Self-Reinforced Grease-Resistant Sheets Produced by Paper Treatment with Zinc Chloride Solution

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A method for the production of paper with high strength and grease resistance was developed. Filter paper was impregnated by an aqueous solution of zinc chloride at a fixed temperature for several seconds. Swelling and partial dissolution of the cellulose fibers resulted in strong and compact paper. Various influencing factors were investigated in an attempt to improve the grease resistance of the paper. In addition, the structural properties of the zinc chloride-treated paper were investigated using a Fourier transform infrared (FT-IR) spectrometer, X-ray diffraction (XRD), and a scanning electron microscope (SEM). Paper treated in this manner was completely grease resistant, had greater stretch, and twice as high tensile strength when compared with untreated paper, while its burst strength more than doubled. Paper treated according to this method had the skeleton of un-dissolved cellulose fibers and the matrix of gelled cellulose. The cellulose of the paper was not chemically modified during this process.

Keywords: Cellulose fibers; Grease barrier; Mechanical properties; Zinc chloride solution

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INTRODUCTION

Paper is widely used for wrapping and packaging because of its excellent biocompatibility and good thermal and mechanical properties. Furthermore, paper is a natural material and represents a promising solution to the environmental problems caused by plastic wastes; however, grease permeates through paper pores, which is driven by capillary forces (Kjellgren 2005). To extend the use of paper to some specific applications, the grease resistance of paper must be improved (Yang *et al*. 1999; Andersson 2008; Shen *et al*. 2014).

The grease resistance of paper is commonly improved by applying a thin, grease-impervious coating layer on the paper surface. Grease barrier materials from renewable resources, such as polysaccharides (*e.g*., starch (Tippit 2011), cellulose (Osterberg *et al*. 2013; Chen *et al*. 2014; Saarikoski *et al*. 2014), alginate (Jost *et al*. 2014), and chitosan (Kjellgren *et al*. 2006)) and proteins (*e.g*. corn zein (Anderson and Lamsal 2011), wheat gluten (Guillaume *et al*. 2010), whey protein isolate (WPI) (Chan and Krochta 2001), and isolated soy protein (ISP) (Bai *et al*. 2013)) have been employed for this purpose, alone or in various combinations. Chitosan, zein, and cellulose, however, have limited commercial applications owing to their high cost (Kjellgren *et al*. 2006; Elsabee and Abdou 2013), and the strength of films made from ISP and WPI are not sufficient for packaging. The addition of plasticizers (*e.g.*, glycerol) into ISP and WPI improves the mechanical properties of the coatings but the migration of the plasticizer into the paperboard can lead to cracking of the

coating during extended application, thereby weakening the grease resistance of the coated paperboard (Lin and Krochta 2003; Nerin and Asensio 2007).

Chemical treatment to the structure of paper is an alternative approach to increasing its grease resistance. Specifically, if the cellulose fibers can be swollen and partially dissolved in a suitable solvent system, then after drying the swollen and dissolved cellulose can fill the pores between fibers, thus reducing the sheet porosity, and serving as a glue binding the un-dissolved fibers. After regeneration, a continuous barrier is formed either on the paper surface or within the fiber network, which prevents oil or grease penetration. The known cellulose solvent systems include sodium hydroxide (NaOH) (Kihlman *et al*. 2012), NaOH or LiOH /urea or thiourea solutions (Yan *et al*. 2007; Li *et al*. 2010), mineral acids (Vaha-Nissi *et al*. 2001), N-methylmorpholine-N-oxide (NMMO) (Ouajai and Shanks 2009), lithium chloride/N, N-dimethylacetamide (LiCl/DMAc) (Nishino *et al*. 2004; Arevalo *et al*. 2010), various ionic liquids (ILs) (Duchemin *et al*. 2009; Huber *et al*. 2012), and various molten salt hydrates (Xiong *et al*. 2010; Chen and Wu 2011). Among these chemical agents, inorganic salt hydrates are inexpensive, environmentally friendly, and efficient solvents for cellulose and its derivatives with a wide range of degrees of polymerization (Leipner *et al*. 2000). The paper mechanical properties and grease resistance could be improved as it was treated in 7% NaOH/12% urea solution at -12 °C for 120 min in our previous study (Ma *et al.* 2014). However, the revere treating condition at -12 °C limits the possibility in pilot and industrial production. Zinc chloride is also a well-known effective swelling agent of cellulose in inorganic salt hydrates (Lu and Shen 2011; Zhu *et al*. 2013; Jiang *et al*. 2015).

Concentrated zinc chloride solutions under certain conditions such as higher temperature cause either swelling or dissolution of cellulose, which could serve for mercerization of cotton, manufacture of vulcanized paper or cellulose film, preparation of spinning solutions, and forming of regenerated cellulose fibers. Moreover, zinc chloride could been completely recycled through a recovery process. (Phillips 1965; Hamed *et al*. 1995; Xiong *et al*. 2010; Zhu *et al*. 2013; Jiang *et al*. 2015). Compared with the NaOH/urea system, the operation and chemical recovery are much easier to operate in industrial scale. Until now, however, zinc chloride has not been used for the production of grease-resistant paper. This study explores the treatment of paper by zinc chloride solution and the effects of various process parameters on the grease resistance, mechanical properties, and structure of the product. The key objective of this work is the development of an environmentally friendly and easy technology for the production of paper with high grease resistance and improved mechanical strength.

EXPERIMENTAL

Materials

Filter paper with a base weight of 103 g/m^2 and diameter of 18.5 cm (P4 qualitative and slow flow rate) was purchased from Fisher Scientific International Inc. (Pittsburgh, UK). The paper was made from cellulose fibers with a degree of polymerization (DP) of about 830. Zinc chloride was purchased from Fisher Scientific International Inc. (Ottawa, CA). All chemicals were of analytical grade and used as received.

Preparation of Paper Treated with Zinc Chloride Aqueous Solution

Zinc chloride aqueous solution was prepared by mixing zinc chloride and distilled water (from 60:40 to 80:20 by weight). The filter paper was immersed for several seconds in the solution preheated to the desired temperature. Subsequently, the samples were pressed for 5 min at 3.85 kPa between two clear plastic sheets and kept humid for a few minutes at an ambient temperature. Then, the treated papers were rinsed with deionized water to extract the zinc chloride. Finally, the samples were constrained on a stainless-steel disk with clips and dried in an oven for 12 h at 60 °C. The yield was determined based on the sample weight before and after the treatment.

Mechanical Properties

Samples were conditioned at 23 °C and 50% relative humidity (RH) for 48 h before measuring the mechanical properties, including tensile strength, stretch, tear strength, and burst strength. Tensile strength and stretch were measured in accordance with TAPPI method T 494 om-01 (2001) using a Lorentzen and Wettre (L&W) tensile tester (063, L&W, Sweden) and the tear strength was measured according to TAPPI method T 414 om-04 (2004) using a Lorentzen and Wettre (L&W) tear tester (045, L&W, Sweden). The burst strength was determined by TAPPI method T 403 om-02 (2002) with a TMIC burst-200 tester (200, TMIC, Canada). Reported results are the average values of 10 parallel tests.

Density and Porosity of Paper

The density was calculated from the grammage and thickness of the paper. The grammage was measured based on TAPPI method T 410 om-02 using an electronic balance. The thickness was measured based on TAPPI method T 551 om-12 (1998) using a Lorentzen and Wettre (L&W) paper thickness tester (250, L&W, Sweden). The porosity of the samples was measured in accordance with ISO 15901-1:2005 using a mercury intrusion porosimetry (Autopore IV 9500 V1.06, Micromeritics, USA).

Testing of Grease Resistance

The grease resistance of the papers was determined according to a modified TAPPI method T-507 cm-99 "Grease Resistance of Flexible Packaging Material". Paper samples (9 × 9 cm) were cut and then placed between two sheets: one clean sheet (10 × 10 cm) on the bottom and one dyed fat-saturated sheet (7.5 × 7.5 cm) of bibulous blotting paper on the top. 1.0 mL of the stained fat was applied to saturate the blotter paper sheet. Stacks of the three-layered system were separated by aluminum foil sheets (15 × 15 cm), and a stainless-steel disk (d = 15.5 cm) with a weight of 700 g were placed on top of each other of up to 10 layers. The assembly was placed in an oven and incubated at 60 °C for 4 to 24 hours, and then the amount of grease that passed through the samples to the clean blotters was measured by a point-counting method (Trezza and Vergano 1994).

Characterization

SEM images

The cross-section and the surface of the samples were observed using a scanning electron microscope (SEM) (JSM-6400 (JOEL)) operated at an accelerating voltage of 10 kV. The cross-section was prepared by cutting the samples with a glass knife in the normal direction. The samples were mounted on a bronze stub and sputter-coated (Sputter coater SPI-Module, PA, USA) with gold prior to imaging.

FTIR measurements

5.0 mg of each dried and ground paper sample was dispersed in 200 mg of KBr and pressed into a disk for FTIR measurement, which was carried out using a Nicolet 30 spectrometer (Thermo Electro, USA). Thirty-two scans were taken for each sample at a resolution of 4 cm^{-1}.

X-ray diffractions

X-ray diffraction graphs were produced by a D8 ADVANCE machine (Bruker, Germany). The Cu Kα radiation generated at 40 kV and 40 mA was irradiated on the specimen perpendicular to the surface. The scanning range was from 10° to 40° with a step length of 0.02° and scanning speed 17.7 s/step. The crystallinity (Cr) was calculated using the following Segal's equation according to the general method (Zhu *et al*. 2013),

$$Cr=\frac{I_{002}-I_{am}}{I_{002}} \quad (1)$$

where I_{002} and I_{am} are the peak intensities for (002) (2θ =22.6°) and peak intensity at 2θ = 19°, respectively.

Determination of the amounts of zinc ion

To examine the release behavior of Zn^{2+} from the treated papers, the corresponding samples were weighed. Paper samples (2 cm × 2 cm) were immersed in vials with 10 mL of distilled water and treated up to one week in 37 °C in an orbital shaker at 200 rpm shaking. Then the samples were removed and then solutions were analyzed by an AA900T flame atomic absorption spectrometry (FAAS) (Perkin Elmer, USA) with HCl-HNO_3 digestion. The residual Zn^{2+} in the treated paper was also evaluated. The sample was burned to ash, and digested with HCl-HNO_3, then measured by FAAS.

RESULTS AND DISCUSSION

Effect of Treatment Time on the Grease Resistance of Paper

A very fast dissolution of cellulose in the zinc chloride aqueous solution was found at a 1:4 molar ratio of $ZnCl_2$:H_2O and temperatures higher than 65 °C. Moreover, the maximal concentration of the dissolved cellulose in the zinc chloride aqueous solution reached 5.5 wt%, and was homogenous at room temperature (Leipner *et al*. 2000; Xiong *et al*. 2010; Lu and Shen 2011). The intention of the present study was to make the fibers in the paper swollen and partially dissolved, but not completely dissolved, in which the partially dissolved cellulose is still associated with the fibres, and serves as a glue to join the un-dissolved fibers together when the cellulose comes out of solution. Various parameters of the zinc chloride aqueous solution were investigated. In the first series of experiments, the filter paper was immersed in the zinc chloride solution for different time intervals to allow the zinc chloride to penetrate into the interior of the paper over various durations. The zinc chloride concentration was 65% and the treatment temperature was 70 °C. The control sample was a blank filter paper not treated by $ZnCl_2$ solution.

As shown in Table 1, cellulose swelling and dissolution resulted in some yield loss caused by the dissolution of cellulose during impregnation and washing. Cellulose was dissolved much more when the treatment time was longer than 5 s, suggesting that the dissolution of cellulose in the zinc chloride solution was very fast. Table 1 also illustrates

that the zinc chloride solution treatment had also a significant effect on the grease resistance of the paper when the treatment time was longer than 2 s. When the paper was treated longer than 5 s, no grease passed through the paper in a 24-h period; however, the product yield was decreased dramatically. At the longer treatment times, the fibers severely swelled, the gel of partially dissolved cellulose covered the fiber surfaces, and, upon regeneration, an all-cellulose composite was formed. This process decreased paper porosity, and increased its density and grease resistance. Taking yield and grease resistance into consideration, 5 s was chosen as the optimum treatment time.

Table 1. Effect of Treatment Time on the Grease Resistance of Paper

Treatment Time (s)			Control	2	5	10	15
Yield (%)		Mean	100.0	98.0	94.1	70.2	59.6
		Std. Error	0	0.7	2.1	5.4	4.8
Density (g/cm^3)		Mean	0.56	0.73	1.30	1.33	1.32
		Std. Error	0.03	0.02	0.01	0.01	0.01
Porosity (%)		Mean	63.9	52.9	16.1	14.2	14.8
		Std. Error	3.2	2.6	0.8	0.7	0.7
Stained Area (%)	4 Hours	Mean	60.3	32.6	0	0	0
		Std. Error	9.1	7.3	0	0	0
	8 Hours	Mean	74.4	69.7	0	0	0
		Std. Error	11.3	8.9	0	0	0
	24 Hours	Mean	94.2	86.9	0	0	0
		Std. Error	1.5	5.4	0	0	0

Effect of $ZnCl_2$ Concentration on the Grease Resistance and Strength of Paper

To reveal the effect of zinc chloride concentration on the paper grease resistance and strength, the samples were treated with various zinc chloride concentrations at 70 °C for 5 s. The results are shown in Table 2 and Fig. 1.

Table 2. Effect of $ZnCl_2$ Concentration on the Grease Resistance of Paper

$ZnCl_2$ Conc. (%)			Control	60*	65	70	75	80
Yield (%)		Mean	100	97.3	94.1	94.5	84.1	74.2
		Std. Error	0	1.7	2.1	2.1	4.6	4.3
Density (g/cm^3)		Mean	0.56	1.13	1.30	1.30	1.32	1.33
		Std. Error	0.03	0.02	0.01	0.01	0.01	0.01
Porosity (%)		Mean	63.9	27.1	16.1	16.1	14.8	14.2
		Std. Error	3.2	1.4	0.8	0.8	0.7	0.8
Stained Area (%)	4 Hours	Mean	60.3	10.8	0	0	0	0
		Std. Error	9.1	1.3	0	0	0	0
	8 Hours	Mean	74.4	29.7	0	0	0	0
		Std. Error	11.3	4.2	0	0	0	0
	24 Hours	Mean	94.2	40.9	0	0	0	0
		Std. Error	1.5	3.9	0	0	0	0

* This sample was full of grease after 72 h.

As seen in Table 2 and Fig. 1, zinc chloride concentration had an important effect on the yield, paper porosity, paper grease resistance, and paper strength. At a high zinc chloride concentration, the yield and porosity decreased, and the grease resistance and strength of the paper increased. When the zinc chloride concentration was 65 wt%, the paper samples reached excellent grease resistance and the highest strength. It is well known that zinc chloride aqueous solutions less than 65 wt% concentration are not able to dissolve cellulose (Leipner *et al*. 2000; Xiong *et al*. 2010; Chen and Wu 2011; Lu and Shen 2011). At a zinc chloride concentration greater than 65%, Zn^{2+} interacts with the hydroxyl oxygen of the cellulose molecular chain. This weakens the intermolecular hydrogen bonding and diminishes the crystalline regions. As a result, more fibers swell, and become more flexible or even partially dissolved. Fiber swelling increases the contact between the fibers. Partially dissolved cellulose is mixed with swollen fibers to form a matrix that anchors the un-dissolved fibres during regeneration to form a strong, impermeable sheet.

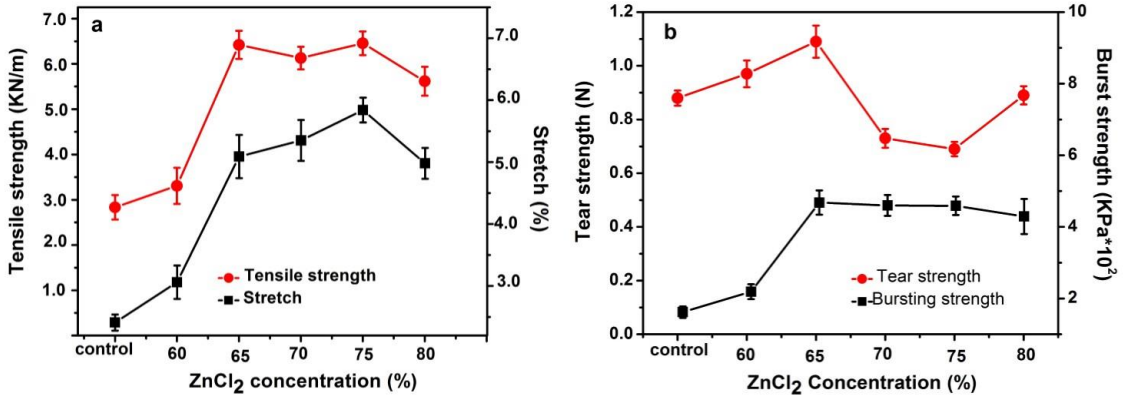

Fig. 1. Effect of $ZnCl_2$ concentration on paper properties: (a) tensile strength and stretch and (b) tear and burst strengths

Effect of Treatment Temperature on the Grease Resistance and Strength of Paper

The swelling and dissolution rate of cellulose fibers in zinc chloride solution depend heavily on the temperature (Lu and Shen 2011). The effect of treatment temperature on the grease resistance and paper strength was investigated at a fixed concentration of 65 % and a reaction time of 5 s.

Table 3 and Fig. 2 show that the grease resistance and strength of the paper increased with the increasing temperature. When the treatment temperature was 65 °C, the treated paper completely blocked grease for 24 hours. The stretch increased with temperature up to 70 °C, but was lower at 75 °C. The tensile strength obtained at the treatment temperature of 70 °C was twice as high as that of the control sample. The burst strength more than doubled and the tear strength tripled when the treatment was carried out at 75 °C; however, at this high temperature more fibers were dissolved and lost during washing, decreasing the yield to less than 90%. It has been reported that cellulose fibers of filter paper with high crystallinity and high degree of polymerization (DP) (Nishiyama *et al*. 2002; Nishino *et al*. 2004) need a higher temperature to swell and dissolve. Taking all factors into consideration, 70 °C was chosen as the optimum swelling and dissolution temperature. Under these conditions, the zinc chloride aqueous solution could markedly enhance the grease resistance of the paper and the paper strength.

Table 3. Effect of Treatment Temperature on the Grease Resistance of Paper

Treatment Temperature (°C)			Control	60	65	70	75
Yield (%)		Mean	100.0	96.2	95.5	94.1	84.1
		Std. Error	0	0.5	1.1	2.1	4.6
Density (g/cm^3)		Mean	0.56	1.09	1.28	1.30	1.32
		Std. Error	0.03	0.02	0.01	0.01	0.01
Porosity (%)		Mean	63.9	29.7	17.4	16.1	14.8
		Std. Error	3.2	1.3	0.9	0.8	0.7
Stained Area (%)	4 Hours	Mean	60.3	21.0	0	0	0
		Std. Error	9.1	4.4	0	0	0
	8 Hours	Mean	74.4	49.3	0	0	0
		Std. Error	11.3	7.3	0	0	0
	24 Hours	Mean	94.2	84.3	0	0	0
		Std. Error	1.5	6.9	0	0	0

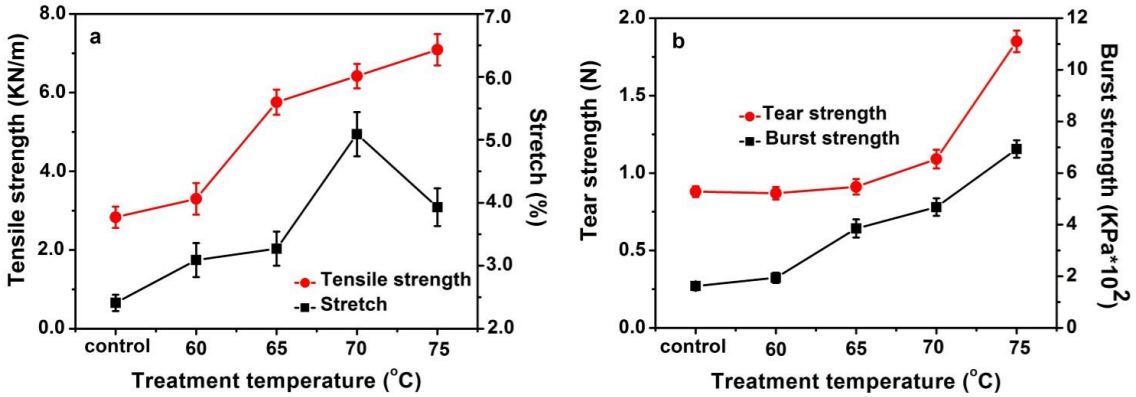

Fig. 2. Effect of treatment temperature on paper properties: (a) tensile strength and stretch and (b) tear and burst strengths

Effect of Aging Time at Room Temperature on the Grease Resistance and Strength of Paper

It was also found that the samples would gradually be dissolved if kept in the $ZnCl_2$ solution at room temperature for a long enough time until full swelling. The effect of aging time at room temperature on the grease resistance and strength of the paper, which was treated at temperature of 70 °C in $ZnCl_2$ concentration of 65 % for 5 s, was investigated.

Table 4 and Fig. 3 demonstrate that the grease resistance and strength of the paper were not significantly improved after a longer aging time at room temperature. When the aging time at room temperature was 30 min, the stretch was lower and the tensile strength was slightly higher. The tear strength, however, increased only after an aging time of 45 min. It can be concluded that longer aging time at room temperature would not offer a better way to prevent the degradation of fibers and improve the properties of the treated paper.

Table 4. Effect of Aging Time at Room Temperature on the Grease Resistance of Paper

Aging Time at Room Temperature (min)			Control	0	15	30	45
Yield (%)		Mean	100.0	94.10	93.73	93.39	83.38
		Std. Error	0	2.1	3.4	2.7	1.3
Stained Area (%)	4 Hours	Mean	60.3	0	0	0	0
		Std. Error	9.1	0	0	0	0
	8 Hours	Mean	74.4	0	0	0	0
		Std. Error	11.3	0	0	0	0
	24 Hours	Mean	94.2	0	0	0	0
		Std. Error	1.5	0	0	0	0

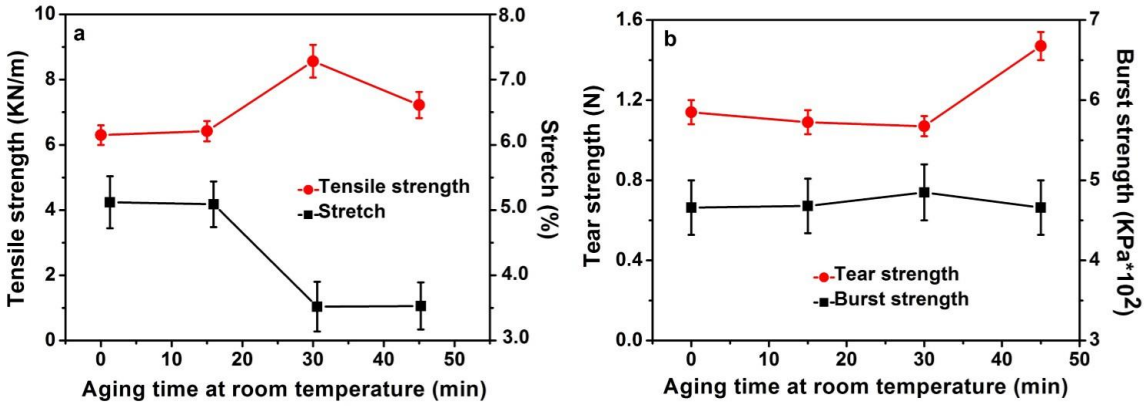

Fig. 3. Effect of aging time at room temperature on paper properties: (a) tensile strength and stretch and (b) tear and burst strengths

Structure Differences of Cellulose and Paper after $ZnCl_2$ Solution Treatment

Morphology of paper

In this work, the swelling and dissolution of cellulosic fibers were studied by observing the progressive morphological changes of the paper fibers using an electron scanning microscope.

Figure 4 shows that there are more pores in the untreated filter paper than in the paper treated with $ZnCl_2$ solution. This is due to the fact that the partially dissolved cellulose covered the surface of the fibers. The SEM images of the cross sections of the treated paper reveal that the paper was highly compact and had low porosity. The $ZnCl_2$ solution treatment made the paper more compact and less porous. One can assume that $ZnCl_2$ caused initial swelling of the readily accessible amorphous regions of the cellulosic fibers. During swelling and partial dissolution of fibers, some intermolecular hydrogen bonds in the fiber are destroyed. Upon regeneration of the partially dissolved cellulose, the swollen cellulose formed a matrix that imbedded the un-dissolved fibers forming an all-cellulose composite. The partial dissolution and regeneration of the cellulose decreased the number of pores in the sheet and the pore size of the remaining pores, thus reducing the sheet porosity; moreover, this matrix improved fiber-fiber adhesion. As a result, the paper becomes less porous, resistant to grease passing, and stronger.

FT-IR results

Figure 5 shows the FT-IR spectra of the original filter paper and the paper treated by the $ZnCl_2$ solution. The FT-IR spectrum of the treated paper was similar to that of the filter paper, implying that there was no significant difference between the chemical bonds of the cellulose in the filter paper and treated paper. As can be seen from Fig. 5, there were characteristic peaks at around 3400 cm^{-1}, which can be assigned to –OH stretching intra-molecular hydrogen bonds. In addition, the peak at 3400 cm^{-1} of treated paper was obviously broadened and shifted to low wavelength, which suggested the increment of the intermolecular hydrogen bonding of cellulose (Abidi *et al*. 2014). The −CH stretching mode at 2901 cm^{-1} also shifted to lower wavenumber at 2891 cm^{-1}. Furthermore, the peaks at 1423 and 899 cm^{-1} were shifted to 1420 and 897cm^{-1}. Shifting to 1420 cm^{-1} suggested formation of new inter- and intra-molecular hydrogen bonds and a change of the conformation of CH_2OH at C-6 from the tg to gt form. The peak at 899cm^{-1} shifted to 897cm^{-1} assigned to C-O-C stretching at β-(1-4)-glycosidic linkage and corroborated some absence of crystalline cellulose I (Oh *et al.* 2005). These results indicated that a crystal transformation of cellulose I to cellulose II occurred in the regeneration process and more intermolecular hydrogen bonds were formed.

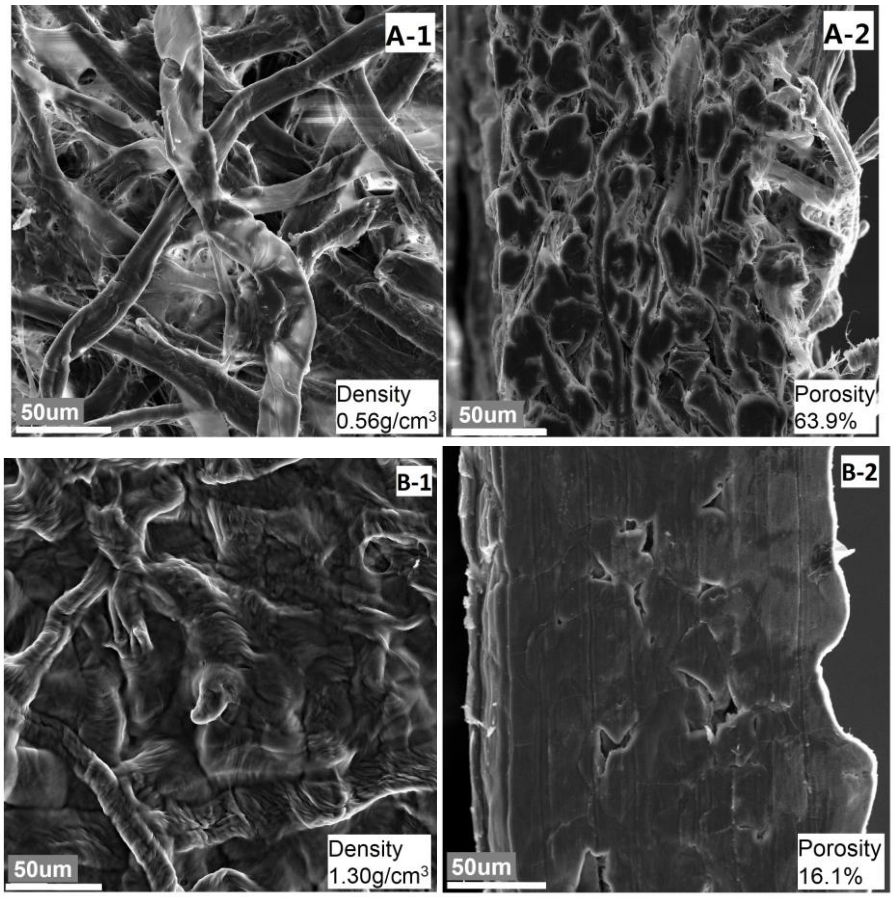

Fig. 4. SEM images of (A-1) the surface of the filter paper; (B-1) the surface of the treated paper; (A-2) the cross-section of the filter paper; and (B-2) the cross-section of the treated paper. The treatment conditions of sample B were 65% zinc chloride by weight at 70 °C for 5 s.

X-ray diffraction results

Figure 6 presents the X-ray diffraction profiles of the filter paper and the paper treated by the $ZnCl_2$ solution. In this figure, the filter paper showed three strong Bragg peaks at about 2θ = 15.2°, 16.8°, and 22.9°, which were indexed as the (101), (10ī), and (002) peaks of the typical cellulose I structure, respectively. Clearly, the filter paper is composed of typical natural cellulose with a crystal modification of cellulose I, which has a high degree of crystallinity (Nishiyama *et al.* 2002). The treated paper also had peaks at similar positions, but they were less clearly defined in (101) and (10ī). The crystallinity of the paper was calculated by Segal's equation. The crystallinity of filter paper dropped from 0.88 to 0.55 after $ZnCl_2$ treatment, which suggested partial crystalline cellulose were dissolved in $ZnCl_2$ solution. In other words, the filter paper had a high crystallinity, whereas the treated paper possessed a lower crystallinity. As the reaction of zinc ion with cellulose weakens the intermolecular hydrogen bonding, part of the crystalline region is damaged so that the crystallinity is decreased; however, the main peak at 2θ=23 is clearly visible even in the treated paper profiles. This indicates that the majority of the crystallinity was preserved even in the treated paper.

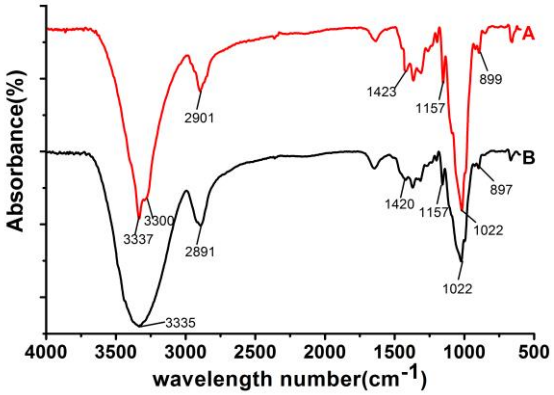

Fig. 5. FT-IR spectra of (A) filter paper and (B) treated paper*

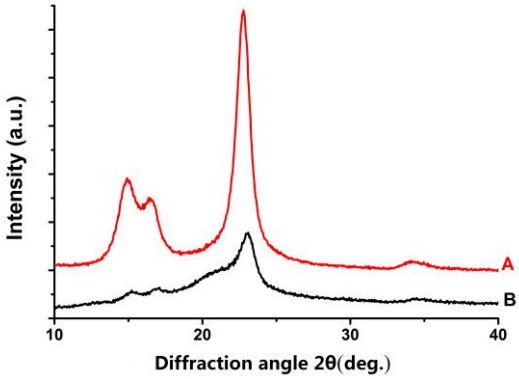

Fig. 6. X-ray diffraction profiles of (A) filter paper and (B) treated paper with $ZnCl_2$*

* The treatment conditions of sample B were 65% zinc chloride by weight at 70 °C for 5 s

As a kind of heavy metal, the residual Zn^{2+} in the treated paper is close to its application of the final product. The amount of Zn^{2+} released from treated paper was determined by flame atomic absorption spectrometry (FAAS). For the solution containing 2cm×2cm paper sample over one week, there was no absorption of Zn^{2+} as detected by FAAS, this implied that there was no Zn^{2+} released from the treated paper. The residual Zn^{2+} in the treated paper was only 3.64 ug/g cellulose and it could be considered the final product was composed by 100% cellulose. The treated paper could be used as a package product with high grease resistance, such as food-wrapping paper.

In the 60 to 70 wt% concentration range, low-DP water soluble and insoluble celluloses could be prepared from native cellulose. The partial dissolution of the cellulose results in the lowering of paper porosity and improving of grease resistance. Moreover, zinc chloride is stable with low toxicity, and can be recovered and reused economically; therefore, zinc chloride treatment of cellulose is a promising route for the production of inexpensive paper with high grease resistance.

CONCLUSIONS

1. A new method to improve the mechanical properties and grease resistance of paper has been developed, which involves the treatment of paper with zinc chloride aqueous solution. The optimal conditions are 65 % zinc chloride by weight at 70 °C for 5 s.
2. This treatment by zinc chloride is relatively easy to operate, and it is possible to realize the pilot and industrial production.
3. The treated paper is a little brittle. Our further work will focus on the application of plasticizing agents to modify the brittle property of the treated paper.

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