ORIGINAL ARTICLE

Reaction behavior of cellulose in an ionic liquid, 1-ethyl-3-methylimidazolium chloride

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Abstract We investigated the reaction behavior of cellulose in an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]), which can dissolve cellulose. The cellulose samples were treated with [C2mim][Cl] at 100, 120 and 140 °C. At the beginning of the treatment, the solubilized cellulose in [C2mim][Cl] is depolymerized into various low molecular weight compounds such as cellobiose, cellobiosan, glucose, levoglucosan and 5-hydroxymethylfurfural. As the treatment continued, some of the low molecular weight compounds reacted with the ionic liquid to form new polymers, which were black and contained nitrogen. [C2mim][Cl] is, therefore, not only a solvent for cellulose, but also a reagent for both depolymerization to produce various low molecular weight compounds, and subsequent polymerization of those compounds.

Keywords Cellulose · Ionic liquid · 1-Ethyl-3-methylimidazolium chloride · Reaction behavior

Introduction

In recent times, several energy and environmental problems from using fossil resources have been identified. To solve these problems, and establish a sustainable society based on renewable resources, efficient utilization of biomass is indispensable. Among various types of biomass, lignocellulosics are most abundant, and do not compete with food resources. To produce various useful materials from lignocellulosics, some methods such as acid hydrolysis [1], enzymatic saccharification [2], pyrolysis [3, 4] and supercritical fluid treatment [5] have been studied.

Recently, much attention has been paid to an attractive novel technology, treatment using ionic liquids. Ionic liquids are organic salts which have low melting points, around ambient temperature. They can be easily modified through changing the structure of the cation and/or anion, which broadens their applications. Because of their negligible vapor pressure, non-flammability and recyclability, ionic liquids are regarded as "green solvents". There have been many fundamental and applied studies of various ionic liquid treatments of wood or cellulose for their chemical conversion, since Swatloski et al. [6] revealed that some imidazolium-based ionic liquids can dissolve cellulose. Miyafuji et al. [7] reported that an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) penetrated into wood and liquefied wood components with depolymerizing them. The reaction atmosphere was revealed to affect the reaction behavior of wood during [C2mim][Cl] treatment [8]. The detailed reaction behavior and mechanisms during ionic liquids treatment of wood have also been clarified [9–12].

Cellulose, which is the main component of wood, has also been investigated to see if useful products can be obtained by treatment with ionic liquids. Ionic liquids comprising imidazolium cations and chloride or acetate anions are often used for cellulose. It was reported by Zhao et al. [13] that 1-butyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride could dissolve Avicel® cellulose up to concentrations of at least 10 wt%. Sun et al. [11] revealed that acetate-based ionic liquids are superior to chloride ones for dissolving cellulose. The solubilization of cellulose in ionic liquids is mainly caused by hydrogen bonding of the hydroxyl groups from the

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cellulose to the chloride or acetate anion and imidazolium cation [14–16].

Cellulose solubilized in 1-n-butyl-3-methylimidazolium chloride or 1-ethyl-3-methylimidazolium acetate can be recovered as amorphous cellulose by adding anti-solvents for cellulose (such as water) [17, 18]. These regenerated celluloses showed enhanced activity for enzymatic hydrolysis by cellulase, compared with the activity of untreated cellulose [18]. After treatment with 1-n-butyl-3-methylimidazolium chloride, 72 % of the treated cellulose could be converted to glucose after enzymatic saccharification using cellulase, while only 30 % of untreated cellulose was converted [17]. Regenerated cellulose can be obtained as films from 1-allyl-3-methylimidazolium chloride. These films showed good mechanical properties, particularly tensile strength [19].

Because conventional organic solvents have limitations of volatility, toxicity and difficulty in their recovery, ionic liquids have also been applied as alternative solvents for cellulose derivatization reactions such as acetylation [20, 21] carboxymethylation [22] and succination [23].

However, the detailed reaction behavior of cellulose in ionic liquids has not yet been clarified. In this study, therefore, we investigated the reaction behavior of cellulose in an ionic liquid, [C2mim][Cl]. Such fundamental information is crucial to understand and apply ionic liquid treatments of cellulose.

Materials and methods

Samples and chemicals

Cellulose samples (Whatman CF1) were dried in an oven at 105 °C for 24 h before use. The ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]), was purchased from Tokyo Kasei Kogyo. Dehydrated dimethylsulfoxide (DMSO) and potassium bromide (KBr) were purchased from Wako Chemicals.

Treatment with [C2mim][Cl]

3 g of [C2mim][Cl] was heated at 100, 120 or 140 °C in a 100 ml glass flask. After melting the [C2mim][Cl], 0.09 g of cellulose was added into the flask and the reaction media were gently stirred. 0 h of treatment was defined as the reaction media became transparent without any cellulose particles in the flask. It took 25, 15 and 10 min to make the reaction media became transparent at 100, 120 and 140 °C, respectively.

Evaluation methods

100 ml of distilled water was poured into the flask at the specified reaction time to quench the reaction, and

precipitate the solubilized polymeric compounds. After stirring overnight at room temperature, the precipitates were filtered, washed several times with distilled water, oven-dried at 105 °C for 24 h and weighed to calculate the yield. The elemental compositions of the obtained precipitates were studied using a Hitachi field emission type scanning electron microscope (S-4800) coupled with an Ametek energy dispersive X-ray spectrometer (EDX) (Genesis XM2). The amounts of carbon, hydrogen and nitrogen in the precipitates were determined by a J-SCIENCE LAB elemental coder (MICRO CODER JM10). Fourier transform infrared (FT-IR) spectra of the precipitates were recorded using a Shimadzu 8200PC spectrophotometer by the KBr pellet method, over a spectral range of 4,000–400 cm^{-1} with 20 accumulations. X-ray diffractograms (XRD) of the precipitates were obtained using an Ultime IV diffractometer (Rigaku) with Cu-K$_\alpha$ radiation ($\lambda = 0.1524$ nm) and a K$_\beta$ filter, operating at 40 kV and 30 mA.

Other experiments were carried out to analyze the molecular weight distribution of the compounds solubilized in [C2mim][Cl]. After starting the treatment of cellulose with [C2mim][Cl] as described above, 125 μl of the reaction medium was withdrawn at a specified reaction time. To this sampled reaction medium, 125 μl of DMSO was added and mixed until homogeneous. The mixture was filtered through a 0.45-μm filter, and gel permeation chromatography (GPC) was carried out on the filtrate. GPC conditions were column, Shodex SB-803 HQ; flow rate, 0.3 ml/min; eluent, DMSO; detectors, refractive index detector (RID) and ultraviolet–visible (UV) detector set at 280 nm; column temperature, 60 °C. Pullulan (Shodex standard P-82) was used as the standard for the molecular weight distribution. The compounds solubilized in [C2mim][Cl] were also analyzed by high performance liquid chromatography (HPLC). The samples for this analysis were prepared as follows: at a specified reaction time, 20 μl of the reaction medium was homogeneously mixed with 180 μl of distilled water and then filtered through a 0.45 μm filter. The filtrates were analyzed under following conditions: column, Shodex Sugar KS-801; flow rate, 1 ml/min; eluent, distilled water; detector, RID; column temperature, 80 °C.

Results and discussion

GPC and HPLC analysis of compounds solubilized in [C2mim][Cl]

The molecular weight distribution of the compounds solubilized in [C2mim][Cl] was studied by GPC, as shown in Fig. 1. Peaks from [C2mim][Cl] appear at around 80-min elution time, and do not overlap any peaks in the figure. For the treatment at 100 °C, after 0 h, a peak is observed

Fig. 1 Gel permeation chromatograms of compounds solubilized in [C2mim][Cl] at **a** 100 °C, **b** 120 °C and **c** 140 °C for various treatment times. *Top* refractive index detector (*RID*), *bottom* UV detector ($\lambda = 280$ nm)
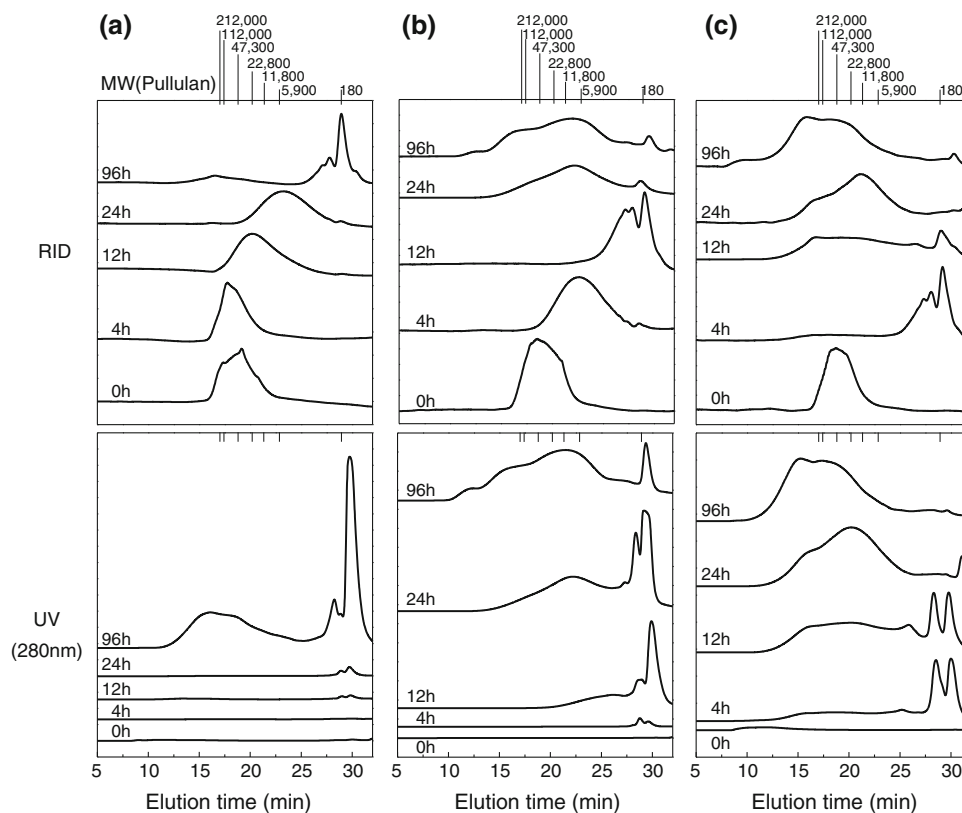
around 47,300 molecular weight (MW) in the chromatogram obtained with the RID, although no peaks are seen in the chromatogram using the UV detector (Fig. 1a). This peak seen with the RID is from cellulose, because cellulose cannot be detected by a UV detector. The cellulose peak shifted to lower molecular weight as the treatment time was extended. After 96-h treatment, a peak can be observed around 180 MW, which is that of glucose. Therefore, cellulose solubilized in [C2mim][Cl] is eventually depolymerized to its monomer level. The similar results of GPC analysis on wood after [C2mim][Cl] treatment were obtained in our previous paper [7, 10]. This is due to the fact that cellulose is a main component of wood contained around 50 % in wood.

The UV-detected chromatograms after 96-h treatment show both low molecular weight compounds (MW < 180) and polymers (>a few thousand MW). This trend is enhanced at 120 °C, as shown in Fig. 2b. Even after 12-h treatment, peaks can be seen around 180 MW (RID) and <180 MW (UV). After 96-h treatment, however, these peaks from low molecular weight compounds are less intense, although peaks from polymers are still observed. At 140 °C, as shown in Fig. 1c, peaks from low molecular weight compounds are seen in both RID and UV-detected chromatograms after 4-h treatment, and are weakened as the treatment time is extended. These peaks become negligible after 96 h of treatment. In contrast, peaks from polymers

increased with prolonged treatment time. These results clearly show that cellulose is decomposed into low molecular weight compounds (<180 MW) during the initial stages of [C2mim][Cl] treatment. These low molecular weight compounds then are polymerized, forming products that are different from cellulose, and are UV-absorbing. This reaction proceeds faster at higher treatment temperature.

HPLC was performed to further study the low molecular weight compounds. Figure 2 shows HPLC chromatogram of compounds solubilized in [C2mim][Cl] after treatment of cellulose at 100 °C for 48 h. Cellobiose, cellobiosan, glucose, levoglucosan and 5-hydroxymethylfurfural (5-HMF) can be identified in the [C2mim][Cl]. Figure 3 shows changes in the yields of these compounds (as calculated using the HPLC chromatograms) as treatment of cellulose proceeds at 120 °C. The yields of all compounds reach a maximum during the treatment, and these maximum values differ. The yield for glucose at 12 h was 23 %, which was the highest among the various compounds shown in Fig. 3. The yields for cellobiose, cellobiosan, glucose, levoglucosan and 5-HMF show their maxima at treatment times of 8, 12, 12, 24 and 24 h, respectively. The higher the molecular weight of the compound, the shorter is the treatment time for maximum yield. Cellobiose appears to be decomposed into glucose and cellobiosan, which are then further decomposed to levoglucosan and 5-HMF. These changes occurred at shorter treatment times
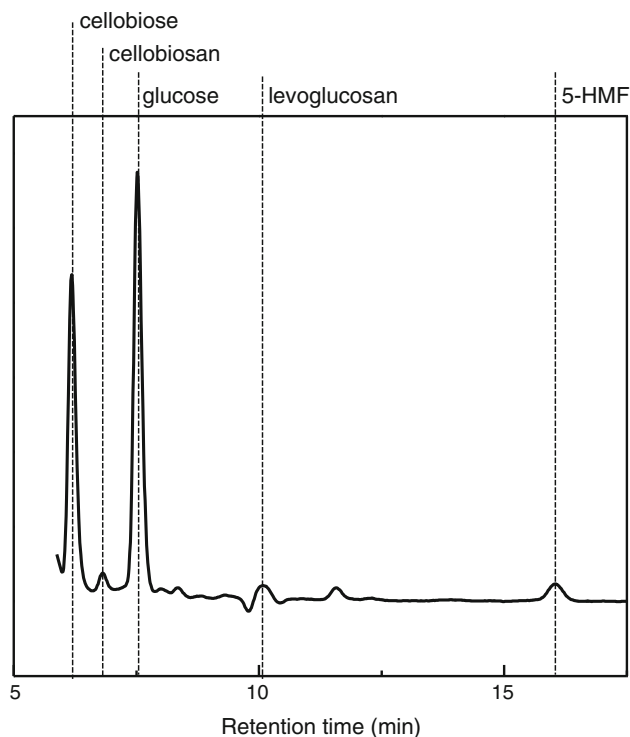
Fig. 2 HPLC chromatogram of compounds solubilized in [C2mim][Cl] after treatment of cellulose at 100 °C for 48 h. *5-HMF* 5-hydroxymethylfurfural

when the treatment was carried out at 140 °C, but took much longer at 100 °C (data are not shown).

Precipitates from [C2mim][Cl]

Figure 4 shows the changes in yields for precipitates obtained at various temperatures. At 100 °C, the yield gradually decreases to 0 % with prolonged treatment time. All precipitates obtained were white in color like cellulose. In contrast, at 120 °C, the yield decreases rapidly after 8-h treatment. After 8 h, the yield gradually increases again to 60 %. As shown in Fig. 5, the precipitates at treatment times up to 8-h treatment are white, while those after 8 h are black unlike cellulose. Similar trends were seen at 140 °C (as shown in Fig. 4), but the changes occurred at shorter times; the yield leveled off at 60 % after 24 h of treatment.

Characterization of the precipitates

The precipitates obtained were characterized using energy dispersive X-ray (EDX) spectrometry, as shown in Fig. 6. All spectra show peaks around 1.5 keV, which are due to the aluminum sample holder, not the samples. Carbon and oxygen peaks are seen in the spectrum from the white precipitate obtained at 100 °C after 4-h treatment (a).
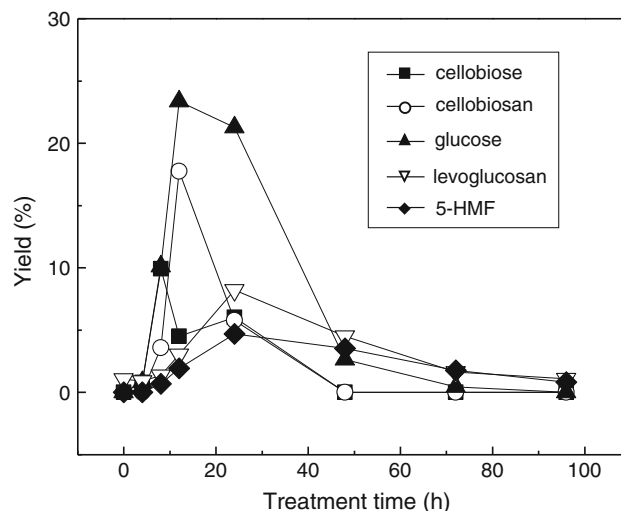

Fig. 3 Changes in yields of various compounds from cellulose treated at 120 °C. *5-HMF* 5-hydroxymethylfurfural
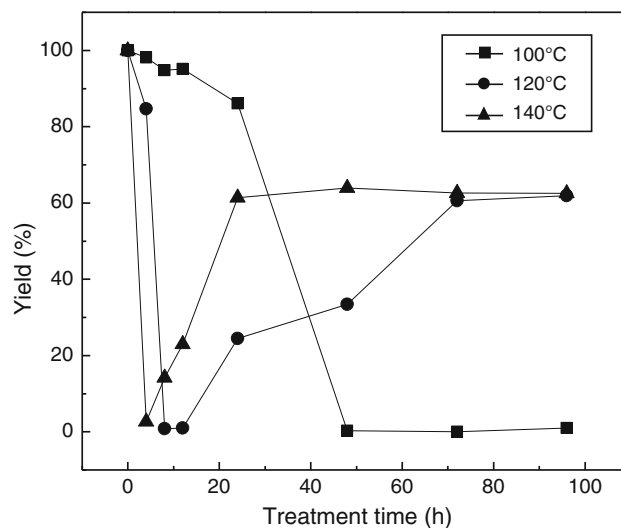

Fig. 4 Changes of yields for precipitates obtained at various temperatures

However, in the spectrum from the black precipitate obtained at 120 °C after 96-h treatment (b), there are carbon, oxygen and nitrogen peaks. This nitrogen might have come from [C2mim][Cl], except that no peak for chlorine was seen. We wondered if there was residual [C2mim][Cl] in the precipitates that had not washed out (although [C2mim][Cl] easily dissolves in water). To remove any free [C2mim][Cl], the precipitate was thoroughly washed again using Soxhlet extraction with distilled water for 24 h. The spectrum for this extensively washed precipitate is shown in Fig. 6c; the nitrogen peak is still apparent, and again no peaks for chlorine occur. This suggests that the imidazolium part of [C2mim][Cl] has become covalently bonded to the black precipitate which is different polymer

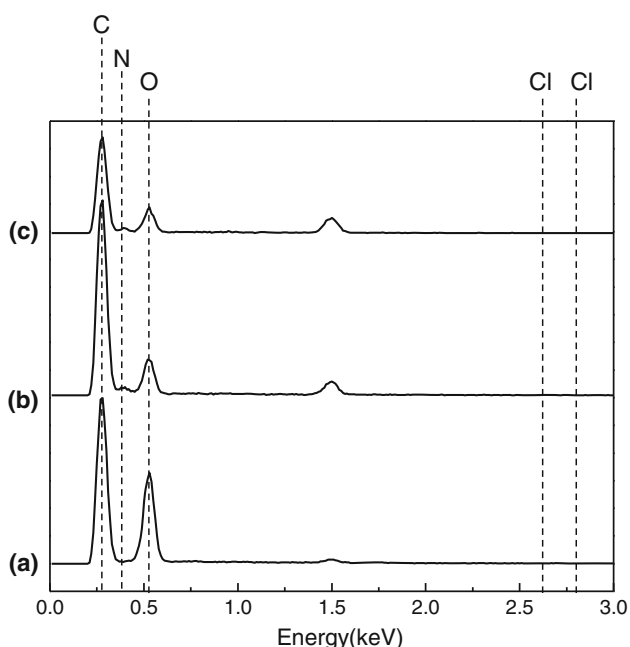Fig. 5 Precipitates obtained after **a** 4-h treatment and **b** 96-h treatment at 120 °C
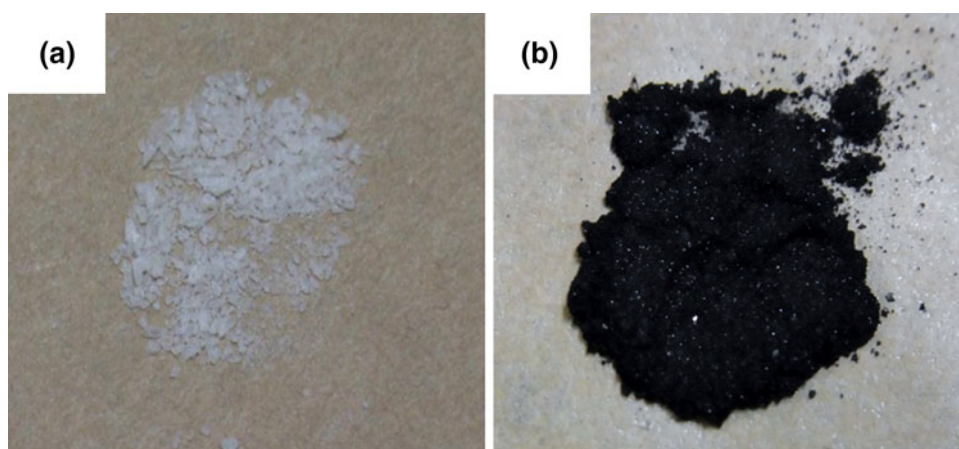

Fig. 6 X-ray spectra of precipitates obtained at **a** 100 °C for 4 h, **b** 120 °C for 96 h and **c** 120 °C for 96 h followed by Soxhlet extraction with distilled water

from cellulose, although chlorine from [C2mim][Cl] was not retained within the precipitate.

The compositions of the precipitates obtained with various treatment conditions, in terms of hydrogen (H), carbon (C) and nitrogen (N) contents, are shown in Table 1. The oxygen content is calculated as the difference between 100 and the total of H, C and N, as shown in Eq. (1).

$$\text{Oxygen (\%)} = 100 - (\text{hydrogen} + \text{carbon} + \text{nitrogen}). \quad (1)$$

For comparison, the results for untreated cellulose are also shown in this table. The precipitates obtained by treatment at 100 °C have similar composition to untreated cellulose, and contain hydrogen, carbon and oxygen,

Table 1 Composition of precipitates obtained with various treatment conditions

Treatment temperature (°C)	Treatment time (h)	Composition (%)			
		H	C	N	O[a]
Untreated		6.2	42.4	0.0	51.4
100	4	6.4	43.5	0.0	50.1
	8	6.5	43.2	0.0	50.3
	12	6.6	43.1	0.0	50.3
	24	6.6	43.2	0.0	50.2
	48	6.9	43.2	0.0	49.9
120	4	6.4	43.3	0.0	50.3
	12	3.9	45.6	3.4	47.1
	24	4.1	58.4	5.4	32.1
	48	4.0	58.0	5.1	32.9
	72	4.1	58.7	6.7	30.5
	96	4.1	58.2	6.3	31.4
140	4	4.1	55.0	3.1	37.8
	8	4.2	59.3	3.7	32.8
	12	3.9	58.7	3.9	33.5
	24	4.1	60.8	6.9	28.2
	48	3.9	59.0	6.9	30.2
	72	3.9	57.6	8.8	29.7
	96	3.9	57.5	8.8	29.8

[a] Calculated values by Eq. (1)

without nitrogen. These precipitates are white, like untreated cellulose, as mentioned above. The white precipitates obtained after 4-h treatment at 120 °C are also similar in composition to untreated cellulose. Ebner et al. [24] reported that ionic liquid with 1-alkyl-3-methylimidazolium cations reacts with cellulose at its reducing end, forming a carbon–carbon bond. However, nitrogen cannot be detected in these white precipitates obtained in this study, indicating that no imidazolium cations of [C2mim][Cl] contain. This may be due to the
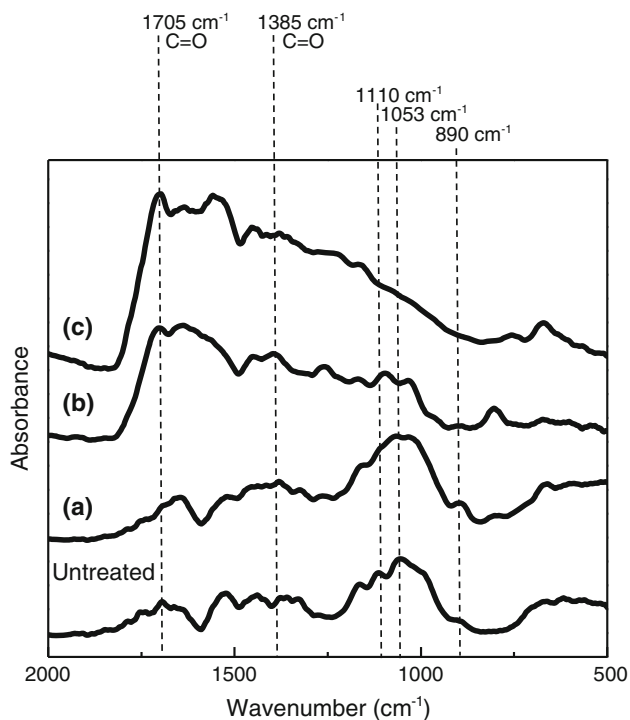
Fig. 7 FT-IR spectra of precipitates obtained after 24-h treatment at **a** 100 °C, **b** 120 °C and **c** 140 °C

Fig. 8 X-ray diffractograms of precipitates obtained after 24-h treatment at **a** 100 °C, **b** 120 °C and **c** 140 °C

difference of ionic liquid and their reaction conditions for cellulose applied. As the treatment is extended, however, the nitrogen content increases to over 6 %. Simultaneously, hydrogen and oxygen decrease, but carbon increases. These precipitates formed at 120 °C, for times over 12 h, are black, as shown in Fig. 5b. All precipitates obtained at 140 °C are black, and show similar compositions (4 % hydrogen, 60 % carbon, 8 % nitrogen and 30 % oxygen). This composition is quite different from that of untreated cellulose. This shows that the compounds which can be precipitated after treatment of cellulose with [C2mim][Cl] at higher temperatures and longer times are different from both the original cellulose and the products formed at shorter times and lower temperatures.

Figure 7 shows the infrared spectra for the precipitates obtained at 100, 120 and 140 °C after 24-h treatment. For comparison, the spectrum of untreated cellulose is also included on the figure. In the spectrum of the white precipitate obtained at 100 °C (a), the peaks at 1110 cm^{-1}, derived from cellulose I [25], and at 1053 cm^{-1}, derived from untreated cellulose [25], are broader. The peak at 890 cm^{-1}, derived from the non-crystalline part of cellulose, is more intense, indicating that some parts of the cellulose change during [C2mim][Cl] treatment. However, general spectrum is quite similar to that of untreated cellulose. Thus, the precipitate obtained at 100 °C has a similar chemical structure to that of untreated cellulose. In
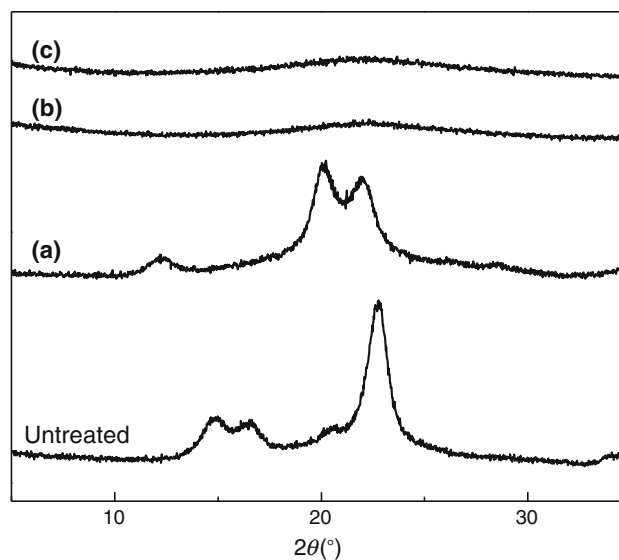
contrast, in the spectrum of the black precipitates obtained at 120 °C (b), peaks at 1705 cm^{-1} and 1385 cm^{-1}, derived from C=O, were observed. This spectrum is quite different from that of untreated cellulose. The spectrum of the precipitate obtained at 140 °C (c) is also different, indicating that the black precipitates obtained after treatments at 120 °C or 140 °C have chemical structures that are different from that of untreated cellulose.

To study the crystalline structure, XRD of the precipitates obtained after 24-h treatment at 100, 120 and 140 °C are shown in Fig. 8. The XRD of untreated cellulose typically have peaks around 14.8°, 16.8° and 22.6° from crystals of cellulose I. In the XRD of the white precipitates obtained at 100 °C (a), two prominent peaks are observed around 20.3° and 21.7°. These are typical peaks for cellulose II. The cellulose solubilized in [C2mim][Cl] is thought to be regenerated as it precipitates upon addition of distilled water after 24-h treatment. It is reported that the solubilized cellulose in 1-ethyl-3-methylimidazoliumacetate can be regenerated as cellulose II [26]. Our results described above coincide with that previous paper, although ionic liquids used are different. In contrast, the XRD of the black precipitates obtained at 120 °C (b) and 140 °C (c) do not show peaks, meaning that these precipitates are amorphous.

Reaction pathway of cellulose in [C2mim][Cl]

Based on the results obtained in this study, a possible reaction pathway of cellulose during [C2mim][Cl] treatment is proposed in Fig. 9. Initially, cellulose dissolves in [C2mim][Cl]. The solubilized cellulose can then be
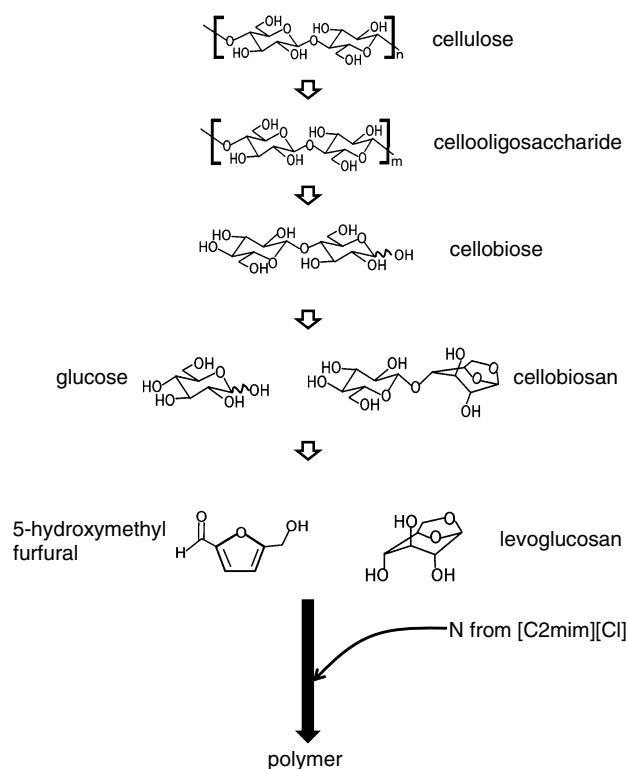
Fig. 9 Proposed reaction pathway of cellulose in [C2mim][Cl]

depolymerized to produce cellooligosaccharides and low molecular weight compounds, such as cellobiose, cellobiosan, glucose, levoglucosan and 5-HMF. The present result showed that the hydrolysis of cellulose into cellooligosaccharide, cellobiose and glucose occurred under the condition without water. Further investigation is indispensable to understand clearly the detail reaction mechanism to produce these various low molecular weight compounds.

During this stage of the [C2mim][Cl] treatment, the amount of precipitates obtained when distilled water is added to the solution decreases. This is because the precipitates are the cellooligosaccharides, which are converted into low molecular weight compounds as the treatment proceeds; the low molecular weight compounds are water soluble, and are not recovered as precipitates. The precipitates obtained are white, and have the cellulose II crystal structure—that is, the crystal structure of regenerated cellulose.

As the treatment continues further, the amount of low molecular weight compounds also decreases, and black precipitates start to be produced. These precipitates are soluble in [C2mim][Cl] and insoluble in distilled water, and are different from cellulose in a number of ways. They are non-crystalline polymers, which can absorb UV light, and are composed of carbon, hydrogen, oxygen and nitrogen. Because [C2mim][Cl] is not polymerized upon heating at the temperatures used in this study, these black

polymers must be from the polymerization of various low molecular weight compounds originally derived from the cellulose. The nitrogen in these polymers is thought to originate from the imidazolium cation of [C2mim][Cl], because the cellulose raw material contains no nitrogen. During the polymerization of the low molecular weight compounds derived from cellulose, the imidazolium cation must be covalently incorporated into the polymers.

Conclusions

We studied the reaction behavior of cellulose in [C2mim][Cl], and found that [C2mim][Cl] is a multifunctional reagent for cellulose. [C2mim][Cl] can dissolve and decompose cellulose, and also react with the compounds produced from the cellulose to form new polymers. Therefore, various products such as polymers, oligomers and low molecular weight compounds can be recovered from cellulose by controlling the reaction conditions. This finding will open new ways to effectively use cellulose via ionic liquid treatment.

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