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Complete conversion of cellulose to water soluble substances by pretreatment with ionic liquids

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Abstract−Pretreatment of cellulose to water soluble substances (WSS) can enhance its efficient conversion in water solvent, such as ethanol fermentation. In this work, we found ionic liquid (IL), 1-methyl-3-methylimidazolium dimethylphosphate ([Mmim][DMP]), could convert efficiently cellulose to obtain WSS, and the product WSS and IL mixture could be separated by ethanol anti-solvent way. Effects of ILs, time, temperature and water on cellulose conversion were investigated. NMR, FTIR, XRD and SEM were employed to study the mechanism of cellulose conversion with ILs. The results indicate that [Mmim][DMP] has a greater ability to interact with cellulose than [Bmim][Cl] under the same conditions. Cellulose can be completely converted into WSS in [Mmim][DMP] under all the investigated temperatures from 140 to 160 °C. Increasing temperature is beneficial to the conversion rate of cellulose. But the presence of water can decrease the conversion rate of cellulose. During the treatment by [Mmim][DMP], the hydroxyls of cellulose can form hydrogen bonds with both anion and cation of [Mmim][DMP], and after the treatment the inter- and intramolecular hydrogen bonds of cellulose and the compact structure of cellulose are collapsed.

Key words: Cellulose, Ionic Liquids, Pretreatment, Hydrogen Bonds, Crystallinity

INTRODUCTION

Cellulose, the most abundant distributed biomass in nature, has been considered as a potential sustainable feedstock for energy production [1-3]. Studies on the conversion of cellulose have drawn much attention [4-8]. As we know, preparation of bio-ethanol by fermentation is a most promising way. However, cellulose forms a highly compact structure due to the presence of extensive intra- and inter-molecular hydrogen bonds, making it difficult to dissolve in water or other conventional solvents [9]. Therefore, cellulose must be first pretreated to deconstruct its compact structure to reactive intermediates before enzymatic hydrolysis [10-13].

The traditional methods of cellulose pretreatment mainly include physical processes [14,15] and chemical processes [16-19]. Physical processes typically have the disadvantages of high energy consumption and low efficiency. Chemical processes mainly use acids, alkalis and organic solvents, leading to pollution, toxicity and additional recovery steps. Ionic liquids (ILs), which are environmentally benign, recyclable and adjustable in structure, have attracted rapidly growing interest in treating cellulose [20-23]. IL 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) has been validated to have great dissolving power for cellulose, since its anion can form hydrogen bond with the hydrogen of hydroxyl group in cellulose [24-26]. However, it has high viscosity and toxic halogen ion that may limit its application. In addition, the regenerated cellulose after treatment with [Bmim][Cl] is still solid and insoluble in water. Yang et al. [25] reported that phosphate based ILs have low viscosity and high thermal stability. Besides, the electronegativity of O (3.5) in anion of phosphate-based ILs is stronger than that of Cl (3.0) in [Bmim][Cl]. This suggests that phosphate-based ILs may also have a strong ability to form hydrogen bonds with cellulose.

In this work, we aimed to deconstruct the crystalline structure of cellulose with a phosphate based IL, and convert cellulose to water soluble substances (WSS), which may be supplied for ethanol fermentation. We found that IL 1-methyl-3-methylimidazolium dimethylphosphate ([Mmim][DMP]) could be used as a solvent to completely convert cellulose to WSS, and the product mixture of WSS and IL could be easily separated by an ethanol anti-solvent method, importantly which might avoid toxic halogen effect on enzyme in fermentation process.

EXPERIMENTAL SECTION

1. Materials

Microcrystalline cellulose and D-(+)-cellobiose were purchased from Bio-Basic Inc. (Canada), which were dried for 24 h at 100 °C under vacuum before use. 1-Methylimidazole was obtained from Linhai Kaile Chemical Co. (Zhejiang, China), which was distilled before use. Trimethylphosphate was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). 1-Chlorobutane was purchased from Beijing Yili Fine Chemicals CO., Ltd. (Beijing, China). N_2 with a volume fraction purity of 0.9995 was supplied by Beijing Haipu Gases. All reagents and solvents above were A. R. grade. [Mmim][DMP] and [Bmim][Cl] were synthesized following the reported procedures [25,27] and the water content of ILs were measured by Karl Fischer analysis.

2. Treatment of Cellulose with Ionic Liquids

A 100 mL round-bottom flask was charged with 5.0 g of IL, placed into an oil bath at a certain temperature and kept stirred for 60 min

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under nitrogen to remove the water in IL (water content was lowered to 0.076 wt%) [28]. Then, 0.250 g of cellulose was added into the IL. The mixture was stirred for the desired time, and then the treatment reaction was stopped by cooling and adding 30 mL of ethanol in the mixture. It is noted that the cellulose after treatment cannot dissolve in ethanol, while the IL is soluble with ethanol. Therefore, the product, treated cellulose, was easily separated by filtration and obtained in a gel form, and the IL can be reused after the removal of ethanol by distillation [29]. To further decrease the residual IL content in the product, we added 2.5 g water to the product above and stirred. Then, the mixture was eluted by adding 25.0 g of ethanol, filtrated and dried at 80 °C. In our work, the dried regenerated cellulose (unconverted cellulose) above was dissolved in water, filtrated, and dried at 110 °C to calculate the conversion of cellulose to water-soluble substances. The residual mass of the regenerated cellulose was weighed by an accurate balance (Sartorius BS224S) with an accuracy of 0.1 mg. The conversion of cellulose was determined by the mass difference in the weight of cellulose loaded before and after treatment by water, and the average reliability is ±1.8% obtained by repeating the same experiment for three times.

3. Interaction Mechanism between Cellulose and [Mmim][DMP]

Cellobiose is the basic repeating units of cellulose and is formed by β-1, 4-glycosidic linkage of two glucose. To clarify the interaction mechanism between cellulose and [Mmim][DMP], we examined ^{1}H-NMR spectroscopy of cellobiose in [Mmim][DMP]. Samples were prepared by adding different weights of [Mmim][DMP] into a solution of 0.6 mL DMSO-d_6 and 10.0 mg cellobiose (with mole ratios of [Mmim][DMP] to cellobiose of 0 : 1, 2 : 1, and 4 : 1). The ^{1}H-NMR spectra were collected on a Bruker Avance 600 NMR spectrometer equipped with a 5 mm BBO probe and a BBI probe.

4. Characterization of Cellulose before and after Treatment

To study the changes of cellulose in structure during the treatment process, we obtained some regenerated celluloses under mild conditions and in shortened pretreatment time, and their properties were characterized by FT-IR, XRD and SEM.

4-1. FT-IR

The original cellulose and the regenerated cellulose were ground into powder for infrared (IR) measurement. IR spectra were recorded on a Thermo Scientic Nicolet 6700 FT-IR spectrophotometer (Thermo, USA) using KBr pellets.

4-2. XRD

The X-ray diffraction analysis was conducted by using a Rigaku D/max2500 VB2+/PC (Rigaku, Japan) equipped with a Cu/K-alpha1 source (0.154 nm) to analyze the structure of cellulose. The samples were scanned within 3.00-45.00° with a scan speed of 5° min^{-1}. The relative crystallinity of cellulose was calculated by the following equations:

$$\text{Crystallinity}\% = (I_{cr} - I_{am}) \times 100 / I_{cr}$$

where I_{cr} and I_{am} are the peak intensities from crystalline and amorphous regions of cellulose, respectively [6].

4-3. SEM

The changes of cellulose in morphology before and after IL treatment were analyzed by scanning electron microscopy (SEM). SEM images were taken on a Philips XL30 SEM instrument operated at 5 kV accelerating voltage. Prior to imaging, the samples were sputter-coated with gold to make the fibers conductive, avoiding degradation and building up the charge of the specimen.

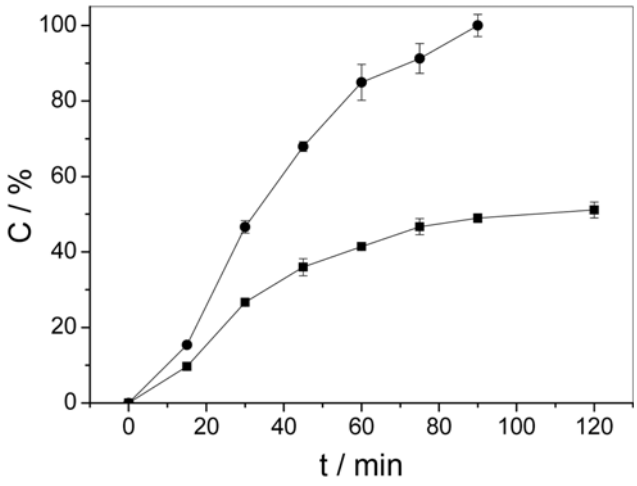

Fig. 1. Effect of time t on the conversion of cellulose C at 150 °C in different ILs: ■, [Bmim][Cl]; ●, [Mmim][DMP].

RESULTS AND DISCUSSION

1. Effect of ILs

Fig. 1 reveals the effect of time on the conversion of cellulose in [Bmim][Cl] and [Mmim][DMP] at 150 °C under identical conditions. From Fig. 1, [Mmim][DMP] has a stronger ability to convert cellulose than [Bmim][Cl]. When treated for 90 min, 100% of cellulose can be converted into WSS in [Mmim][DMP], but only about 50% of cellulose can be converted in [Bmim][Cl]. Particularly, the cellulose conversion of 50% in [Bmim][Cl] is nearly close to the equilibrium value. [Bmim][Cl] has been widely acknowledged as a good solvent for dissolving and converting cellulose. Therefore, [Mmim][DMP] is an excellent solvent for cellulose conversion, which is obviously better than [Bmim][Cl]. Unfortunately, we cannot determine the details about the water soluble substances because of the lack of detection means. Zhang et al. [30] reported that the interactive mechanism between cellulose and [Bmim][Cl] is the formation of hydrogen bonds between Cl in [Bmim][Cl] and OH in cellulose. Based on this point of view, we will explore the reason why [Mmim][DMP] holds a stronger ability to convert cellulose than [Bmim][Cl] in the following studies.

2. Effect of Temperature

The conversion of cellulose was studied at temperatures from 140 °C to 160 °C, and the results are displayed in Fig. 2. Clearly, under all the temperatures we investigated, cellulose can be completely converted into WSS. The higher the temperature that is employed, the higher the conversion rate of cellulose that is achieved, and the shorter time is required for the total conversion of cellulose. The main reason is that the increase of temperature is beneficial to the breakage of hydrogen bonds.

Fig. 2 also shows that the conversion rate of cellulose grows slowly at the beginning, it increases quickly after a certain time, and then the conversion rate increases a little slower again. This may result from the dissolving process of cellulose. Cellulose is solid powder, so it is converted in a heterogeneous system at the beginning. After

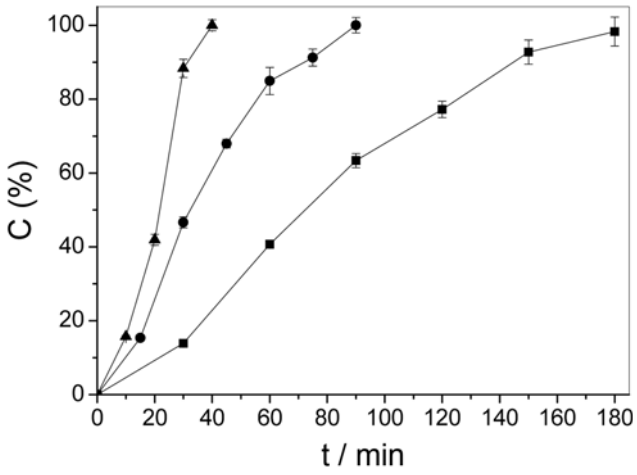

Fig. 2. Effect of time t on the conversion of cellulose C in [Mmim][DMP] at different temperatures: ■, 140 °C; ●, 150 °C; ▲, 160 °C.

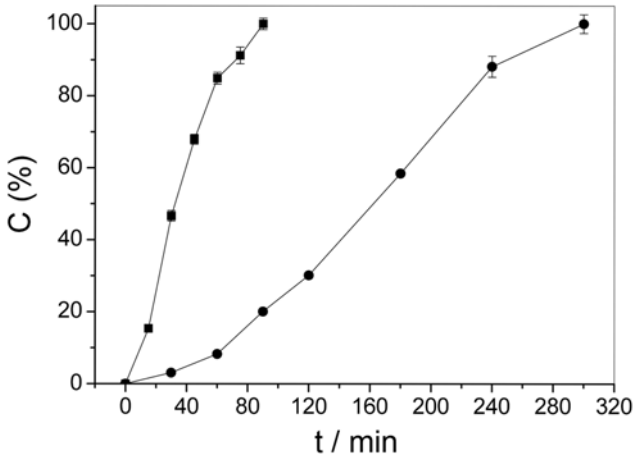

Fig. 3. Effect of time t on the conversion of cellulose C in [Mmim][DMP] with or without water at 150 °C: ■, without water; ●, with water.

a certain time, cellulose will be dissolved in [Mmim][DMP] to form a homogeneous solution, in which the conversion rate of cellulose can surely be promoted. In the final stage, the concentration of cellulose decreases greatly, which may result in the slower conversion rate.

3. Effect of Water

The effect of water on conversion of cellulose is shown in Fig. 3. The results are similar to those reported in the literature [31]. When water is added into the reaction system, the conversion rate of cellulose is reduced. For example, when cellulose is treated in the system without water, it can be completely converted within 90 min. But when 200 mg of water (4.0% of IL in weight) is added, only 21% of the cellulose can be converted in 90 min. Zhang et al. claimed that water is a better hydrogen bond donor than hydroxyls, and also a good hydrogen bond acceptor, so water is more liable to form a hydrogen bond with ILs than cellulose [30]. Thus, the dissolving capacity of ILs for cellulose is reduced. It is better to remove water in ILs and in cellulose to increase the conversion reaction rate.

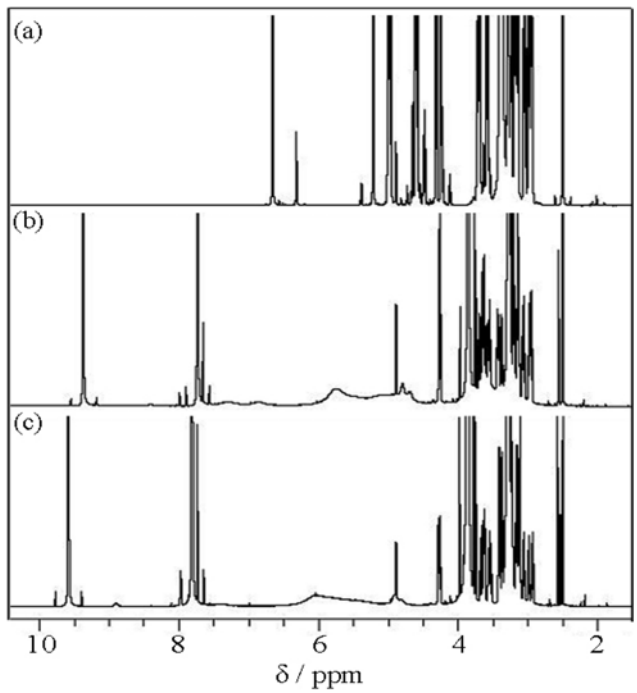

Fig. 4. Effect of molar ratios of [Mmim][DMP]/cellobiose R on the ^{1}H-NMR spectra of cellobiose in DMSO-d_6: (a), pure cellobiose; (b), R=2; (c), R=4.

4. Mechanism of the Interaction between Cellulose and [Mmim][DMP]

Fig. 4 shows the ^{1}H-NMR spectra of cellobiose and (cellobiose+[Mmim][DMP]) mixtures in DMSO-d_6 ranging from 2.0 to 10.0 ppm. The assignment of the resonances has been studied in detail elsewhere [30]. Fig. 4(a) clearly reveals that the proton signals of hydroxyls in cellobiose range from 4.5 to 6.5 ppm. When [Mmim][DMP] is added into cellobiose/DMSO-d_6 solution, the proton signals of hydroxyls merge together, shown in Fig. 4(b). As the proportion of [Mmim][DMP] increases, the proton signals of hydroxyls become broader and move downfield, shown in Fig. 4(c). As we know, the two phenomena above are typically caused by formation of hydrogen bonds. In terms of our system, the hydrogen bonds are undoubtedly formed between the hydrogen atoms of hydroxyls in cellobiose and the oxygen anions in [Mmim][DMP]. In addition, the signal of the acidic protons in the imidazolium cation of [Mmim][DMP], ranging from 9.0 to 10.0 ppm, also moves to lower field. This indicates that hydrogen bonds also occur between the acidic proton in the imidazolium cation of [Mmim][DMP] and the oxygen atoms of hydroxyls in cellobiose.

From the results above, we can see that the dissolution and conversion of cellulose in both [Mmim][DMP] and [Bmim][Cl] are due to the formation of hydrogen bonds. However, Fig. 1 indicates that [Mmim][DMP] shows better property than [Bmim][Cl] in converting cellulose under the identical conditions. This can be explained by the electronegativity of the anion in ILs, since electronegativity determines the intensity of hydrogen bonds. As we know, the electronegativity of O (3.5) is stronger than that of Cl (3.0). At the same time, the atomic radius of O is shorter than that of Cl. Therefore, the hydrogen bond between [Mmim][DMP] and cellulose is obvi-

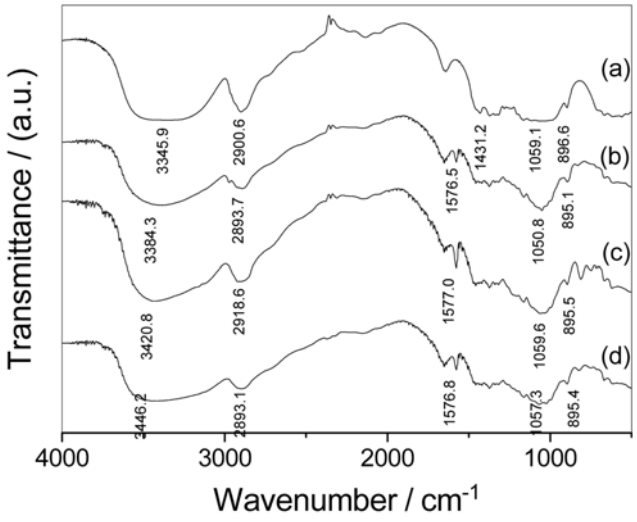

Fig. 5. FT-IR spectra of (a) pure cellulose, (b) regenerated cellulose at 140 °C for 10 min, (c) regenerated cellulose at 160 °C for 10 min and (d) regenerated cellulose at 160 °C for 20 min.

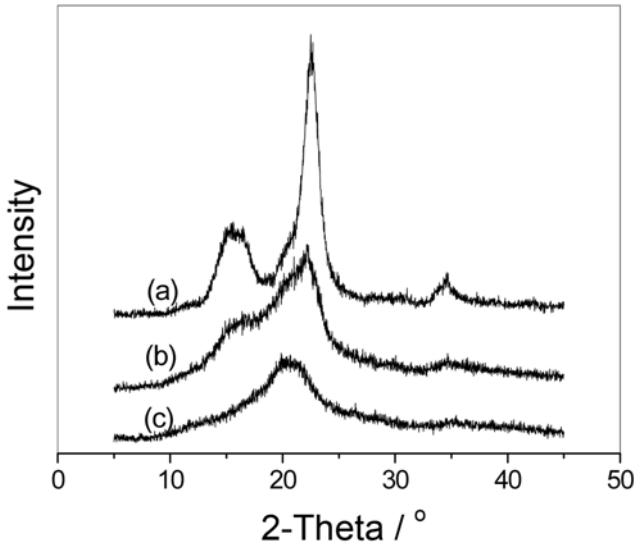

Fig. 6. X-ray diffractograms of (a) pure cellulose, (b) regenerated cellulose at 90 °C and (c) regenerated cellulose at 110 °C.

ously stronger than that between [Bmim][Cl] and cellulose.

5. Characterization of Cellulose before and after Treatment

5-1. FT-IR Spectra

The changes of cellulose in structure before and after the treatment examined with FT-IR are shown in Fig. 5. The new peaks of the regenerated cellulose at 1,576 cm^{-1} come from the C-C in-plane stretching vibration of imidazolium cation in [Mmim][DMP], which is left in the regenerated cellulose after treatment. With the increases of either treatment temperature or time, the stretching vibration peak of O-H in cellulose (at 3,345 cm^{-1}) shifts to a high frequency. For example, when the pure cellulose is treated with [Mmim][DMP] at 140 °C and 160 °C for 10 min, the vibration peaks of O-H shift to 3,384 cm^{-1} and 3,420 cm^{-1}, respectively, and they further move to 3,446 cm^{-1} if the treatment time is prolonged to 20 min at 160 °C. These changes imply that the hydrogen bonds among each O-H of the cellulose are destroyed to some extent. When cellulose is treated with [Bmim][Cl] at 160 °C for 20 min, the vibration of OH only moves to 3,378 cm^{-1}, indicating that hydrogen bond in cellulose treated with [Mmim][DMP] is more broken than that with [Bmim][Cl]. In addition, the peak at 1,431 cm^{-1} in the original cellulose comes from a -CH_2 distortion motion in -CH_2-OH groups of cellulose. After regeneration, this band disappears, indicating that the intra-molecular hydrogen bond at -CH_2-OH is broken. All in all, the FT-IR spectra show that the inter- and intra-molecular hydrogen bonds of cellulose can be significantly broken by the treatment in [Mmim][DMP]. This process makes the cellulose easier to dissolve in water.

5-2. XRD

The cellulose was treated by [Mmim][DMP] at 90 °C and 110 °C for 60 min.

The treated cellulose, which was white and partially soluble in water under these mild conditions, was regenerated by ethanol. The XRD patterns of cellulose before and after treatment with [Mmim][DMP] are shown in Fig. 6. The XRD pattern of cellulose before treatment shows three diffraction peaks at 2θ, 15.16°, 22.52° and 34.44°, and the crystallinity of cellulose is calculated to be about 81.8%. In contrast, the crystalline peaks disappear, but the amorphous peak appears around 20° in the XRD pattern of the treated cellulose, and the relative crystallinity of cellulose is decreased to 56.2% and 29.2% when cellulose is treated with [Mmim][DMP] at 90 °C and 110 °C for 60 min. Therefore, the compact structure and the relative crystallinity of cellulose can be markedly decreased by the treatment with [Mmim][DMP], indicating that the glycosidic bond between each glucose monomer is broken. The XRD spectra of cellulose after treatment by [Bmim][Cl] at 110 °C for 60 min show no significant difference in position of diffraction peak compared with that by [Mmim][DMP].

5-3. SEM

The SEM images of cellulose before and after treatment at 150 °C for 20 min are shown in Fig. 7. The morphology of the cellulose is changed after treatment no matter by [Bmim][Cl] or [Mmim][DMP]. As is shown in Fig. 7(a), the original cellulose is composed of elongated strips with compact structure. After treatment, the regenerated cellulose is arranged in irregular fragments (Fig. 7(d) for [Bmim][Cl]; Fig. 7(g) for [Mmim][DMP]). Under high magnification electron micrograph, the surface of original cellulose is quite smooth and the arrangement of cellulose molecular is in parallel with regular structure (Fig. 7(b) and Fig. 7(c)). But when the cellulose is treated with ILs and regenerated, its surface turns rather uneven with many irregular protrusions, cracks and holes (Fig. 7(e) and 7(f) for [Bmim][Cl], Fig. 7(h) and 7(i) for [Mmim][DMP]). However, it is clear that the cellulose treated by [Mmim][DMP] is better than that with [Bmim][Cl] in breaking the structure of cellulose at the same conditions. All of the phenomena above certify that the compact structure of cellulose has been broken, and [Mmim][DMP] is a better solvent to convert cellulose into water soluble substances than [Bmim][Cl]. The breakage of the compact structure of cellulose makes it easier to access to solvent or catalysts, which is greatly beneficial for the conversion of cellulose.

CONCLUSIONS

In this work, we validate that [Mmim][DMP] shows better dis-

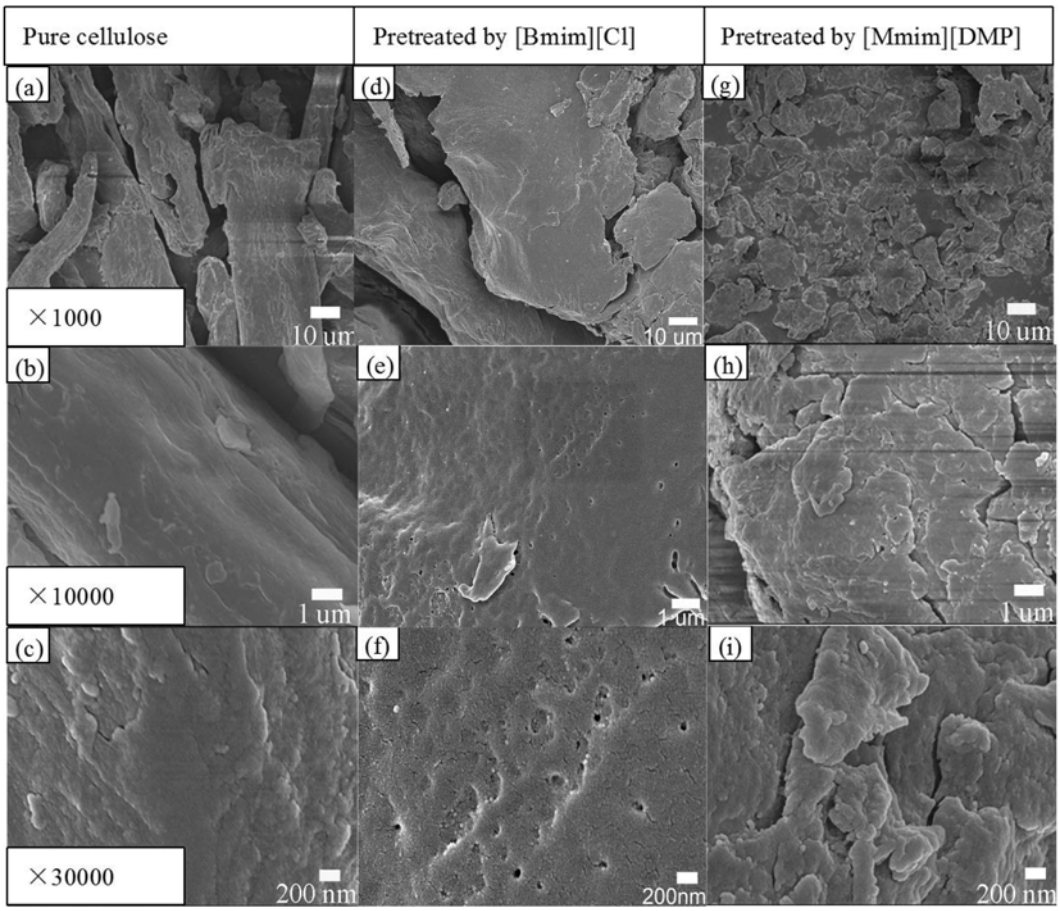

Fig. 7. SEM images of pure cellulose, regenerated cellulose by [Bmim][Cl] and [Mmim][DMP] at 150 °C for 20 min.

solving capacity for cellulose than [Bmim][Cl]. Cellulose can be completely converted into WSS within short time at temperatures from 140 °C to 160 °C, and the higher the temperature is, the shorter the time required for cellulose to be totally converted. The existence of water can decrease the conversion rate of cellulose in [Mmim][DMP]. The main interactive forces of cellulose and [Mmim][DMP] are achieved by the formation of hydrogen bonds between the hydroxyls of cellulose and both the anion and the active hydrogen atoms in the imidazolium cation of [Mmim][DMP]. During the treatment process with [Mmim][DMP], the inter- and intra-molecular hydrogen bonds of cellulose are broken and its compact structure is demolished, resulting in conversion of cellulose into WSS.

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SUPPLEMENTARY MATERIAL

1. Preparation of ILs [32]

[Mmim][DMP] was synthesized as follows: equal molar amounts of 1-methylimidazole and trimethylphosphate were added to a round-bottom flask and stirred vigorously at 150 °C for 10 h under nitrogen atmosphere. After cooling to room temperature, the mixture was washed with ether for three times to remove the residual raw material. Then, the volatile residues were evaporated from the crude product at 60 °C with a rotary evaporator.

[Bmim][Cl] was synthesized as follows: A mixture of 1-methylimidazole, 1-chlorobutane and acetonitrile (with a mole ratio of 1.0 : 1.2 : 1.2) were refluxed at 78 °C for 48 h. Among them, acetonitrile plays a role of co-solvent, making the reaction carried out in a homogeneous solution. After cooling, acetonitrile and volatile residues were evaporated at 60 °C with a rotary evaporator. Then, the solution was recrystallized using ethyl acetate for two times to get a white solid.

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