treated TMP was found to be 0.543, about 0.019 lower than that of the untreated sample. This indicates that the NaOH/thiourea/urea solution did not substantially alter the crystalline structure, and the reaction area was almost entirely confined to the surface of fibers.

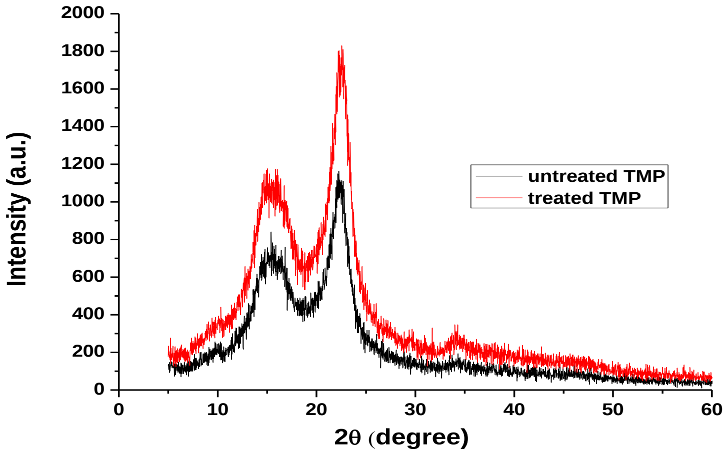

Fig. 2. XRD spectra of treated and untreated TMP

SEM Analysis

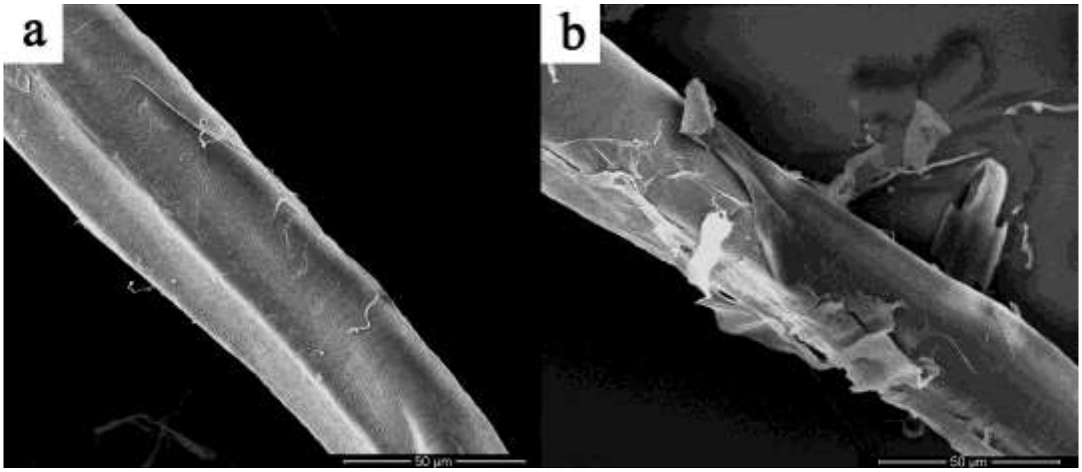

Fig. 3. SEM images of untreated and treated TMP

The surface morphology of the samples was investigated by SEM, as shown in Fig. 3. Figure 3a displays the untreated TMP, and Fig. 3b displays the treated TMP. The results indicate that there was more damage on the fiber surface after chemical treating of the original paper sample. However, the variation of the whole structure of the treated sample was not obvious when compared with the original TMP. This indicates that the NaOH/thiourea/urea aqueous solution only interacted with the fibers on the surface and did not alter the fiber internally under the optimal conditions employed in this work.

Proposed Mechanism

With suitable alkali dosage, some of lignin, existing on the surface of cellulose and hindering soaking process of alkali, can be removed by NaOH first. The value of residual alkali is small after this process, so the range of treatment for polysaccharides is narrow, which means that alkali (NaOH, urea, and thiourea) is mainly used to increase toughness or softness of fibers and the internal bonding have not been affected obviously. Also, as shown above, the content of fines will be increased at the same time. For these reasons, the paper strength will be increased in these contexts. Aspects of this proposed mechanism can be supported as follows:

(1) NaOH is able to remove water-soluble lignin or some lignin with lower molecular weight or phenol structure at room temperature or low temperature (Liu and Lee 1991) in TMP. As shown in the introduction of this paper, fibers will tend to be stiff when they contain more lignin and therefore more difficult to be treated during beating or paper-making process (Laivins and Scallan 1996). Both of these factors may decrease paper strength. Though lower content of lignin is helpful for paper strength, the range of decrease was small in the present work. The extent of removal was about 10% under the optimal condition, which means the effect on paper strength of this process is small, compared to other changes.

(2) Fibers could be swelled by NaOH, and the ability of polymer segments on the fiber surface to take part in bonding will increase (Sang and Dong 2005). As shown in the

introduction above, the amorphous region of fibers can be swelled by NaOH first and then the crystal regions may be swollen by sufficient concentrations of urea or thiourea (Wang *et al*. 2008). The toughness or softness of fibers will be increased by the softening function of these reagents (Chakravarty 1962; Zhang *et al*. 1994). At the same time, paper strength could also be increased (He 2010).

(3) The content of fines can be increased in this process, for the reasons described earlier. Usually, fines possess larger specific surface area than ordinary fibers. Also, fines can be easily swelled by water and more hydrogen bonding will be enabled. Fines will rest in the gaps between longer fibers due to absorption, and hydroxyl bonding of adjacent fibers will become tighter due to the hydrogen bonding of fines (Warwicker *et al*. 1967; Retulainen 1992). For these reasons, paper strength will be increased.

However, according to the results of the present single factor experiments, paper strength will decrease by a large amount with high alkali dosage. Some details are as follows:

(1) The internal bonding of cellulose will be weakened by alkali. The groups C=O, C=S, -NH (urea and thiourea), or OH^- (NaOH) resulting from treatment with various alkaline agents can be expected to combine with cellulose macromolecule and decrease the original hydrogen bonding of the cellulose molecule (Roy *et al*. 2001; Cai and Zhang 2006). NaOH will be consumed on degradation or dissolving of lignin, resins, and hemicellulose of TMP, and the residual content of NaOH is small with lower alkali dosage, which means that the range of cellulose swelling and the weakening of internal bonding of fibers will be relatively small. Alkali is mainly used to increase the toughness or softness with lower alkali dosage, and it is suitable to modify paper strength under this condition. However, with higher dosage, the residual content of NaOH is much larger after the reaction with lignin, resins, and hemicellulose. Then the cellulose will be swollen to a much greater extent by NaOH and urea or thiourea (also with high concentration), and the crystal regions could be affected. Both of these processes are harmful to hydrogen bonding strength or paper strength for the reasons given earlier. So paper strength will be reduced with high alkali dosage.

(2) Lignin can be degraded by NaOH, and cellulose can be dissolved by NaOH-thiourea-urea aqueous solution. So in this paper, if alkali dosage is high enough, more lignin could be removed, then more polysaccharides will be exposed and it is much easier to be degraded. As is well known, paper strength depends on the strength of hydrogen bonding (mainly coming from the polysaccharides), and if the loss of polysaccharides is large, then the number of hydroxyl groups of polysaccharides macromolecule will be decreased, and the strength of hydrogen bonding will be weakened at the same time. For these reasons, paper strength of TMP may be decreased; however, the extent of removal for polysaccharides is low according to subsequent tests (6.5% under the optimal condition and 11.8% with alkali dosage of 15%) in this paper, and it can be affirmed that essentially all of the polysaccharides can be retained in TMP, and the effect of polysaccharides degrading on paper strength with the optimal condition is smaller than that of the internal bonding weakening for fibers.

CONCLUSIONS

1. The optimal conditions for pretreatment with a NaOH/thiourea/urea aqueous solution were determined to be 15% pulp concentration, 8% alkali dosage, soaking for 15 min, and freezing for 60 min.
2. In this process, the content of fines were increased, the surface of fibers was broken, and more hydroxyl and other functional groups were exposed, all of which led to a tighter combination of fibers. At the same time, the solution did not damage the fiber structure or functional groups under the optimal conditions described in this paper.
3. However, the solution did remove much of the lignin. Thus, the resulting paper was still just as brittle. There was almost no variation in fold strength.

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