High-Permeability Filter Paper Prepared from Pulp Fiber Treated in NaOH/Urea/Thiourea System at Low Temperature

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Pulp fibers were treated in aqueous NaOH/urea/thiourea solution at low temperatures (from -14 °C to 8 °C) to prepare high-permeability filter papers. The effects of treatment temperature and time were investigated to control the permeability of the filter paper. SEM images were taken to observe the physical configuration of fibers, and fiber quality analysis was used to characterize the properties of the fibers. The main parameters of the filter papers (permeability and bulk) were increased markedly. The permeability was increased from 150.1 L/(m^2·s) for the untreated paper to 1136 L/(m^2·s) for the treated paper, and from 4.3 cm^3/g for the untreated paper to over 5.5 cm^3/g for the treated paper. The zero-span tensile strength changed only slightly. Moreover, the characteristics of the pulp fibers underwent some positive changes. These results demonstrate that the permeability of paper sheets can be preferably improved by treating fibers in NaOH/urea/thiourea solution at -2 °C for 30 min.

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INTRODUCTION

Cellulosic fiber is the most abundant renewable resource and has attracted increasing attention for applications in many fields (Klemm *et al.* 2005). Cellulosic fibers are the basic materials involved in the production of various paper-based products. One driving force for the rising demand for fibers possessing various properties is a growing demand for various specialty papers. Different grades of paper products are strongly dependent upon the characteristics of their fibers. Essentially, treating fibers allows for vital cost reduction and value-added use of pulp fibers by the pulp and paper industry (Xu *et al.* 2013).

Filter paper is a high value-added specialty paper possessing extremely high permeability, low pore size, and high porosity (Ma *et al.* 2014). Filter paper with high bulk (large dust-containing capacity) and high air permeability (low air resistance) is significant to its subsequent processing. In the conventional filter paper industry, the performance requirements of filter paper are often met *via* mercerization, a common method for preparing pulp fibers with highly swollen, reactive surfaces (Dinand *et al.* 2002; Halonen *et al.* 2013). It is now well established that native cellulose (cellulose I) becomes swollen after alkali treatment and, upon washing, shrinks to yield a new allomorph with an antiparallel structure (cellulose II) (Yoshiharu *et al.* 1998, 2000). In general, filter paper is prepared such that the bulk is much greater than that of ordinary

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paper, and this is done to maintain high permeability after the impregnation post-treatment. In a sense, mercerizing pulp fibers with smooth, rounded surfaces is critical to the filter base paper to improve its bulk and permeability. On the other hand, impregnating the base paper with resin to improve its quality and performance is a typical post-treatment used in current automobile filter paper production (Francucci *et al.* 2010; Lebrun *et al.* 2013). Chemical methods, based on the differences in cellulosic and non-cellulosic materials' stability in chemical solutions, are most commonly used to treat fibers (Liu *et al.* 2011).

Cellulose is composed of β-(1→4)-linked D-glucopyranosyl units with three hydrogen groups, which can form tight arrays of inter- and intra-molecular hydrogen bonds (Klemm *et al.* 2005). Thus, the structure of cellulose is not easy to damage in common solvents. Historically, alkali solutions have been used to treat cellulose. As always, Zhang's group used an alkali/additive solvent system to dissolve cellulose. They found that alkali/urea or thiourea can readily dissolve cellulose (Cai *et al.* 2005; Yang *et al.* 2005; Cai *et al.* 2008; Xiong *et al.* 2014). OH^- groups break the hydrogen bonds and Na^+ hydrations stabilize the hydrophilic hydroxyl groups. Urea, with high polarity and thus strong van der Waals forces, may accumulate on the hydrophobic cellulose regions, preventing cellulose molecules from gathering and damaging the hydrogen bonds between the fibers (Xiong *et al.* 2014). The low temperature effect is thought to be driven by entropy hydrate formation kinetics, which strengthens the network of the solvent hydrates such that they act on the fiber to a greater extent (Zhang *et al.* 2010). It is assumed that the network of the solvent hydrates becomes stronger and breaks the intra- and inter-molecular hydrogen bonds of cellulose at low temperature, smoothing and curling fibers, thus improving permeability. Moreover, these solvents are inexpensive and less toxic than conventional solvents.

Recently, many studies of aqueous NaOH/urea/thiourea solution dissolving fibers have been conducted (Ruan *et al.* 2008; Jin *et al.* 2007; Mohsenzadeh *et al.* 2012; Xiong *et al.* 2014; Liu *et al.* 2015), but none have focused on swelling the fibers to improve the permeability of filter paper. Alkali is a simple chemical that can swell or even dissolve cellulose at high concentration. And addition of chemicals such as urea, thiourea, or a combination of urea and thiourea can provide a benefit to improve the dissolution behavior of cellulose in the alkali solution (Mohsenzadeh *et al.* 2012). It is worthy noting that the thiourea leads to better solubility of cellulose than the urea in alkali solution (Jin *et al.* 2007; Ruan *et al.* 2008). In this case, both thiourea and urea are supplied in alkali solution to treat pulp fibers. Compared with the mercerization (the alkali dosage was about 20%), the NaOH/urea/thiourea solution to treat pulp fibers only requires low alkali dosage (under 10%), and also the permeability of filter paper can be improved immensely. Unlike previous studies, pulp fibers are treated in alkali solution with additives such as urea and thiourea under mild operating conditions. Such an approach supplies a novel and simple method to prepare high-permeability filter paper.

The overall objective of this work was to evaluate the effect of NaOH/urea/thiourea processing on the characteristics of cellulosic fibers and the permeability of paper and to consider the mechanism of swelling fibers in the solvent system. It was hypothesized that fibers treated by the NaOH/urea/thiourea solution system can improve the permeability of paper sheets and be used in the production of high value-added specialty papers requiring high permeability. The goal is to gain some meaningful information for the purpose of fundamental research.

EXPERIMENTAL

Materials

Fully bleached softwood kraft pulp (BSKP) fibers imported from Canada were supplied by Hengfeng Paper Co., Ltd. (Mudanjiang, China) and were soaked in water for 12 h, drained, and torn into grain-size (length of about 1 cm) pieces. The pulp fibers were put into plastic bags, their moisture contents were measured after 24 h, and they were stored at 5 °C prior to use. All reagents were of analytical grade, were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. of China, and were used as received without further purification. An aqueous mixture of 6/6/8 parts NaOH/urea/thiourea was pre-cooled at corresponding temperatures (8 to -14 °C).

Fiber Treatment

First, 15 g of dry pulp fibers was added to 300 mL of pre-cooled solution. Continuous stirring was done with a screw rotating at 600 rpm for 5 min. The mixture was immediately put into the treatment environment for 30 min, after which the mixture was extruded with a net and waste liquid was recycled. The treated fibers were washed with tap water several times, then the yield of treated pulp fiber was measured.

Hand-sheet Preparation

A JY98-DNⅢ ultrasonic cell crusher, supplied by Scientz Biotechnology Co., Ltd. (China), was employed to refine the fibers with the same power output, followed by measuring the moisture (referred to as materials preparation) to make sure the same basis weight was achieved. Handsheets with a target basis weight 80 g/m^2 were made on a ZCX-200 handsheet former (China) without pressing to maintain high air permeability. The wet filter papers were dried at 80 °C for 15 min. Paper sheets were stored in a constant temperature and humidity room prior to testing. The methodologies of fiber treatment and hand-sheet preparation were determined from preliminary experiment and conventional experience.

Fiber Analysis, FTIR Analysis and SEM Observations

A Motic BA300 Microscope (Motic China Group Co., Ltd) equipped with Panasonic WV-CP470/CH Surveillance Cameras (Japan) was employed to observe and compare the shapes of treated fiber and the fiber without treatment. The fiber length, width, shape factor, curl index, coarseness, fines, kink angle, and kink index were determined using a 912 Lorentzen & Wettre fiber tester (Sweden). The paper sheet samples were broken apart with a fiber mill, and the powder was further used for analysis with FT-IR spectrum (Nicolet 6700, Thermo Fisher Scientific, USA). For each sample, the data were recorded at a resolution of 4 cm^{-1} with an accumulation of 32 scans. Then, paper sheet samples were rapidly cut with a scalpel after they were placed onto supports with tape to obtain planar views. After the gold-coating procedure, an FEI Quanta-200 environmental SEM (USA) was used to further observe the surface of paper and the cross-section of paper. The magnifications were 100X, 1000X, and 5000X, respectively. The value of the untreated fiber was used as the blank.

Property Tests

The principle of the YG461E Numerical Air Permeability Instrument, supplied by Ningbo Textile Instrument Factory (China), depends on the measurement of the air

passing through the sheet per unit area (φ 50.0 mm) at a certain pressure gradient, Δp (20.0 mm water column), according to the ISO 9237: 1995 (E) (Zupin *et al.* 2012). In many filter products, appropriate air permeability is an important feature, as it helps to evaluate the performance of the industrial filter material (Tokarska 2008).

The pore size of the filter paper was measured by an MP-10K Hole Size Reflectscope Reflector (Xinxiang Dongfeng Filtration Technology Co., Ltd. China) with isopropanol as the test medium. To regulate the valve, pressure was increased slowly. The pressure value P_1 was recorded when the first series of bubbles were observed. Then, pressure value P_2 was recorded when three series of bubbles appeared. P_1 was used to characterize the maximum pore size, and P_2 was used to characterize the average pore size. The pore size of the filter paper was defined as,

$$D = 4 \times \frac{S}{P} \tag{1}$$

where D denotes the pore size. The quantity S represents the test medium surface tension and was taken to be 21.35×10^{-3} N/m, and P indicates pressure.

A Z-span1000 troubleshooter was supplied by Pulmac Instruments International (USA) to measure the zero-span tensile strength. The width of the sheet specimen was 15 ± 0.1 mm and the length was 100 mm. At least twelve data points were gathered for each sheet sample.

A ZUS-4 paper thickness tester, supplied by Chang Chun Yueming Mini Testing Machine Co., Ltd (China), was employed to measure the thickness of the filter paper. The relationship of bulk with basis weight was,

$$B_u = \frac{d_a \times 1000}{q} \tag{2}$$

where bulk is B_u, d_a represents the thickness of the filter paper, and q denotes the basis weight. Fifteen data points were gathered for each sheet sample.

RESULTS AND DISCUSSION

Fiber Morphological and Quality Analysis

The fiber morphology after various treatment stages is shown in Fig. 1. Fibers treated in aqueous NaOH/urea/thiourea solution underwent crucial changes in morphology. As can be seen from Fig. 1(a) and (c), fibers exhibited swelling and their cell wall became thickened after treatment. Broken fibers and fines were dissolved or sieved, which Table 1 also verifies. In some sense, the decrease in fines improved the permeability of the filter paper. Previous reports suggest that urea can form inclusion complexes in the presence of guest molecules through van der Waals force (Vasanthan *et al.* 1996; Rusa and Tonelli 2000). Figure 1(b) shows that the surface of the fibers forms a kind of cellulose/urea/thiourea complex that can prevent the dispersed fibers from re-agglomerating. A tentative explanation about the power of urea/thiourea in altering the hydrogen bonding is given in Fig. 2, which is based on the following literature (Vasanthan *et al.* 1996; Rusa *et al.* 2000; Cai *et al.* 2005; Mohsenzadeh *et al.* 2012; Xiong *et al.* 2014; Liu *et al.* 2015) and micrographs of fibers (Fig. 1(b)). As shown in Fig. 2, the hydrogen bonds between fiber and other fibers or water make full swelling of fibers

difficult. The urea/thiourea solution treats pulp fibers and accumulates on them by forming hydrogen bonds with them, damaging the hydrogen bonds between fibers. Improvement of the fiber swelling can be obtained. This mechanism also applies to the fibrils of the pulp fibers.
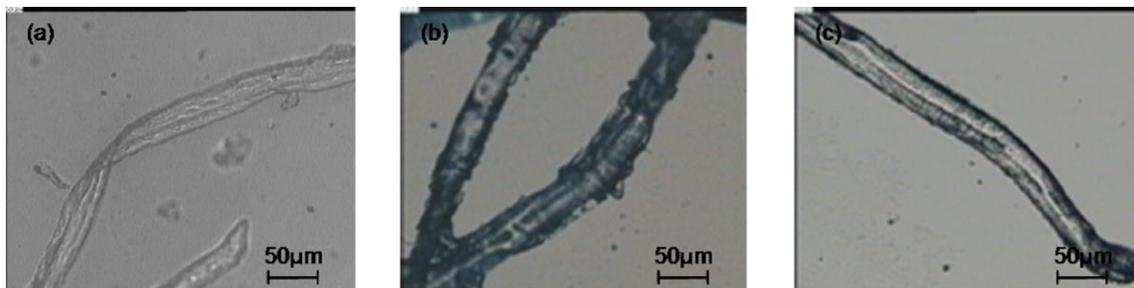

Fig. 1. Micrographs of fibers. Untreated fiber (a); Fiber during the treating process (b); Treated fiber (urea/thiourea complex was washed away) (c)
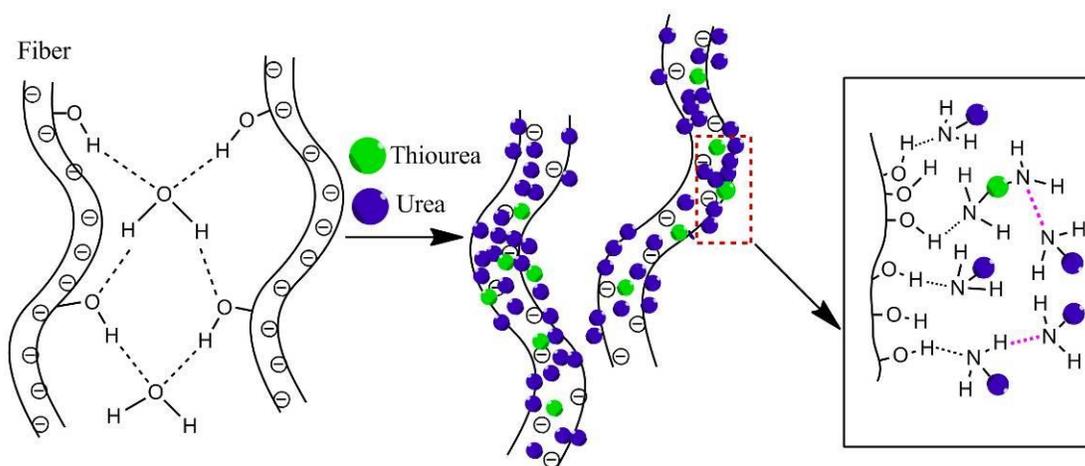
Fig. 2. Schematic of change in hydrogen bonding

Figure 3 shows SEM images papers and fibers. As can be seen from Fig. 3(a), (b), (c) and (d), the shape of the untreated fiber was ribbon-like, while that of the treated fiber was pole-like. The surface of the treated fiber was smooth. And the porosity values of treated papers were higher than those of untreated papers. Figure 3(e) and (f) reveal that the cross-section of the untreated fibers was flat and the lumen was large, whereas that of treated fibers was tumid and the lumen became small. Moreover, the cell wall of treated fibers became loose and fibrillated. In addition, the treated fiber exhibited marked swelling without breakage of its structure. This provides visual evidence that treating the fiber imparts high bulk to the sheet of paper, enhancing its permeability. SEM observation showed that the treated fibers had the potential to improve paper's permeability and perform to a greater degree than ordinary fibers.

The properties of fiber were determined using a 912 Lorentzen & Wettre fiber tester (Sweden). The results of fiber quality analysis are listed in Table 1. The value are averaged over the three data points for each sample. The properties of treated fibers (length, width, curl index, coarseness, fines, kink angle, and kink index) changed following treatment.
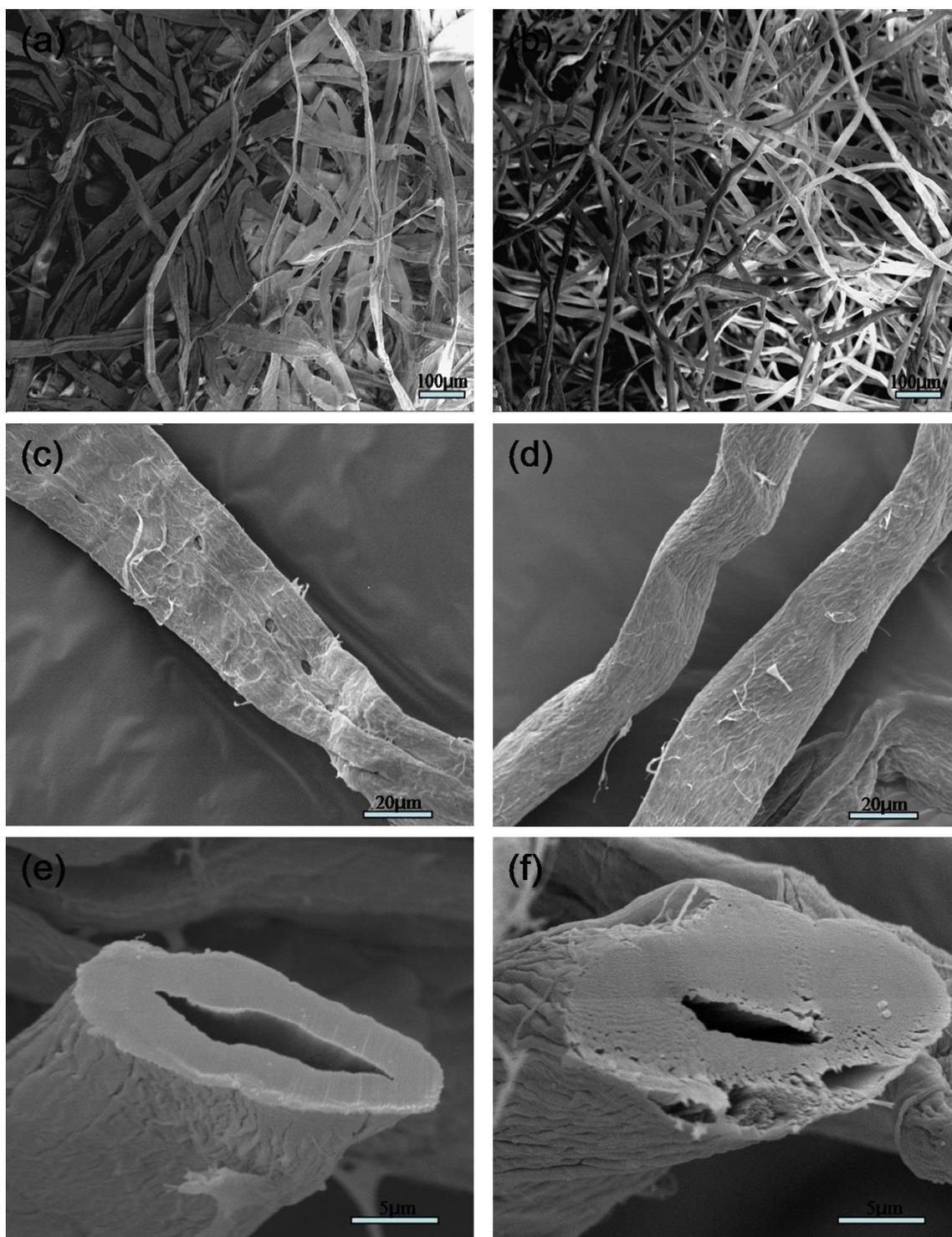
Fig. 3. SEM images of papers and fibers. (a) untreated paper; (b) treated paper; (c) and (e) untreated fiber; (d) and (f) treated fiber

The greatest increases, in the curl index (22.3% to 27.1%) and coarseness (160.8 to 179.1 µg/m), suggest that aqueous NaOH/urea/thiourea solution facilitated the swelling of fibers. The kink index of treated fiber dramatically increased, by 42.3% (2.175 to 3.094), indicating that the treatment destroyed hydrogen bonds in the fiber. Moreover, the

fines content decreased to 0.3% (from 2.3%). It was found that broken fibers and fines were dissolved or sieved by the treatment. Therefore, treating fibers with aqueous NaOH/urea/thiourea solution caused varying degrees of distortion in the fibers and made them swell. This had a great effect on the paper's permeability.

Fiber Analysis

To further understand the changes of the components, the FT-IR spectra of untreated and treated fiber are shown in Fig. 4, and the peaks are assigned by comparing with the literature data (Li *et al.* 2010; Zhai *et al.* 2015). As shown in the figure, both samples basically exhibited similar spectra, which indicated that the treatment did not change the structure of pulp fiber.

The peak at 1103 cm^{-1} is indicative of associated OH groups from cellulose and hemicellulose. The band at 1161 cm^{-1} arises from C-O-C stretching of the β- (1,4)-glycosidic linkages. The peak at 3331 cm^{-1} is attributed to the stretching of OH groups, and the absorption at 2895 cm^{-1} is attributed to C-H stretching in CH_2 groups in cellulose. A strong signal at 1030 cm^{-1} is indicative of C-O at C-C stretching.
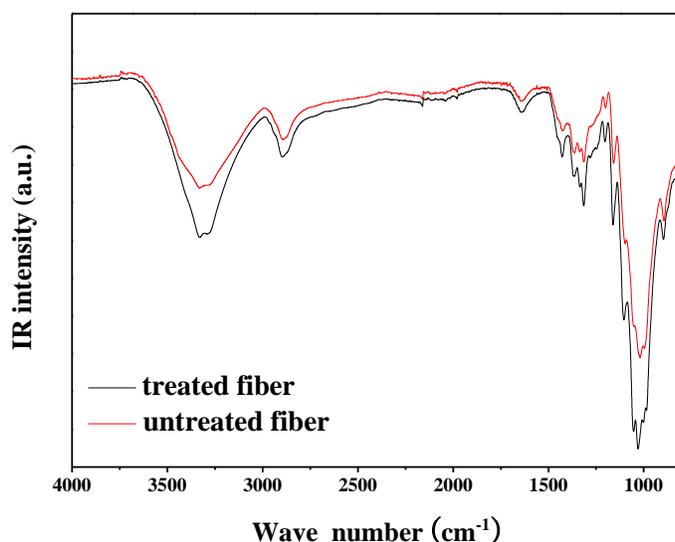

Fig. 4. FT-IR spectra of untreated fiber and treated fiber

Table 1. Fiber Quality Analysis Results

Variable	BSKP Fiber	Treated Fiber
Mean Length (mm) / Weighted (μm)	2.444 / 28.3	2.145 / 26.8
Curl Index (%)	22.3	27.1
Coarseness (μg/m)	160.8	179.1
Fines Content (%)	2.3	0.3
Kink Angle (°) / Kink Index	54.8 / 2.175	58.5 / 3.094

Effect of Treatment Temperature on the Properties of the Filter Paper

Temperature appeared to have an important role in the treatment, which promotes the formation of a stable inclusion complex hosted by urea, thiourea, and NaOH hydrates through hydrogen-bond networks at low temperature (Ruan *et al.* 2008). In this work, a large number of experiments were carried out to investigate the influence of treatment temperature on the properties of the filter paper, with treatment time fixed at 30 min. The results were evaluated and studied for pore size, permeability, bulk, and zero-span tensile strength, as shown in Fig. 5. The properties of the paper without treatment are shown in Table 2.

Table 2. Properties of Paper without Treatment

| Property	Maximum Pore Size (µm)	Average Pore Size (µm)	Permeability (L/(m²·s))	Bulk (cm³/g)	Zero-pan Tensile Strength (N)
Value	41.0	39.0	150.1	4.3	164.3

The pore size of paper has an impact on its filtering accuracy. Generally, the filtering accuracy increases with decreasing void fraction and pore size. It makes no sense to investigate the pore size separately. Thus, the pore size and permeability are always considered together. Generally, large pore size corresponds to high permeability. As Fig. 5(a) and Table 2 show, the maximum pore size was increased by treatment from 41.0 µm for untreated paper to 50.5 µm for treated paper, and from 39.0 µm for untreated paper to 45.6 µm for treated paper, which Fig. (a) and (b) also verified. This finding is likely a consequence of treated fiber's swelling and smooth surface. Treatment increases the pore size of paper by deteriorating hydrogen bonds between fibers. However, the maximum pore size and average pore size decreased with increasing treatment temperature from -6 to 8 °C. Otherwise, pore size was larger and decreased slightly from -14 to -6 °C. As is well known, an increase in temperature weakens the hydrogen bonding between the fiber and the solvent, such that the structure may collapse when the temperature is increased from -14 to 8 °C. Figure 5(a) shows that lower temperature equates to the larger pore size and that the effect of fiber treatment is unsatisfactory at high temperatures.

It is generally accepted that the permeability of filter paper depends on its pore size and bulk. The effect of treatment temperature on the permeability of filter paper is depicted in Fig. 5(b). The permeability increased from 795.8 to 1184.2 L/(m²·s) with an increase in treatment temperature from -14 to -6 °C and decreased from 1184.2 to 537.4 L/(m²·s) with an increase in treatment temperature from -6 to 8 °C. This indicates that temperature is quite important to the treatment of pulp fibers in aqueous NaOH/urea/thiourea solution. Interestingly, the permeability of the paper was 379.89 L/(m²·s) after it was treated at room temperature, and that of paper without treatment was 150 L/(m²·s). With an increase in temperature, the hydrogen-bonding network structure of inclusion complex could be destroyed, depending on the relationship between the stability of the hydrogen bonds and temperature. At room temperature, the structure of inclusion complex had been destroyed seriously, and the increase in permeability may have been mainly due to alkali swelling at room temperature. Moreover, 379.89 L/(m²·s) is far below the requirements for high-permeability filter paper. Thus, low temperature favors effective fiber treatment in aqueous NaOH/urea/thiourea solution and greatly improves permeability.

Bulk affects the sheet's dust-containing capacity and the service life of the filter paper. It is accepted that, per unit mass of filter paper, greater volume reflects a greater

capacity of the filter paper to contain dust, which relates to its service life. The effect of treatment temperature on the bulk of filter paper is depicted in Fig. 5(c), and the values display a similar trend with Fig. 5(a). Table 2 and Fig. 5(c) indicate that the bulk of filter paper increased significantly (the bulk of paper without treatment was 4.3 cm^3/g, while treatment increased the bulk to more than 5 cm^3/g), and lower processing temperatures led to higher values of bulk. This may be attributed to the high treatment intensity, making fibers smooth and curled at low temperature.

Zero-span tensile strength (ZSTS) characterizes the strength of single fibers. Generally, chemical processing causes fibrous fracture and ZSTS reduction. As can be seen in Fig. 5(d), the ZSTS gradually increased with increasing treatment temperature from -10 to 2 °C. Otherwise, treatment resulted in minor decreases in ZSTS with increasing treatment temperature from 2 to 8 °C. Moreover, the ZSTS of paper without treatment was 164.3 N, and the ZSTS slightly decreased after treatment. As explained above, the decrease was likely due to the solvent damaging the fibers. However, dissolving broken fibers and fines during treatment led to an increase of ZSTS to a certain degree. Based on the analysis of various properties, to obtain high permeability and damage the fiber slightly, the treatment process was most favorable at -2 °C.
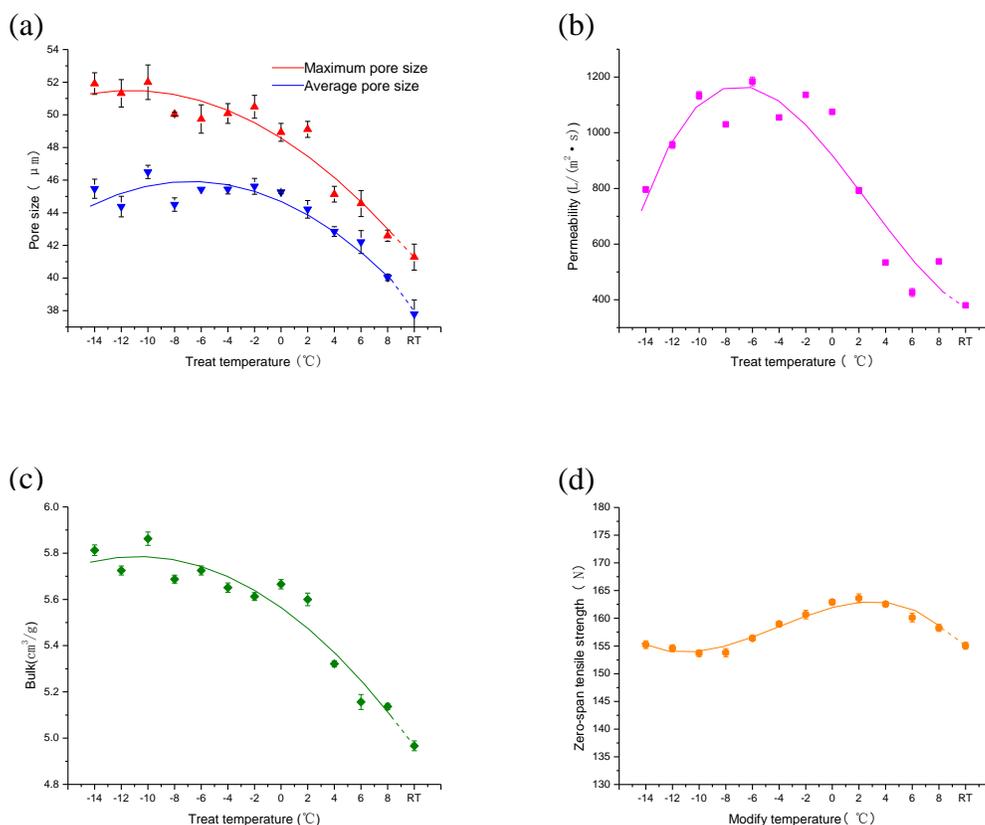
Fig. 5. Effect of temperature on filter paper properties: (a) pore size; (b) permeability; (c) bulk; (d) zero-span tensile strength. RT represents room temperature (25 **°**C)

Effect of Treatment Time on the Characteristics of the Filter Paper
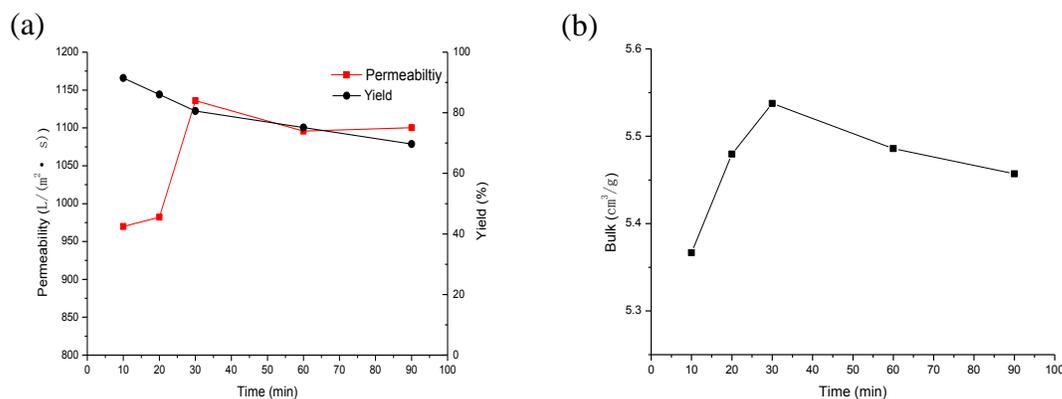
Fig. 6. Effect of treatment time on the permeability, yield (a) and bulk (b) of the filter paper

The solvent molecules (NaOH, urea, thiourea, and water) and the cellulose macromolecules lead to inclusion complex formation through hydrogen bonds, which are relatively stable at low temperature. The treatment of pulp fibers in NaOH/urea/thiourea system can be described as two parts: first, the fibers are immersed in the precooled solvent and dispersed as cellulose chains; second, NaOH, urea, thiourea hydrates form an inclusion complex at the surface of fibers (Cai *et al.* 2008). Short treatment time is not favorable for the dispersion of cellulose, leading to unsatisfactory treatment. However, a lot of pulp fibers are dissolved in the solvent if a long treatment time is provided, leading to low treated pulp fiber yield. Figure 6(a) and (b) show the effects of treatment time on the characteristics of the filter paper at -2 °C. The results in Fig. 6(a) revealed that the paper permeability was sharply increased with increasing of the treatment time from 10 to 30 min and there were minor decreases after 30 min; meanwhile the yield of the treated pulp fiber was considerably decreased. The highest permeability at 30 min, which was 80.6% of the yield, was obtained by treatment with NaOH/urea/thiourea at -2 °C. The effect of treatment time on the bulk of filter paper is depicted in Fig. 6(b), and the values display a similar trend with permeability in Fig. 6(a). In the early stages of the treatment, Na^+ of the alkali existed as $[Na(H_2O)m]^+$ and OH^- existed as $[OH(H_2O)n]^-$. $[OH(H_2O)n]^-$ broke hydrogen bonds, and $[Na(H_2O)m]^+$ stabilized the hydrophilic hydroxyl groups (Xiong *et al.* 2014). Urea/thiourea accumulated on the cellulose's hydrophobic region. The hydrogen bonds of the amorphous zone were quickly damaged with the cooperation of the solvent system. The proper time was favorable for the treatment of components in aqueous NaOH/urea/thiourea solution. As can be seen in Fig. 6, 30 min was found to be the most efficient, time-saving duration for treating pulp fibers and was suitable for preparing filter paper with high permeability.

CONCLUSIONS

1. Pulp fibers were treated in an NaOH/urea/thiourea system in this study, and the effects of treatment temperature and time on filtration properties of filter paper were investigated. According to the experimental data and fiber morphology observations,

the permeability and bulk of the filter paper were improved by the solvent treatment at low temperatures.

2. The fibers curled noticeably increased (from 22.3% to 27.1% in curl index), and obviously swelled (increased from 160.8 to 179.1 µg/m in coarseness) with treatment, leading to higher permeability.

3. When the treatment was conducted at -2 °C for 30 min, the permeability increased to 1136 L/(m^2·s) and the treatment resulted in only a slight reduction in the zero-span tensile strength (164.3 to 160.4 N).

4. This study provides a novel and simple method to achieve high-permeability filter paper production *via* the treatment of fiber in alkali solution with additives such as urea and thiourea under mild operating conditions.

ACKNOWLEDGMENTS

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