Ionic Liquids as a New Platform for Fiber Brittleness Removal

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In the present study, three ionic liquids, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-allyl-3-methylimidazolium ([AMIM]Cl), and 1-ethyl-3-methylimidazolium chloride dimethyphosphate ([EMIM]DMP), were used to eliminate the brittleness of recycled fibers. The results showed that the pretreatments with ionic liquids were able to modify and improve the properties of recycled fibers even at high moisture contents. [EMIM]DMP gave better performance compared to [BMIM]Cl and [AMIM]Cl, which can tolerate higher moisture contents. The optimal conditions of EMIM]DMP pretreatment were moisture content of 65%, [EMIM]DMP dosage of 20 wt-%, 80 °C, and 60 min, for which a higher brittleness removal was obtained. The tensile index, bursting index, and tearing index of handsheets were increased by 32.4%, 57.0%, and 46.5%, respectively. Fiber quality was improved as demonstrated by fiber length, lowered fines content, and increased swellability. Such results imply that ionic liquids pretreatment can promote the swelling of recycled fibers and remove their brittleness.

Keywords: Recycled fibers; Ionic liquids; Pretreatment; Brittleness

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INTRODUCTION

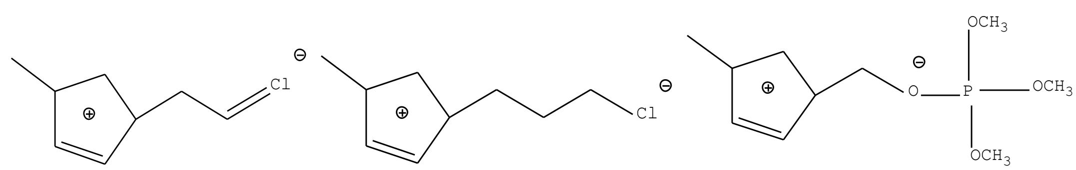
Recycled fibers are an important feedstock for addressing shortfalls in the availability of lignocellulosic materials and reducing environmental concerns (Abbasi and Abbasi 2010). Worldwide, the amount of paper recycled *per annum* has increased, but the quality of recycled paper has been deteriorating (Ampulski 1985; Waterhouse and Liang 1995; Xiao 1999; Wahlstrom 2000). This reduction is principally due to reduced bonding between fibers because of their stiff structure, which results from the formation of internal hydrogen bonds and contraction of the cell lumen, a phenomenon known as “hornification” (Barzyk and Page 1997; Tze and Gardner 2001). Consequently, the physical properties of final paper products diminish (Carlsson and Lindström 1984; Seth 2006). In particular, the drying of kraft fibers leads to a decrease of water absorption capacity and an increase of brittleness (Thode *et al.* 1955; Stone and Scallan 1968) and poorer properties in the final products (Somwang *et al*. 2002).

Several methods, such as mechanical refining, chemical treatment, and enzyme modification, have been used to mitigate the effects of brittleness. Mechanical refining can damage the brittle fibers, producing more fines and reducing drainability (Howard 1990). Chemical treatment can improve the properties of recycled fibers at the expense of high pollution and costs (Shen *et al.* 2002). Enzymatic treatment, using cellulase products, is generally conducted at mild conditions with low efficiency, resulting in only slight improvements (Burton 2003; Nicotra *et al.* 2004a,b; Mohandass *et al.* 2008; Witayakran *et al.* 2009; Yang *et al.* 2011). Therefore, an environment-friendly and low-cost method to remove brittleness is needed.

Ionic liquids (ILs), salts that melt near ambient temperature, demonstrate total non-volatility, high oxidative and thermal stabilities, and possess a wide liquid temperature range. Based on such attributes, they can be regarded as green solvents for biomass. Specifically, ILs containing chloride and similar anions are able to effectively dissolve lignocellulosics by disrupting the network of recalcitrant and extensive intermolecular and intramolecular hydrogen bonds. ILs are believed to be non-derivatizing solvents for cellulose dissolution (Zhu *et al.* 2006; Fort 2007). Swatloski first demonstrated that 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) can solubilize cellulose under conventional heating to dissolve up to 25 wt-% cellulose for a homogeneous solution (Swatloski *et al.* 2002), while 1-propylene-3-methylimidazolium chloride is only effective up to 5 wt-% (Ren *et al.* 2003).

Only approximately 20 kinds of ILS have been verified to dissolve cellulose effectively (Lee *et al.* 2009). 1-allyl-3-methylimidazolium ([AMIM]Cl, Structure I) and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl, Structure II) show powerful dissolving abilities, while 1-ethyl-3-methylimidazolium dimethyphosphate ([EMIM]DMP, Structure III, phosphate salts) also has good dissolving power with decreased viscosity.

The increase of brittleness is considered to be an irreversible physical and chemical change in plant cell walls that leads to diminished surface area and increased crystallinity. Therefore, brittleness of recycled fibers is a limiting factor in their effective utilization. In previous studies, ILs were found to effectively disrupt hydrogen bonds (Pang *et al.* 2013). However, high water content during pretreatment process has been shown to have a detrimental effect on the performance of ILs. The current report shows an improved performance in recycled fibers from ionic liquid(IL) pretreatment, even at high moisture contents.



(I) (II) (III)

Fig. 1. Structures of cations/anions of ionic liquids

EXPERIMENTAL

Materials

Recycled fibers were taken from a paper mill in Shandong Province, China, as feedstock. Recycled fibers used in the experiment were deinked chemical pulp. The contents of cellulose, hemicellulose and lignin were respectively 80.6%, 18.4%, and 2.2%. The feedstock was repulped using a H-272M Formax Micro-Maelstrom high-consistency hydropulper (Dover, NH) in a lab at a consistency of 10% at 60 °C for 30 min.

The ILs of [AMIM]Cl, [BMIM]Cl, and [EMIM]DMP, with purities of ca. 99.0%, were purchased from Shanghai Chengjie Chemical Co., China and were used as received without further purification.

Methods

Ionic liquid pretreatment

Twenty grams of feedstock was mixed homogeneously with an IL in a polythene bag and treated at a given temperature with a residence time of 60 min. Then, 40 mL of ethanol was added to terminate the pretreatment, followed by thorough washing with water. The control group was treated with water alone in a volume commensurate to the IL used.

Fiber quality analysis

Fiber quality was analyzed using a fiber quality analyzer (FQA; Canada OpTest Company, model LDA02), to report fiber length, fines content, and width.

Methods of papermaking and testing

After pretreatment, the fibers were dispersed by a laboratory-scale defibrizer at concentration of 1.5% for 5000r without beating and diluted with water to a concentration of 0.3-0.5%. Then they were added into the automatic sheet-making apparatus to make the sheets. All of the sheets were treated at the environmental condition of constant temperature of 23 °C and humidity of 52% for more than 24 h before the testing. The tensile, tear, and bursting indices of sheets were respectively tested according to the TAPPI Methods T494, T414, and T810.

FTIR analysis

The FTIR spectra of the handsheets were recorded using a spectrophotometer (IRPretige-21, Shimadzu, Japan), scanning KBr-pellets from 4000 to 500 cm^{-1}.

Scanning Electron Microscope (SEM)

The sample was prepared as typically done: the freeze dried samples were spread on a circular base with double sided tape that has high conductivity and covered with a thin layer of gold. The samples were interrogated by SEM microscopy (Quanta 200, FEI) at 4,000× the original size.

RESULTS AND DISCUSSION

Effect of Moisture Content

Moisture content is known to significantly affect the performance of ILs. Specifically, the presence of water reduces the IL dissolving power while simultaneously maintaining the internal hydrogen bonding in the recycled fibers (Pang *et al*. 2014). Therefore, controlling moisture content during pretreatment is essential. The effects of moisture content on the physical properties of recycled pulp, *i.e.*, CSF, tensile indices, and burst indices, are reported in Fig. 2.

CSF increased with an increase of moisture content after [BMIM]Cl and [AMIM]Cl pretreatment, while the physical properties decreased. However, for [EMIM]DMP pretreatment, the CSF slightly decreased with an increase of moisture content. The tensile, tear, and bursting indices all increased and then decreased. At a moisture content of 65%, the tensile, tear, and bursting indices were improved to 6.44 N·m·g^{-1}, 0.38 mN·m^2·g^{-1}, and 0.23 kPa·m^2·g^{-1}. These results represent increases by 21.86%, 6.99%, and 14.33%, respectively. The improvement in physical properties demonstrated that ionic liquids can promote swelling, remove brittleness, and improve strength and toughness.

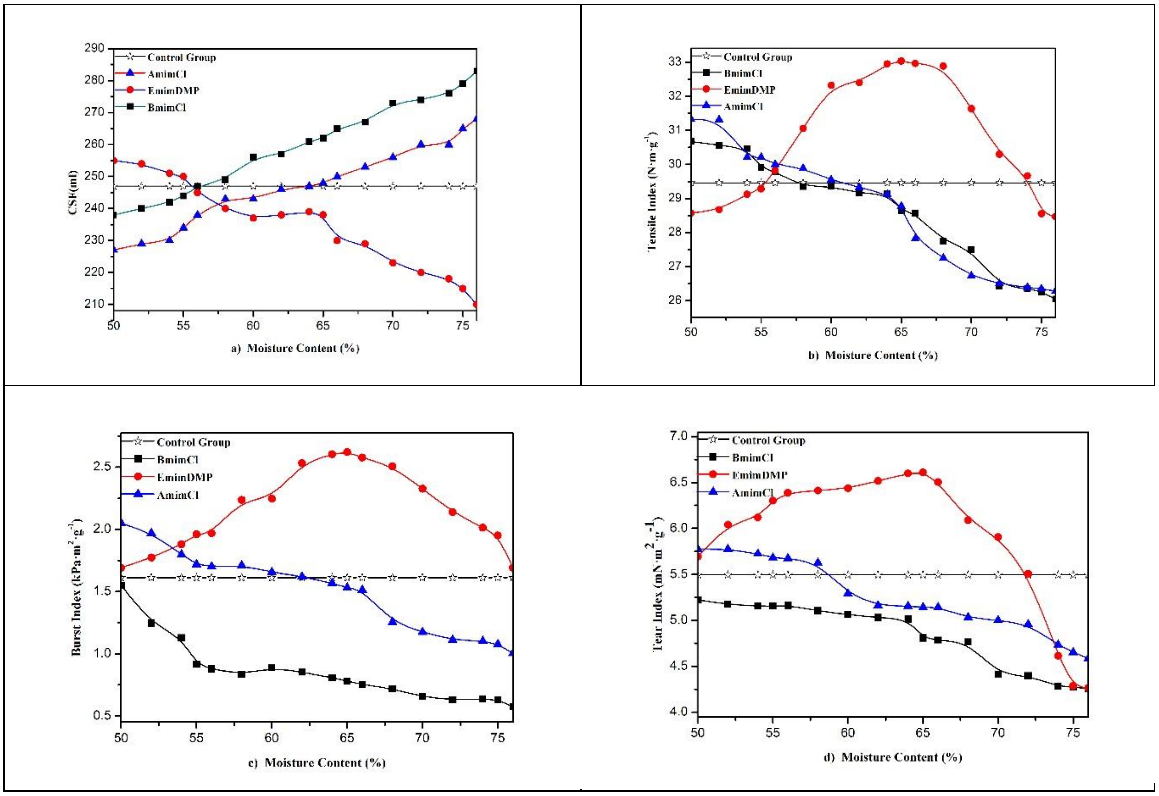


Fig. 2. Effect of moisture content on the physical properties of recycled fibers; the pretreatment was conducted at an IL concentration of 30 wt-% (based on oven-dried pulp) at 60 °C for 60 min

The improvements were not obvious when the moisture content was below 50%, which may be due to the high consistency, resulting in poor dispersion and stirring. Compared to that of [BMIM]Cl and [AMIM]Cl, the optimal properties of recycled fibers from [EMIM]DMP pretreatment were obtained at moisture contents up to 65% (Table 1). A decrease in pulp freeness value occurred at high levels of hydrogen bonds cleavage caused by fiber swelling. In addition, reducing the moisture of the recycled pulps can consume a large amount of energy, especially in the case of pulps with low moisture contents.

Moreover, flocculation occurred when the moisture content was lower than 50%. Such flocculation resulted in the formation of bridges among the recycled fibers, such that it was difficult to disperse pulp or fasciculi into single fiber during the defibering process, consequently leading to inferior uniformity of formation of the papers. After ILs pretreatment, the recycled fibers were partly oxidized, and also a part of fines were dissolved into the aqueous phase, both of these would loosen the fibers to facilitate easy separation. In other words, the treatment decreased the bonding between fibers.

Effect of IL Dosage

Having a sufficient dosage of ILs is critical for the dissolution of lignocellulose. However, overdosage can destroy the structure of recycled fibers, and the cost of IL recovery or regeneration can increase. The effect of [EMIM]DMP dosage on pretreatment is shown in Fig. 2. When the dosage of [EMIM]DMP was increased from 5 to 50 wt-%, the CSF values decreased from 297 to 230 mL, which indicated that a high level of cellulose swelling was achieved. When the [EMIM]DMP dosage was 20 wt-%, the tensile and tearing indices reached maximum values of 34.26 N·m/g and 5.88 $mN \cdot m^2 \cdot g^{-1}$, respectively. The burst index and folding endurance gradually increased with an increase of [EMIM]DMP dosage.

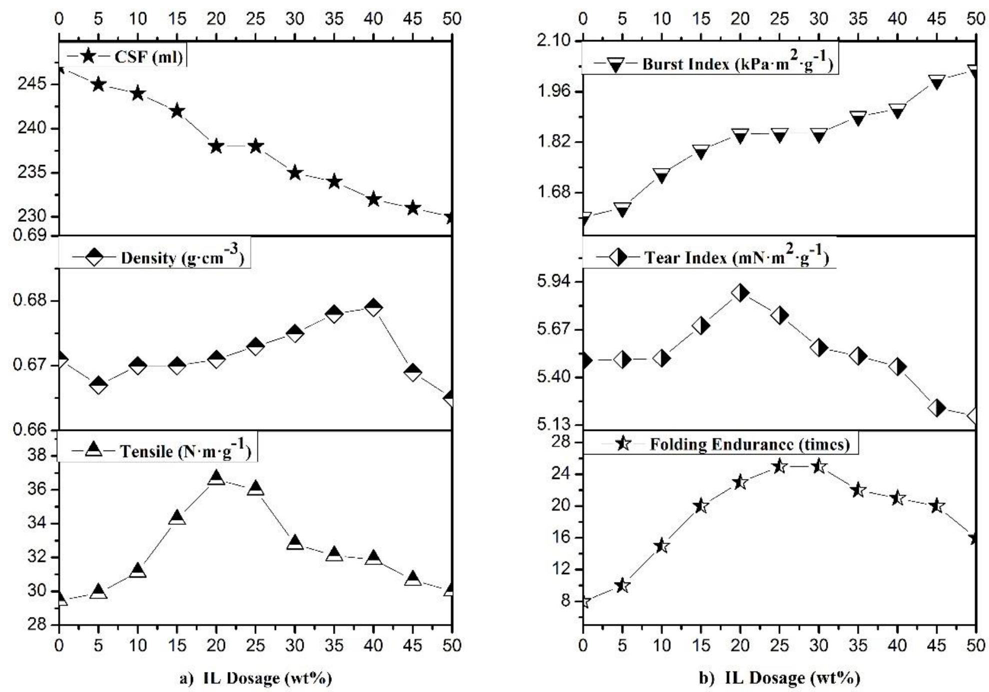


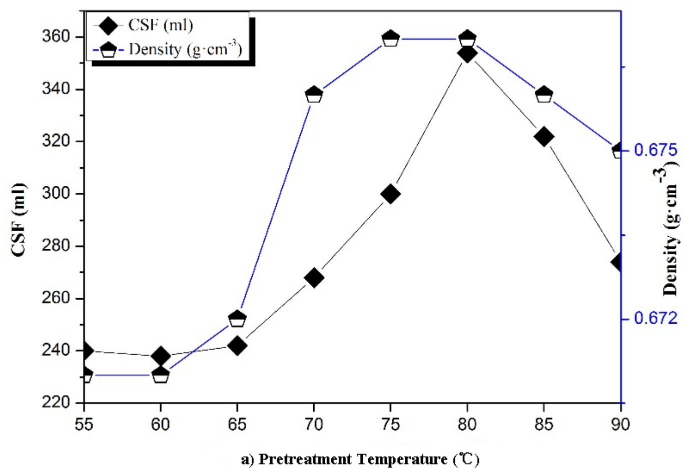
Fig. 3. Effect of IL dosage on the physical properties of the recycled fibers; pretreatment was conducted at a moisture content of 65% at 60 °C for 60 min

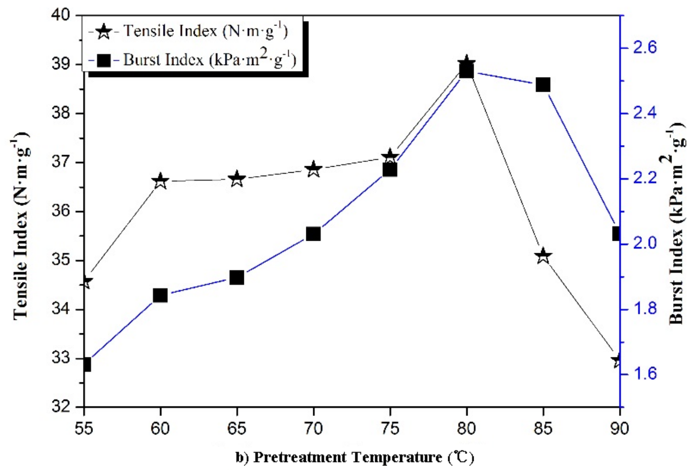
Effect of Temperature

The dissolution and regeneration rates of fibers increased at high temperatures, and degradation also occurred at the same time. A high pretreatment temperature led to severe fiber degradation with a decrease of physical strength and fiber quality. When the temperature was increased from 60 to 80 °C, the physical properties increased substantially (Fig. 4). However, reduction in physical properties was observed when the pretreatment temperature was increased to 90 °C.

Comparisons were made between different ionic liquids (Table 1). It can be seen from Table 1 that, compared to the control group, the freeness, tensile index, tearing index, and bursting index were improved 43.32%, 32.45%, 46.47%, and 56.95%, respectively, and the folding resistance was increased to 10 times that of the control. The ionic liquid pretreatment might decrease fiber shortening or fiber curl, allowing for more bonding sites. In addition, fiber width increased as a result of fiber swelling. Compared to [AMIM]Cl and [BMIM]Cl, improvement of recycled fibers was achieved at lower [EMIM]DMP dosage and temperature. The order of physical properties increase was as follows: [EMIM]DMP

> [AMIM]Cl > [BMIM]Cl. After [EMIM]DMP pretreatment, the fiber length and width had been increased by 4.50% and 3.03%, respectively, whereas the fines content decreased by 10.20% relative to the control. The effect of [EMIM]DMP was more favorable than that of other two ILs in reducing brittleness and improving physical properties.





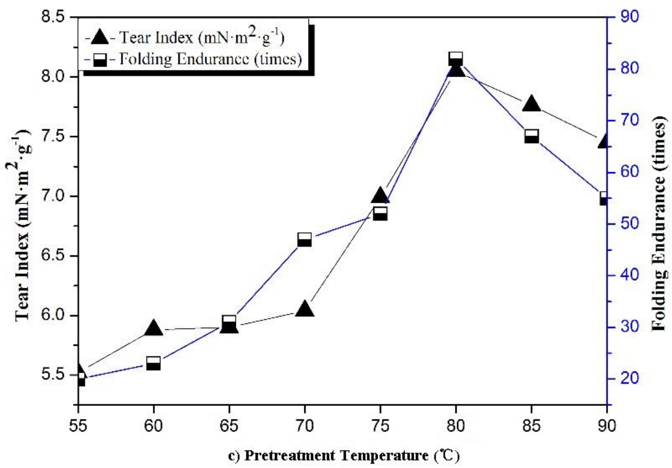


Fig. 4. Effect of temperature on physical properties; the pretreatment was conducted at a moisture content of 65% for 60 min with an [EMIM]DMP dosage of 20 wt-%

Table 1. Physical Properties of Handsheets Pretreated with Various ILs

ILs	Control group	[AMIM]Cl	[BMIM]Cl	[EMIM]DMP
Dosage (wt%)	--	25	30	20
Temperature (°C)	--	85	85	80
Fiber length (mm)	0.555	0.569	0.561	0.580
Fiber width (μm)	16.5	16.7	16.6	17.0
Fines content (%)	48.01	46.52	46.98	43.11
CSF (mL)	247	360	375	354
Tensile index (N·m/g)	29.46	28.85	26.74	39.02
Bursting index (kPa·m^2/g)	1.61	2.08	1.84	2.53
Tearing index (N·m/g)	5.49	7.09	7.93	8.05
Folding endurance (times)	8	61	45	82

Infrared Spectroscopy

FT-IR spectra were used to identify changes in the functional groups of the recycled fibers (Fig. 5). The peak of C=C stretching vibration in benzene occurs at 1510 cm^{-1}, which was unchanged after IL pretreatment, so it was selected as the internal standard. Correspondingly, the absorbance of the other peaks were expressed relative to the absorbance at 1510 cm^{-1} (Yang *et al.* 2013). Compared to the control group, the relative absorbance of the band at 3404 cm^{-1} increased 4.50%, which indicated a high level of exposed hydroxyls to promote fiber bonding and ultimately addressing the adverse effects of brittleness. A comparison of the samples revealed that minor chemical changes occurred during ILs pretreatment process.

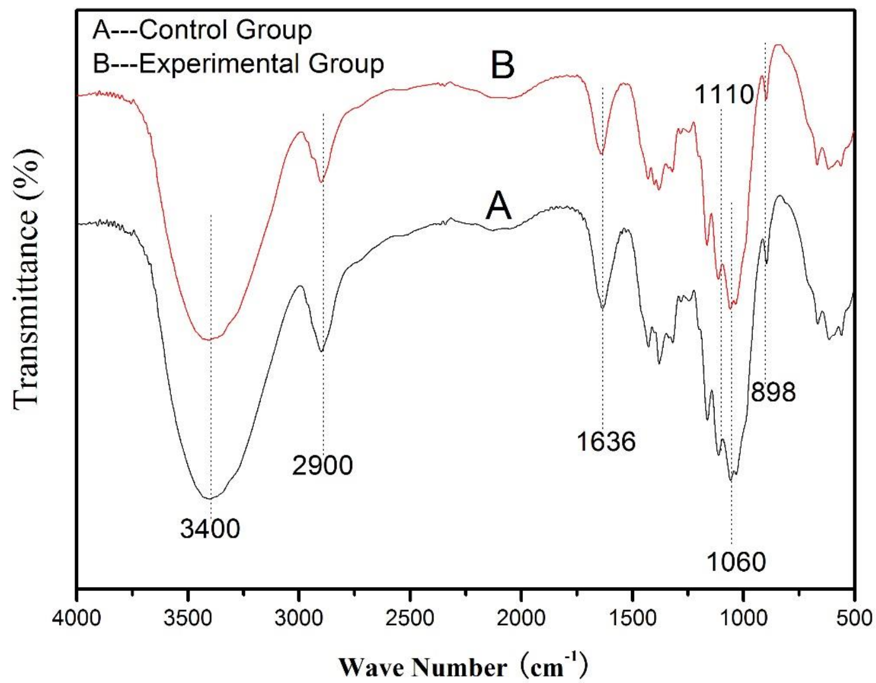
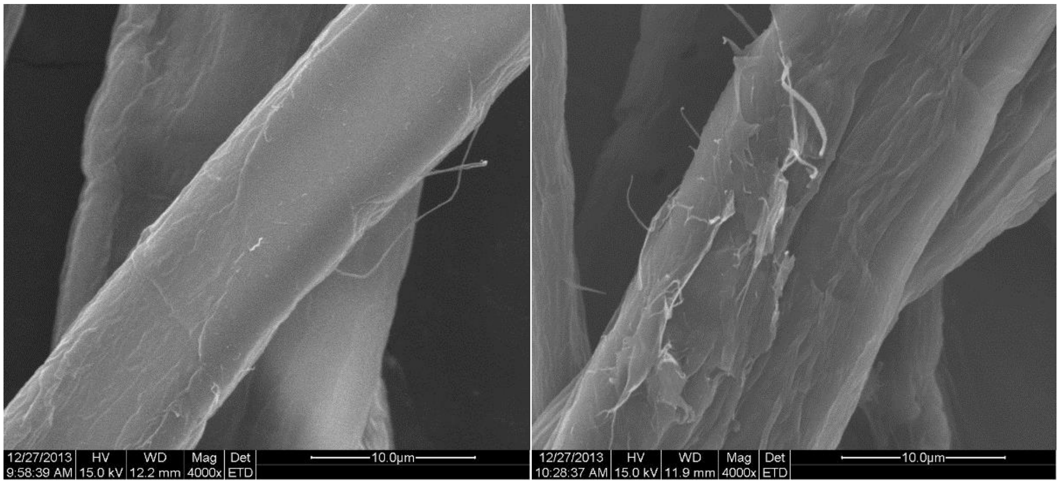


Fig. 5. FTIR spectra of (A) the control group and (B) the sample pretreated with [EMIM]DMP; pretreatment was conducted with a moisture content of 65% at 80 °C for 60 min at a dosage of 20 wt-%

SEM

The experimental samples were characterized by SEM (Fig. 6). As can be seen from Fig. 6, the smooth surface of the control group showed that part of fines would lie down and become attached closely to the fiber surface after repeated recycling. This would reduce the water-holding ability of the recycled fibers. On the other hand, the contraction of the cell lumen of recycled fibers (called hornification) would further decrease the water-holding ability. However, there was a greater degree of fibrillation on the surfaces of pretreatment fibers, which indicated that ILs treatment could promote fibrillation and the combination between fibers, thus increasing the physical properties of the paper. These changes on the fibers surface were conducive for fibers to absorb water and then to reduce brittleness of fibers.



(A) Control Group **(B) Experimental Group**

Fig. 6. SEM images of (A) the control group and (B) the sample pretreated with [EMIM]DMP; pretreatment was conducted with a moisture content of 65% at 80 °C for 60 min at a dosage of 20 wt-%

CONCLUSIONS

1. Ionic liquids treatment was able to improve the bonding ability of recycled fibers of deinked chemical pulp.
2. The effects of the ionic liquids [BMIM]Cl and [AMIM]Cl pretreatment decreased at high moisture contents, whereas [EMIM]DMP was tolerant of high water contents, resulting in brittleness removal.
3. The optimal conditions for [EMIM]DMP pretreatment were moisture content of 65%, dosage of 20 wt-%, 80 °C, and 60 min, in which the optimal physical properties and brittleness removal were obtained.
4. The quality of recycled fibers was obviously improved after [EMIM]DMP pretreatment as demonstrated by longer fiber length, reduced fines, and optimal swellability.

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