Highly permeabale paper fabricated with Cold NaOH/Thiourea Treated Smooth Cellulose Fibers

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Abstract： High-permeability paper has a wide range of applications in air filtration media, packaging materials, sound insulation or insulation materials. However, there are still some limitations in the current method for preparing high-thickness and high-permeability paper. In this paper, NaOH/thiourea is used to gently treat wood pulp fibers to improve the bulk of paper. The effects of low temperature treatment time on the surface morphology and physical properties of the paper were investigated. The results showed that, with the increase of mild pretreatment time, the length of fiber decreased slowly, the content of fine fiber was less, and the fiber became swollen and bent and kinky. The effect of thiourea dosage on fiber was further investigated when the treatment time was 20 min. The results showed that when the treatment condition was NaOH of 8 wt% and thiourea of 8 wt%, the length was shorten by 14.51%, the fine fiber content was reduced by 60.62%, and the surface etching phenomenon was aggravated compared with the untreated fiber. The SEM and AFM analysis showed that the fiber surface was obviously folded and the roughness increased by 158%. At the same time, the bulk of paper increased by 39.53% and the average pore diameter of the paper increased from 28.79 μm to 49.62 μm, the air permeability increased by 105.38%. FT-IR indicated no new changes in the chemical structure after treatment. XRD indicated that the fiber crystallinity after treatment decreased by 2.17%.

1. Introduction

Due to the bulk, light-weight, and high porous properties, high-bulk papers are getting more and more attention in the fields of air filter media, insulation media or sound insulation materials. Traditionally, paper bulk can be improved by increasing the content of high yield pulp (such as mechanical pulp, chemical mechanical pulp) and the use of paper bulking agents[1-2]. (1) The high yield pulp has a high content of lignin and cellulose exposed limitely, leading to less hydrogen bonding between intermolecular cellulose chains, a large gap between fibers. Therefore, a loose and porous structure was obtained, leading to the resultant paper with a high bulk[3-5]. However, the high content of high yield pulp commonly lead to a decease of the strength and whiteness of papers and the acceleration of paper aging[6-7]. (2) Bulking agent covers on the surface of cellulose fibers during the process of paper drying, leaving cellulose fibers with hydrophobic surfaces. Thus, the hydrogen bonding between the cellulose molecules were hindered, resulting in a loosly porous paper structure. However, the commonly used bulking agents such as alkyl ether, alkyl amide organic bulking agent, are toxic.

In the traditional production of high-bulk and high-permeability materials (such as air filter paper), mercerization of cellulose fibers is a common method to prepare fibers with high swelling degree and high reactivity[8-10]. The smooth surface of cellulose fibers after mercerization are critical to increasing

the permeability of filter papers. In recent years, NaOH/urea aqueous solution is demonstrated an effective inorganic dissolution system for cellulose[11-13]. All cellulose samples with molecular weights below 1.29×10^5 can be quickly dissolved completely of 7 wt% NaOH/12 wt% urea aqueous solution at -12°C[14-15]. The solubility of cellulose in NaOH/urea aqueous solution depends on the temperature and the mass ratio of the individuals, the molecular weight, and the crystallinity of the cellulose[16]. Therefore, we can anticipate that the surface morphologies of cellulose fibers, and even the mechanical properties of the resulting papers can be tailored by controlling the above mentioned factors. Recently, Fan et al. use NaOH/urea solution to slightly dissolve the surface layer of natural cotton fibers, which can enhance the wrinkle resistance of cotton fabrics without leaving any adhesive resin on the fibers[17]. The ramie fabric is treated with NaOH/urea to micro-dissolve the superficial zone of ramie fabrics and dissolve part of the hairiness to reduce scratchiness[18]. High permeability air filter paper was prepared by treating pulp fibers with NaOH/urea/thiourea mixtures[19]. The bulk and softness of papers can be improved using NaOH/thiourea pretreated hardwood pulp[20]. However, the pretreatment of cellulose fibers is time-consuming and the process is complicated.

Herein, we studied the effect of mild treatment of cellulose fibers using NaOH/urea (or thiourea) system on the performance of softwood pulp. We compared the treatment effects of NaOH/urea and NaOH/thiourea. The data showed that under the same conditions, thiourea was superior to urea in improving paper bulk and air permeability. In this study, the bleached kraft pulp was treated with a low content of NaOH/thiourea aqueous solution, and the fibers were gently pretreated with a low content of alkali and thiourea for a short time (figure 1). The effect of NaOH/thiourea on the surface morphology and paper forming properties of the fibers was investigated. Compared with previous studies, the processing of this paper was simple and the time was short. The bulk of the prepared paper was 6.1 cm^3/g.

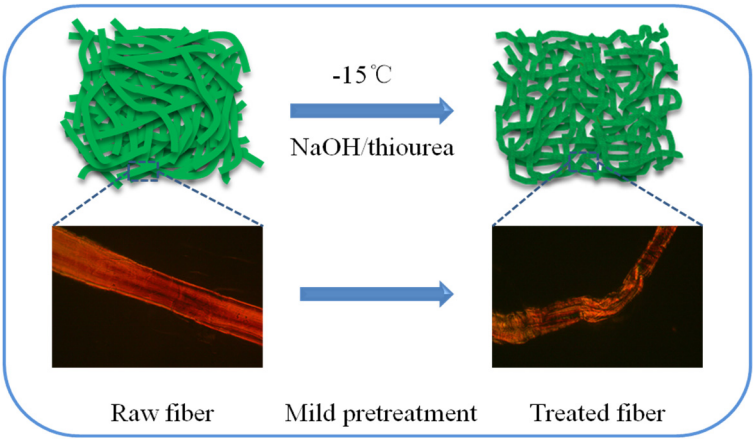

Figure 1. Schematic diagram of pretreatment process

2. Materials and methods

2.1. Materials

Bleached softwood kraft pulp was provided by Vida paper co. LTD(Shan Dong, China). The solid content was 46 wt%. NaOH and thiourea were purchased from Hengxing Chemical Reagent (Tianjin, China). All reagents were used as received without further purification.

2.2. Pretreatment of fiber

8 wt% NaOH/thiourea aqueous solutions with thiourea contents of 2 wt%, 4 wt%, 6 wt%, and 8 wt% were prepared, separately. The solutions were stored at room temperature for further use. 42 g cellulose fibers were immersed in 300 mL NaOH/thiourea aqueous solutions and magneticly stirred for 3 min, followed by placing in a refrigerator at -15℃ for 5 min, 10 min, 15 min, 20 min, 25 min, 30 min, 35 min and 40 min, separately. Subsequently, the treated cellulose fibers were filtered (120 mesh

filter) and washed thoroughly with deionized water until a pH of 7.0. For comparision, cellulose fibers without NaOH/thiourea treatment were prepared under the same conditions. Paper sheets with a basis weight of 100 g/m^2 were made from treated or untreated cellulose fibers.

2.3. Measurements and Characterization

The dimensions including length, width, and curl degree of cellulose of fibers were measured by a Fiber Quality Analysis system (LDA02 Canada). We examined the morphology at the surface of cellulose fibers and papers using an optical microscope, atomic force microscopy (AFM), and scanning electron microscope (Hitachi Regulus8220 Japan). The AFM analysis of fiber was carried out using a bruker AFM (Multimode 8 Germany). The fiber was placed onto a freshly cleaved mica surface and air dried. All images were obtained using a tapping mode at room temperature. The pore size distribution of the paper was determined by an aperture analyzer (Porometer 3G Quantachrome USA). The sample was cut into a circular shape with a diameter of 20 mm. The air permeability of the paper was measured using an air permeability tester (FX3300-IV Switzerland), and the test process pressure was 100 Pa.

3. Results and discussion

3.1Morphological analysis of cellulose fibers

To study the morphological changes of fibers before and after pretreatment, they were observed by polarizing light microscopy. The samples of untreated and NaOH/8 wt% thiourea treated for 20 min were shown in Figure 2. Obviously, there were many fine fibers around the untreated fibers (small bright spots in the figure), and the fibers were flattened (Figure 2a, c). With the increase of thiourea dosage, there were few fine fibers at the fiber backbone. The fine fibers were dissolved, and the fibers were swelling and round, with etched folds on the surface, showing a curved and kinky shape (Figure 2b, d). Alkali dissolved the residual lignin and wax on the surface of the fiber, which made the fiber embellish and rough.

3.2Surface roughness analysis of cellulose fibers

Figure 2e, f showed the measurement of the untreated and treated fiber surface roughness. AFM analysis helped us to measure the surface texture parameters of the fiber quantitatively. As shown in Figure 2e, the untreated fiber surface was relatively uniform and the fluctuation range was small, and the treated sample was shown in Figure 2f, its surface exhibits irregular pleats, and the range of undulation was relatively large. As far as the quantitative measure of the roughness was concerned, untreated fiber showed average roughness of 80.6 nm and RMS roughness of 105 nm, whereas for treated fiber these values were 209 nm and 271 nm respectively. The above data showed more clearly that the treatment of NaOH/thiourea exacerbates the surface etching and grooves of the fiber, increasing the surface roughness of the fiber, which was similar to the morphology of the mercerized fiber. The deepened grooves on the surface of the rounded fibers made the contact area between the fibers smaller, from flat faces to dots and lines.

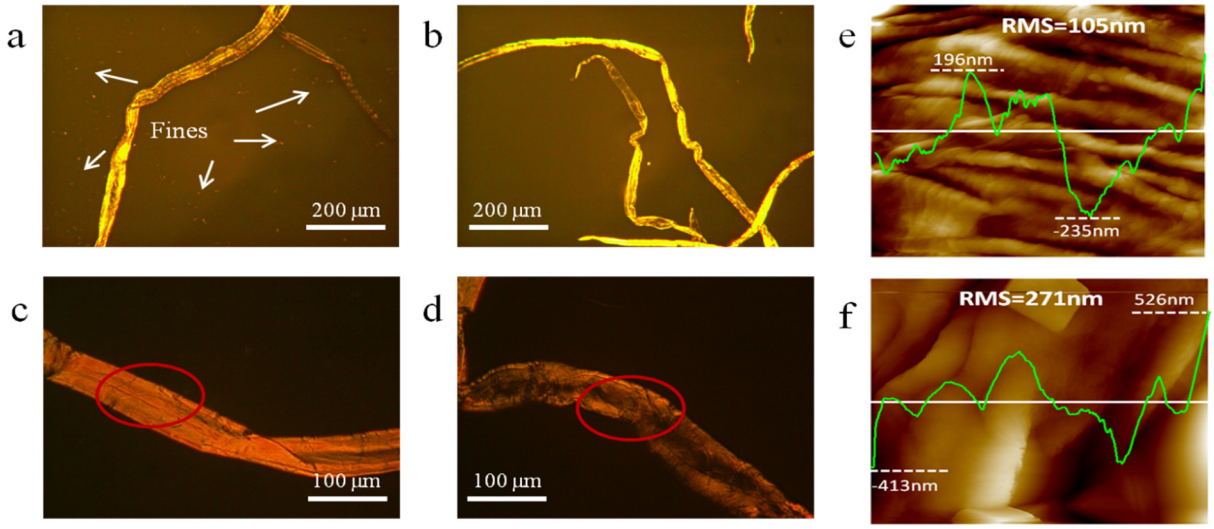

Figure 2. Polarized light microscope image of fibers without pretreated (a, c) and with pretreatment using aqueous NaOH/8wt% thiourea solution (b, d) and AFM images of untreated fiber and treated fiber(e, f).

3.3Surface morphology of cellulose fibers

Figure 3 showed the surface morphology of untreated fibers and treated fibers at magnifications of 1k and 3k. As seen in the untreated fibers (Figure 3a, c), the relatively smooth surface of the fibers, the fibers were intertwined in a flat shape. The band shape made the contact area between the fibers become larger and the fibers bind relatively tightly. However, the surface morphology of treated fibers changed when the fiber was pretreated with the NaOH/8 wt% thiourea as shown in Figure 3b, d. Many wrinkles and grooves on the surface of the fiber could be obviously observed, which led to a coarser surface. Meanwhile, the fibers form become rounded and present a twisted structure, and the paper-forming structure was loose and porous. Figure 3e, f graphically illustrate the difference in cross-sectional thickness of untreated and treated fiber-forming paper. In the case of the same weight, the thickness of the paper made from the untreated fiber was small, the flat fibers were interwoven, and the bonding between the fiber layers was relatively tight. However, the thickness of the paper made by the treated fiber was large, the fiber was rounded and twisted, and the irregularly bent fibers cause loose bonding between the layers. Therefore, the paper structure of the treated fiber was loose and porous and had good air permeability.

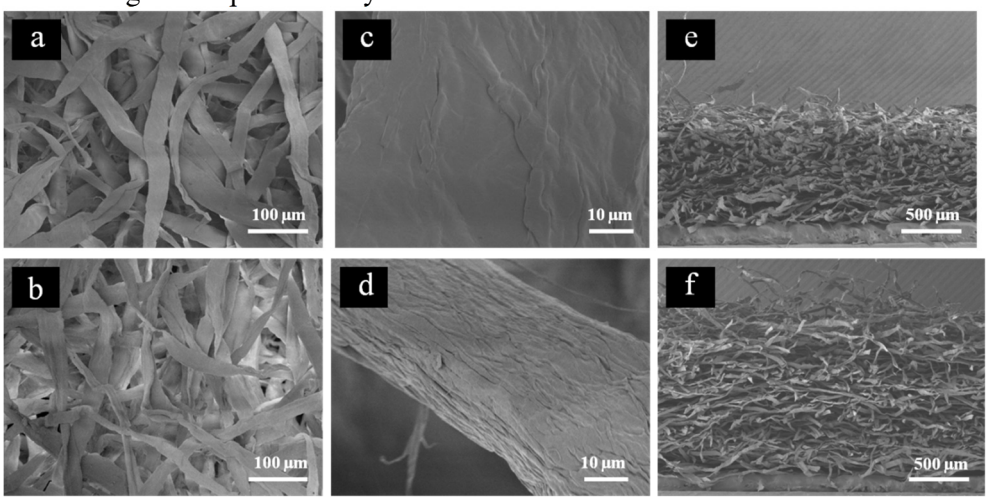

Figure 3. SEM image of untreated fiber (a, c) and its cross section (e) and image of fiber treated with NaOH/8 wt% aqueous solution of thiourea (b, d) and its cross section (f).

3.4Dimensions of cellulose fibers

The dimensions of cellulose fibers and the fines content treated with 8 wt% NaOH/6 wt% thiourea for different time durations were shown in Table 1. It clearly showed that the length of cellulose fiber decreased with the increase of treatment time, which was mainly due to the partial dissolution at the fiber ends or breakage, leading to a shorter fiber. Meanwhile the number of fine fibers decreased significantly, the fiber became curly. As the solution of NaOH/thiourea had a solubility effect on cellulose, the fine fiber in the solution system was partially dissolved in a short time, resulting in a decrease in the content of fine fiber. Fiber kink refers to a sudden and rigid transition due to the damage in the fiber cell wall. The treatment of the alkali caused the fiber to swell and deform, change fiber morphology, caused kinking and bending, and the average width slightly fluctuated. Table 2 showed the relationship between the amount of thiourea and the fiber quality at a freezing time of 20 min. The increase in the amount of thiourea promotes the tendency of the fiber to become shorter slowly and the dissolution of fine fibers. At the same time, due to the swelling and surface micro-dissolution of NaOH/thiourea, the cell wall thickness of the fiber was changed from 10.35 μm to 8.75 μm, and the cell cavity diameter was changed from 24.9 μm to 16.56 μm. This is consistent with the fiber morphology mentioned above from flat to round.

Table 1. The morphology parameters of various fiber samples from FQA

Time/min	L_{ww}/mm	Fines content/%	Curl index/%	Width/μm
0	2.288	2.26	19.5	29.0
5	2.165	1.73	33.5	29.0
10	2.106	1.52	31.2	29.6
15	2.058	1.44	32.3	29.9
20	2.079	1.29	31.9	30.2
25	1.941	1.43	32.6	30.5
30	1.964	1.36	32.3	30.0
35	1.972	1.28	31.9	29.7
40	1.963	1.27	33.2	29.6

Table 2. The morphology parameters of various fiber samples from FQA

Dosage of thiourea/wt%	Lww/mm	Fines content/%	Curl index/%	Width/μm
untreated	2.288	2.26	19.5	29.0
2	2.030	1.29	29.3	30.3
4	1.993	1.06	30.6	30.4
6	1.970	1.10	30.1	30.6
8	1.956	0.89	30.9	30.2

3.5Paper Physical properties

Figure 4 showed the effect of different thiourea dosages on paper performance at a treatment time of 20 min. The relationship between the amount of thiourea and the bulk and air permeability of the paper was seen in Figure 4a. As the amount of thiourea increases, the bulk and air permeability of the paper showed an upward trend. The bulk of the paper increased significantly from the original 4.3 cm^3/g to 6.0 cm^3/g, while the air permeability increased from 222 mm/s to 458 mm/s. The NaOH/thiourea aqueous solution dissolved some of the fine fibers, reducing the hydrogen bonding between the fiber molecules, and the paper tightness was lowered. Aperture was a key indicator of paper bulk and air permeability. Figure 4b showed the effect of the amount of thiourea on the paper pore diameter. The amount of thiourea played a significant role in the pore size distribution of the paper. Compared with the average pore size of untreated paper (28.79 μm), the average pore size after treatment with NaOH/8 wt% thiourea reached 49.62 μm. As a mild fiber treatment method for preparing high-thickness paper, this paper compared the previous research results on high-thickness

paper[21-22], such as fiber silk photochemical treatment, NaOH/urea/thiourea treatment (Figure 4c). The process mentioned in this paper was more effective in improving the bulk. The experiment measured the thermal insulation performance of the product by infrared thermometer. Figure 4d showed the thermal insulation performance of the commercial cup sleeve and the cup sleeve produced in this study. The commercial cup sleeve had a basis weight of 200 g/m^2, and the inner wall of the cup sleeve was corrugated; the sample prepared in this study had a basis weight of 100 g/m^2, which was thick and soft. As can be seen from the figure, the thermal insulation performance of the two products was similar. Therefore, in the case of similar thermal insulation performance, the samples prepared in this study had the advantages of light weight, saving raw materials and soft texture.

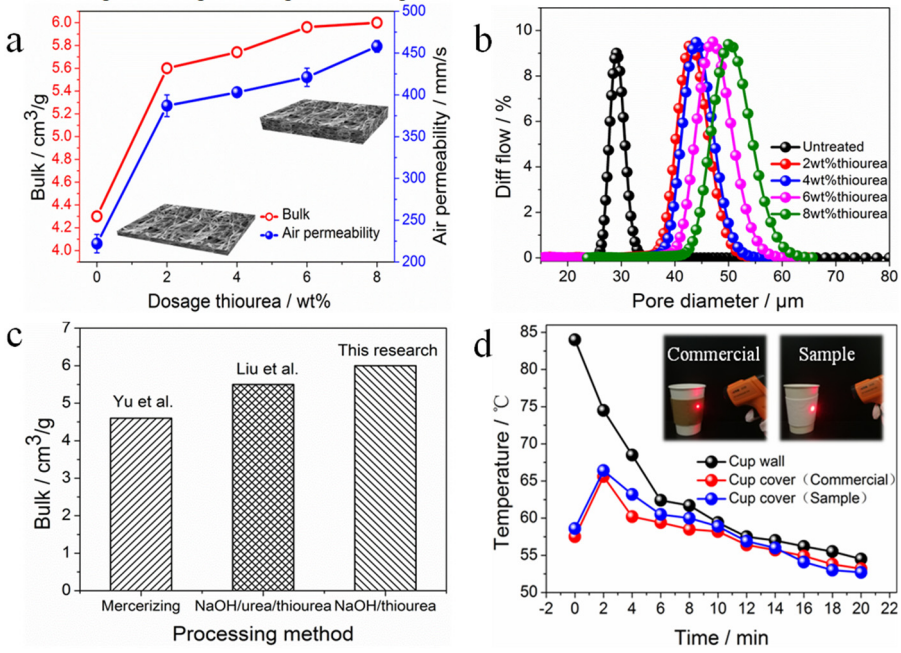

Figure 4. Effect of the amount of thiourea on the bulk and air permeability of paper (a) and effect of the amount of thiourea on the pore diameter of paper (b) and comparison of paper bulk obtained by different fiber treatment methods (c) and thermal insulation test of sample(d).

4. Conclusion

We studied the effect of low-level NaOH/thiourea mildly treated softwood pulp on the surface morphology and paper-forming properties of cellulose fibers. The results show that the NaOH/thiourea pretreatment makes the fiber swell, bend and kink, and can partially dissolve the fiber surface and the tail end, the paper has a high bulk, good air permeability, and is soft and porous. This high-bulk paper has potential development prospects in air filtration media and insulation materials. The samples prepared in this experiment have the advantages of light weight, softness and fast heat dissipation compared with commercial insulated sleeves for coffee cups. The shape of the bent-wound fiber destroys the structure in which the original flat fibers are closely packed and forms a large number of voids. The formation of a thiourea-hydroxy complex during the reaction can also significantly reduce the formation of hydrogen bonds between the cellulose molecules, the paper structure is more swelled and has a higher bulk.

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