Carbohydrate Polymers 87 (2012) 1058–1064

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Investigations about dissolution of cellulose in the 1-allyl-3-alkylimidazolium chloride ionic liquids

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ARTICLE INFO

Article history:
Received 28 October 2010
Received in revised form 5 August 2011
Accepted 12 August 2011
Available online 31 August 2011

Keywords:
1-Allyl-3-alkylimidazolium chloride ionic liquids
Carbon atom
Cellulose dissolution
Regenerated cellulose

ABSTRACT

In this work, the 1-allyl-3-alkylimidazolium chloride ionic liquids were synthesized and characterized by increasing carbon atoms ($n \leq 6$) of alkyl chains on a cationic 3-imidazole ring. The results indicated that 1-allyl-3-alkylimidazolium chloride with asymmetrical structure on the two sides of a cationic 3-imidazole ring (i.e., $n = 1$, 2, 6) exhibited alkalinity and lower thermal stabilities, and showed better solubility to the cellulose samples at 60–120 °C than those with symmetrical structures ($n = 3$, 4). The cellulose samples treated by 20% (w/w) ethylenediamine solution showed better solubility in 1-allyl-3-ethyl, hexyl-imidazolium chloride ionic liquids than that treated with 20% (w/w) NaOH solution at 5 °C for 72 h. XRD and TG analysis indicated that 0 0 2 plane apparent crystallite size as well as thermal stability of the regenerated cellulose samples from the ionic liquids decreased significantly compared with the untreated cellulose samples.

1. Introduction

The growing concern about environmental pollution from the manufacture of synthetic polymers, biodegradable plastics, and biocompatible composites from natural resources has become an important technology of next-generation polymers. Cellulose is a linear homopolymer of $\beta(1 \rightarrow 4)$-linked D-glucopyranose (Glc) unit that can aggregate to form a highly ordered structure due to its chemical constitution and spatial conformation (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998). The three hydroxyl groups, C_6–O_6H, C_3–O_3H, and C_2–O_2H, in each Glc can form intermolecular hydrogen bonds (Oh et al., 2005). The highly ordered structure of cellulose is the reason for its desirable mechanical properties but is also the barrier to its dissolution in common solvents. However, in the last few years, several suitable solvents for dissolving cellulose have been found, e.g., N-methylmorpholine N-oxide (NMMO) (Doganand & Hilmioglu, 2009), LiCl/DMAc (Nattakan, Takashi, & Ton, 2009), and NaOH/urea (Song, Zhang, Gan, Zhou, & Zhang, 2010). Recently, ionic liquids have been found to be suitable green media for dissolving cellulose by destroying hydrogen bonds (Cao et al., 2009). Almost all ionic liquids consist of negative ions (i.e., Cl^-, Br^-, CH_3CHOO^-, NO_3^-, and BF_4^-, CF_3COO^-) and positive ions (i.e., alkyl-imidazolium) (Pinkert et al., 2010). Wu and his group (Ren, Wu, Zhang, He, & Guo, 2003; Wu et al., 2004; Zhang, Wu, Zhang, & He, 2005) developed a novel ionic liquid, 1-allyl-3-methylimidazolium chloride (AMIMCl), thus offering a new ionic liquid for dissolving cellulose.

The previous studies reported that the molecular structure of ions in ionic liquids plays an important role in dissolving cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002). In this study, 1-allyl-3-methylimidazolium chloride ionic liquid (AMIMCl), 1-allyl-3-ethylimidazolium chloride ionic liquid (AEIMCl), 1-allyl-3-propylimidazolium chloride ionic liquid (APIMCl), 1-allyl-3-butylimidazolium chloride ionic liquid (ABIMCl), and 1-allyl-3-hexylimidazolium chloride ionic liquid (AHIMCl), which are derivatives of increasing carbon atoms ($n \leq 6$) in the alkyl chains on a cationic 3-imidazole ring, were synthesized and investigated for their effects on the dissolution of cellulose.

2. Material and methods

2.1. Materials

Microcrystalline celluloses (MCC) (column chromatography grade; 99.99% purity) were purchased from Shanghai Hengxin Chemical Reagent Co., Ltd., Shanghai, China. Bleached Kraft softwood pulp (Pulp) was kindly supplied by Guangdong Eagle Force Paper Co., Ltd., Guangzhou, China. A total of five imidazole derivatives (i.e., N-methyl, ethyl, propyl, butyl, and hexyl-imidazole; analytical reagent; 98% purity) were purchased from Shanghai Aoke Industrial Co., Ltd., Shanghai, China. The above five imidazloe derivatives are purified under reduced pressure distillation before the syntheses. Allyl chloride (RS-Aldrich; analytical reagent grade; 98% pure) with a specific gravity of 0.935 kg/m^3 was

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doi:10.1016/j.carbpol.2011.08.026

purchased from Sigma–Aldrich (Shanghai) Trading Co., Ltd., Shanghai, China. The fresh deionized water was prepared through a QHY-LO-6000 model lab water purification system equipped with 8040 Dow's reverse osmosis membranes. This water purification system is made in Guangdong Huankai Microbial Sci & Co., Ltd., Guangzhou, China.

2.2. Pretreatment of MCC and pulp

A certain amount of the pulp was dispersed in water using a high-shear ZBJ-1 Model fiber kneader (Changchun Paper Test Depots Co., China), soaked in water for 24 h, and diluted to 5% (w/w) consistency by magnetic stirring. Subsequently, the pulp slurry was treated respectively with 20% (w/w) aqueous NaOH and 20% (w/w) ethylenediamine (EDA) solution. Both the above two treatments were performed at 5 °C for 72 h. The MCC were prepared at a 5% (w/w) consistency by magnetic stirring and treated with aqueous 20% (w/w) NaOH solution at 5 °C for 72 h. After the treatments, the pulp slurry and MCC were washed with water until the washings were of pH 7. After filtration by a 60 mL G3 sand core bush funnel with vacuum assistance, the treated MCC samples were dried in DZF-6210 vacuum drier (Shanghai Permanent Science and Technology Co., Shanghai, China) at 80 °C for 24 h. From this process, the cellulose samples, i.e., pulp, pulp samples treated with aqueous 20% (w/w) NaOH solution (Pulp–NaOH) and in aqueous 20% (w/w) EDA solution (Pulp–EDA), and MCC treated in aqueous 20% (w/w) NaOH solution (MCC–NaOH), were obtained. The mean degree of polymerization of the pulp, Pulp–NaOH, Pulp–EDA, and MCC–NaOH was measured by the viscosity method (GB, 1986), and was respectively 826, 705, 801, and 141.

2.3. Synthesis and characterization of 1-allyl-3-alkylimidazolium chloride ionic liquids

The general synthesis procedure of AMIMCl was performed according to the method by the reports (Ren et al., 2003). To N-methylimidazole in a 500 mL glass-lined reactor, approximately 1:1.2 molar ratio of allyl chloride was added dropwise under argon gas atmosphere at room temperature. After completely adding the allyl chloride, the reaction mixture was stirred magnetically with reflux at 55 °C for about 10 h. After removing the residual allyl chloride under reduced pressure, the resulting liquid was repeatedly washed with an excess amount of ether to eliminate the residual N-methylimidazole. The resulting ionic liquids was analyzed for pH value and zeta potential under PHS-3D pH equipment (Shanghai Jingke Equipment Co., Ltd., Shanghai, China), and was subsequently dried in vacuum drier at 80 °C for 72 h. Thus, AMIMCl was obtained. The derivatives AEIMCl, APIMCl, ABIMCl, and AHIMCl were synthesized according to the above method. The density of AMIMCl, AEIMCl, APIMCl, ABIMCl, and AHIMCl was measured by density bottle method (GB, 1985), and was 1.2096, 1.1735, 1.1375, 1.1288, and 1.2211 g/mL, respectively. The ^{1}H NMR spectra of the 1-allyl-3-alkylimidazolium chloride were obtained using an AVANCE Digital 400 MHz NMR (Bruker Company, Germany) showing the following peaks: ^{1}H NMR (400 MHz, DMSO), AMIMCl, $\delta = 9.60$ (–N–CH–N–); 7.85 (–N–CH–CH–N–); 5.98 (=CH–); 5.28 (=CH_2); 4.89 (CH_2–N–); 3.87 (–N–CH_3). AEIMCl, $\delta = 9.86$ (–N–CH–N–); 8.08, 7.95 (–N–CH–CH–N–); 6.09 (=CH–); 5.37 (=CH_2); 4.99 (–CH_2–N), 3.56 (–N–CH_2–); 1.45 (–CH_3). APIMCl, $\delta = 9.80$ (–N–CH_2–N–); 8.05, 7.95 (–N–CH–CH–N–); 6.10 (=CH–); 5.35 (=CH_2); 5.00 (–CH_2–N–), 3.41 (–N–CH_2–); 1.84 (–CH_2–) (a); 0.86 (–CH_3). ABIMCl, $\delta = 9.76$ (–N–CH–N–); 8.01, 7.91 (–N–CH–CH–N–); 6.08 (=CH–) 5.34 (=CH_2); 4.97 (–CH_2–N–), 3.47 (–N–CH_2–); 1.82 (–CH_2–) (a), 1.27 (–CH_2–) (b); 0.90 (–CH_3). AHIMCl, $\delta = 9.72$ (–N–CH–N–); 8.02, 7.96 (–N–CH–CH–N–); 6.09 (=CH–); 5.36 (=CH_2); 5.00 (–CH_2–N–), 3.96 (–N–CH_2–); 3.64 (–CH_2–) (a), 2.57 (–CH_2–) (b), 1.09 (–CH_2–) (c), 0.86 (–CH_2–) (d); 0.62 (–CH_3).

2.4. Dissolution of cellulose

The pulp, Pulp–NaOH, Pulp–EDA, and MCC–NaOH were used as the cellulose samples to study their dissolution in AAIMCl ionic liquids under argon protection. The dissolution rate of the above-mentioned cellulose samples in the ionic liquids was investigated at 60–100 °C as a result of dissolution time. In the dissolving process, a certain amount of cellulose sample was added into the ionic liquids. After the emergence of a blackburst in the cellulose solution was determined on a JPL-1350 polarization microscope (Guangzhou LISS Optical Instrument Ltd., Guangzhou, China), the succeeding amount of cellulose sample was added again into the dissolved cellulose solution. The above experimental procedure was repeated for several cyclic numbers. The solubility of cellulose corresponding to dissolution times in ionic liquids for each cyclic number was recorded. The solubility and dissolution rate of the cellulose samples in the above five species of ionic liquids were calculated as shown in Eqs. (1)–(3):

$$T(n) = \sum_{1}^{n} (t_n) \tag{1}$$

$$S(n) = \sum_{1}^{n} \left(\frac{G_n}{G_{ILs}} \right) \times 100\% \tag{2}$$

$$V(n) = \left(\frac{G_n}{G_{ILs} \times t_n} \right) \times 100\% \tag{3}$$

where n is the cyclic number of dissolving cellulose samples in the ionic liquids ($n = 1, 2, 3, 4, \ldots, n$); t_n is the dissolution time (min) required for dissolving completely the mass (g) of the cellulose samples; (G_n) in the ionic liquids at the n cyclic number; G_{ILs} is the mass (g) of the ionic liquids; T is the dissolution time required for dissolving completely the cellulose sample in the ionic liquids (%, w/w) as a function of cyclic numbers; S, V is respectively the solubility (%, w/w), dissolution rate (%/min) of the cellulose sample in the ionic liquids as a function of dissolution time.

Different cellulose samples were investigated in terms of solubility in AAIMCl ionic liquids. The solubility of the pulp, Pulp–NaOH, Pulp–EDA, and MCC–NaOH samples were compared in each ionic liquid at 100 °C under argon gas protection. The effects of the dissolution temperatures (i.e., 60 °C, 100 °C, and 120 °C) on the solubility of the MCC–NaOH samples in ionic liquids were also studied.

2.5. Preparation of the regenerated cellulose

After complete dissolution of the cellulose samples in the ionic liquids, the resulting cellulose solution was washed with ~20 mL absolute ethyl alcohol 3–5 times to regenerate the cellulose samples. Subsequently, an excess amount of deionized water was used to wash the regenerated cellulose. The regenerated cellulose samples were vacuum freeze-dried under ModulyoD-230 Freeze Dryer (Thermo Savant, USA) at −50 °C for 24 h.

2.6. Scanning electron microscopy analysis

The two regenerated MCC samples, one obtained by vacuum freeze drying and the other by air drying method, were fixed to a metal–base specimen holder using double-sided sticky tape. The samples were then coated with gold using a vacuum sputter-coater. Afterwards, the fracture surfaces were observed using an S-3700N scanning electron microscope (Hitachi, Ltd., Japan).

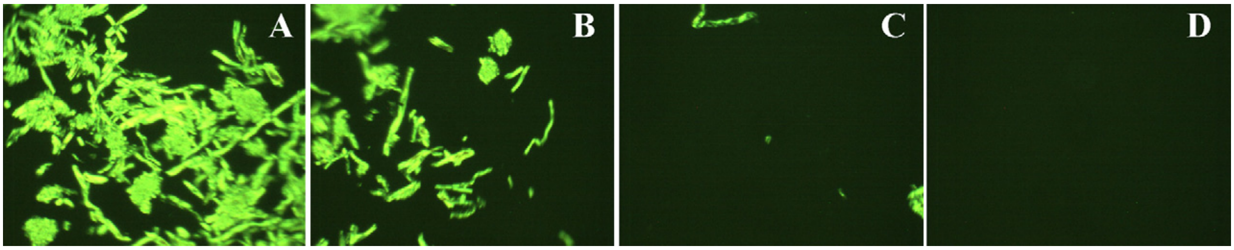

Fig. 1. Dissolution of cellulose in AHIMCl in the starting stage (A); initial partial dissolving stage (B); later dissolving stage (C); and completely dissolved stage (D).

2.7. X-ray diffraction (XRD) analysis

The crystal structures of the MCC, MCC–NaOH, and the regenerated MCC–NaOH samples treated with AMIMCl and AHIMCl at 100 °C were studied using an XRD analyzer (Rigaku D/max-III X-ray diffractometer) set at 40 kV and 30 mA. Wide-angle X-ray intensities were collected for 2θ, ranging from 4° to 60°, with a step scanning rate of 8°/min and step increment of 0.04°.

The 0 0 2 plane apparent crystallite size of the cellulose samples was calculated by the Scherrer formula (Cao & Tan, 2002), described in Eq. (4) as follows:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (4)$$

where K is the Scherrer constant (0.89); D is the 0 0 2 plane apparent crystallite size (nm); λ is the wavelength of the X-ray (0.154056 nm); β is the full width at half maximum (rad); and θ is the diffraction angle.

2.8. Thermogravimetric analysis (TGA)

TGA was used to study the thermal stability of the 1-allyl-3-alkylimidazolium chloride ionic liquids by Q500 TGA instrument (TA instruments, USA), the MCC, MCC–NaOH, and the regenerated MCC–NaOH samples treated with AMIMCl and AHIMCl at 100 °C. Weight loss was recorded in the range of room temperature to 500 °C, with a heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Characteristics of 1-allyl-3-alkylimidazolium chloride ionic liquids

Based on the currently developed AMIMCl (Wu et al., 2004; Zhang et al., 2005), AMIMCl and the series of its derivatives, AEIMCl, APIMCl, ABIMCl, and AHIMCl, were successfully synthesized in this study. The newly developed AEIMCl and AHIMCl in this study exhibited reasonable capability to dissolve cellulose (e.g., in MCC and pulp), as observed by polarization microscopy. Fig. 1A and B shows that dissolution of the cellulose samples commenced due to the dispersion of numerous cellulose fibers in the ionic liquids. Eventually, the cellulose fibers disintegrated and finally disappeared, while the blackburst structure emerged on polarization microscope (as shown in Fig. 1D).

In the synthesis route (see Fig. 2), the electrophilic attack of the 2-allyl cation on alkylimidazolium formed the bigger alkylimidazolium cation, which underwent further nucleophilic reaction with chloride anion. This finding indicates that the symmetry on the two sides of the cationic 3-imidazole ring was destroyed by the increase in alkyl chain length, which also affected the electron cloud distribution in the cationic 3-alkylimidazolium ring. Fig. 3 shows that AMIMCl and AHIMCl, which contain micro-moisture, exhibited alkalescent environment with a pH value of 8.82 and 9.72, respectively, whereas AEIMCl, APIMCl and ABIMCl were nearly neutral. Asymmetry in the distributions of the groups on both sides of the imidazolium cation probably distorted the electron cloud distribution, which facilitated the

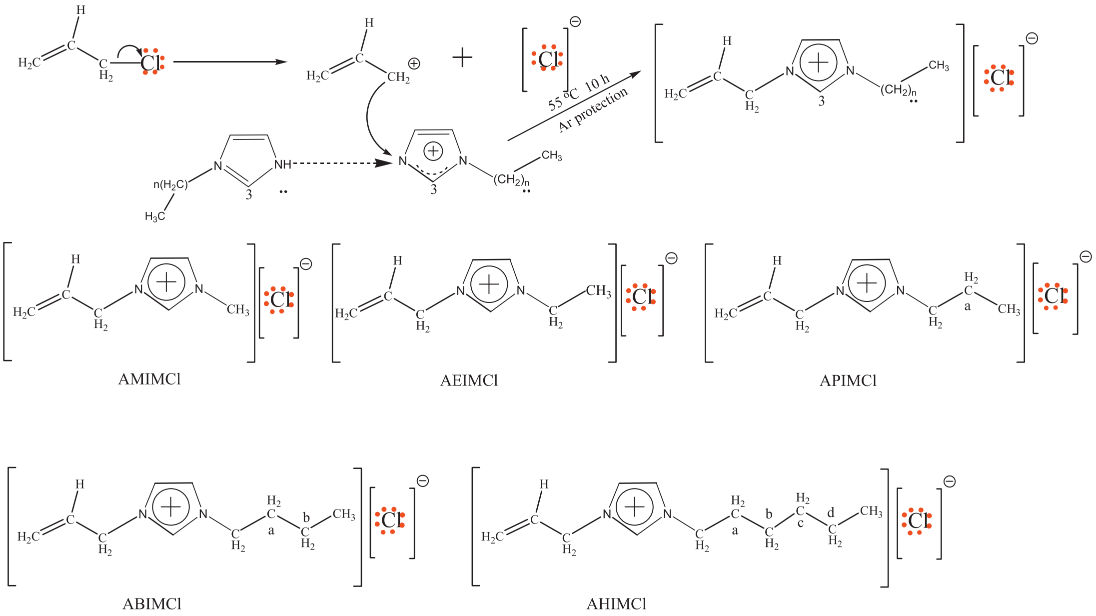

Fig. 2. Synthesis route and chemical structures of 1-allyl-3-alkylimidazolium chloride ionic liquids.

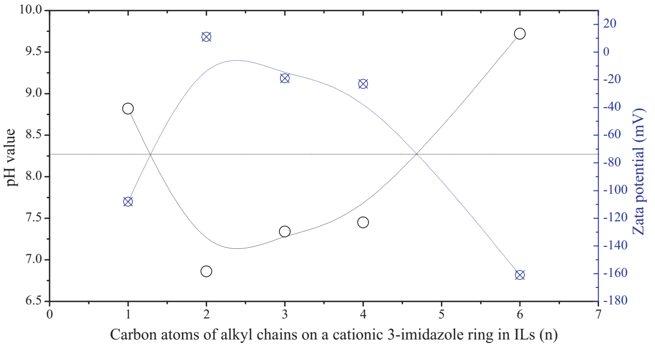

Fig. 3. Dependence of carbon atoms ($n \leq 6$) of alkyl chains on the cationic 3-imidazole ring on the pH and zeta potential of ionic liquids.

interaction of chlorine atoms with H⁺ from H_2O. The differences in stability in ionic liquids were evaluated from the zeta potentials. The zeta potentials of AMIMCl and AHIMCl were much higher than 100 mV, whereas AEIMCl, APIMCl, and ABIMCl had zeta potentials lower than 20 mV. These findings imply that asymmetrical distributions of groups on both sides of the imidazolium cation benefit the systematic stability of the ionic liquids.

3.2. Dissolution of cellulose

The cellulose of the MCC–NaOH samples at 100 °C completely dissolved in AMIMCl, AEIMCl, and AHIMCl, whereas the solubility of APIMCl and ABIMCl was lower than 0.42% within 740 min (Fig. 4A). AEIMCl showed relatively higher capacity to dissolve the cellulose samples than AMIMCl and AHIMCl at 100 °C. The solubility of MCC–NaOH samples in AMIMCl, AEIMCl and AHIMCl initially increased rapidly with dissolution time and then increased slowly with further dissolution time. Accordingly, the dissolution rate increased quickly in the initial stage ($\leq$300 min) and subsequently slowed with further dissolution time (Fig. 4B).

Fig. 4C illustrates the affects of the dissolution temperature on the solubility of the MCC–NaOH samples in the ionic liquids. The AMIMCl, AEIMCl, APIMCl, ABIMCl, and AHIMCl almost did not dissolve the cellulose samples when the dissolution temperature was lower than 60 °C. This finding agrees with the present ionic liquid of AMIMCl (Zhang et al., 2005). The time required for dissolving completely 1% cellulose of the MCC–NaOH samples at 60 °C for AMIMCl, AEIMCl, and AHIMCl was about 419, 685, and 422 min, respectively.

At a low dissolution temperature, AMIMCl and AHIMCl had nearly the same solubility, showing easier dissolution of cellulose than AEIMCl. APIMCl and ABIMCl did not dissolve the cellulose of MCC–NaOH samples at 60 °C regardless of the duration (Fig. 4D). Increasing the dissolution temperature to 120 °C resulted in a much faster dissolution of 1% cellulose of MCC–NaOH sample. ABIMCl was also found to dissolve the cellulose of MCC–NaOH completely at 120 °C by 718 min. This result suggests that increasing the dissolution temperature improved the solubility of cellulose in 1-allyl-3-alkylimidazolium chloride ionic liquids. The result also shows that cellulose dissolved more easily in AEIMCl at a higher dissolution temperature but not at a low dissolution temperature.

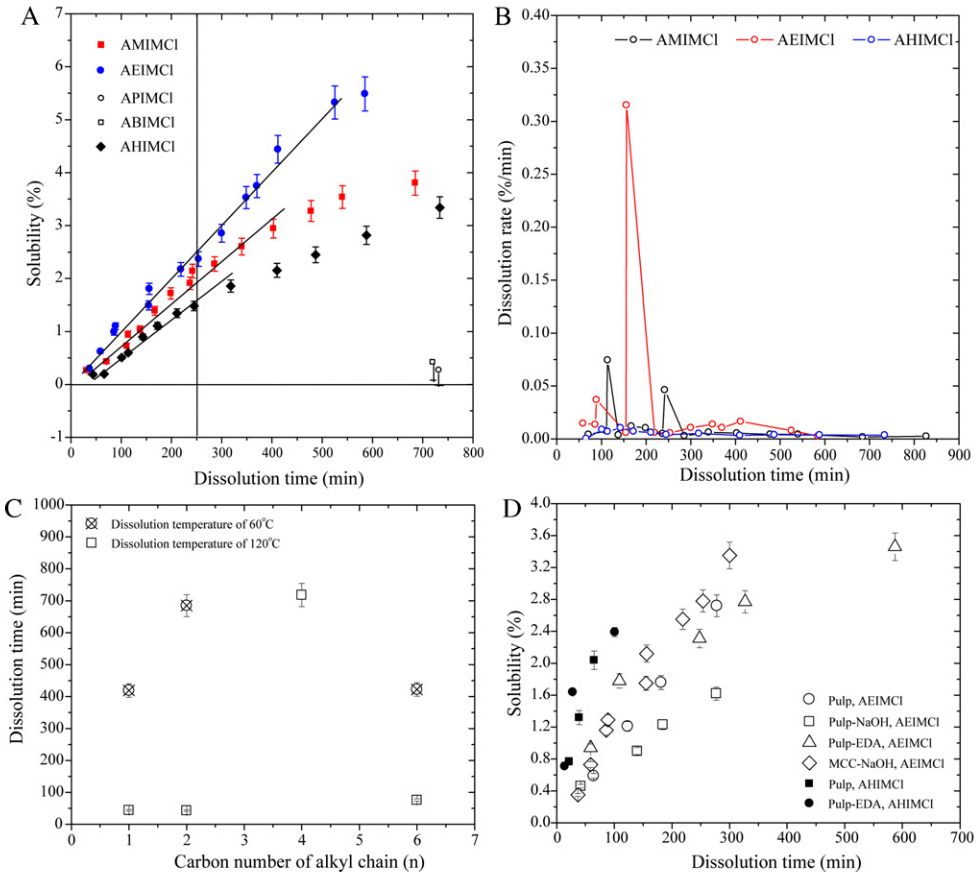

Fig. 4. Comparisons of solubility (A) and dissolution rate (B) of the MCC–NaOH samples in 1-allyl-3-alkylimidazolium chloride ionic liquids at 100 °C; effects of dissolution temperature (C) on the dissolution time of 1% MCC–NaOH samples in AMIMCl, AEIMCl and AHIMCl; comparison (D) of the solubility of pulp, Pulp–NaOH, Pulp–EDA, and MCC–NaOH samples in AEIMCl and AHIMCl at 100 °C.

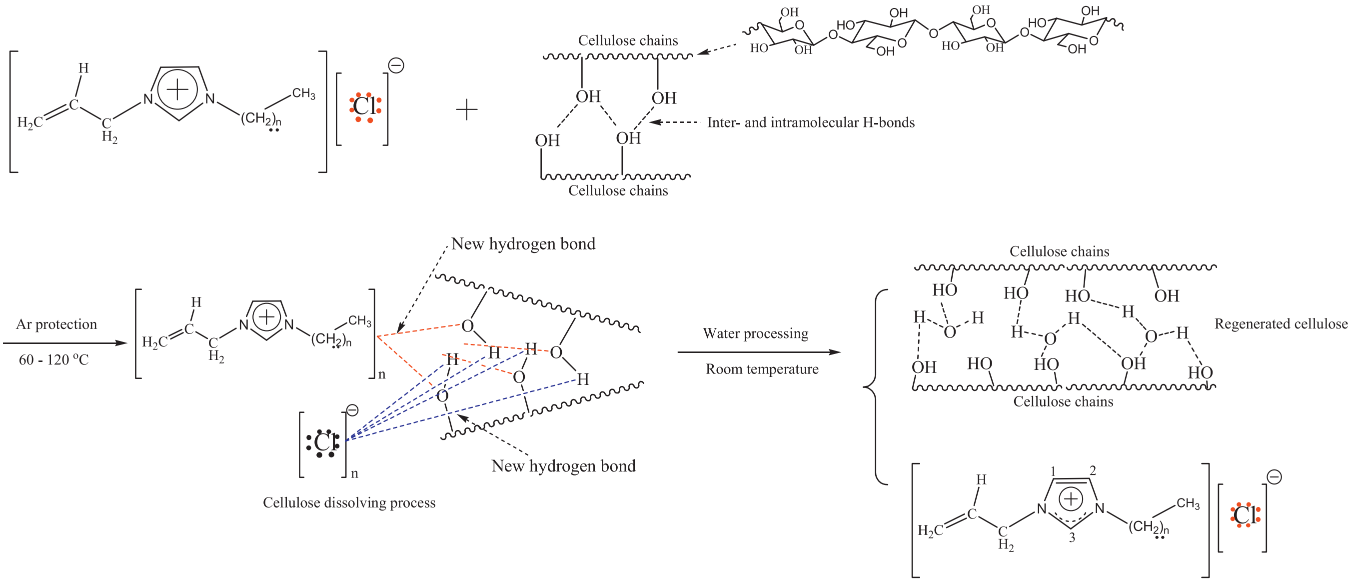

Fig. 5. Mechanism of processing cellulose with 1-allyl-3-alkylimidazolium chloride ionic liquids.

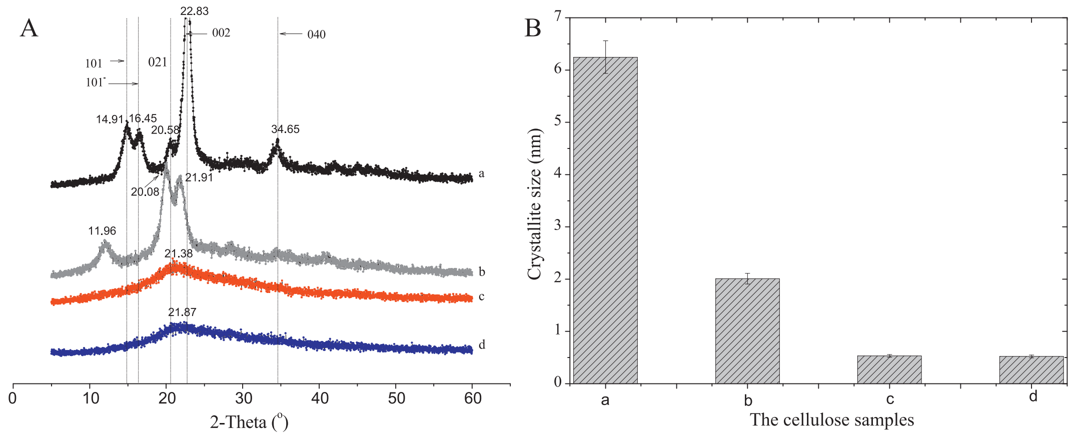

Fig. 6. XRD patterns (A) and crystallite sizes (B) of the MCC (a), MCC–NaOH (b), and the regenerated MCC–NaOH samples from AMIMCl (c) and AHIMCl (d).

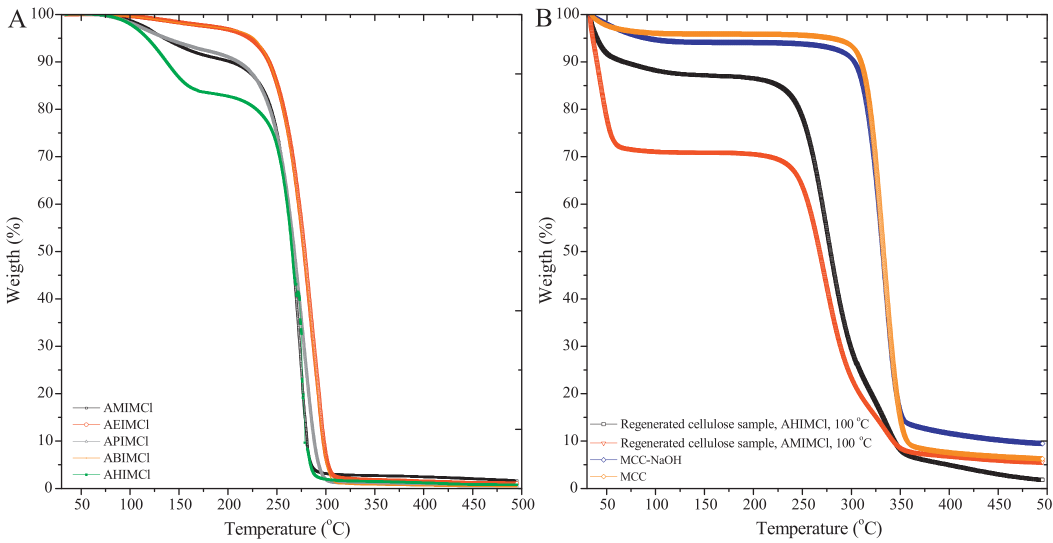

Fig. 7. Temperature dependencies of weight loss for 1-allyl-3-alkylimidazolium chloride ionic liquids, the MCC, MCC–NaOH, and the regenerated MCC–NaOH samples in a nitrogen atmosphere.

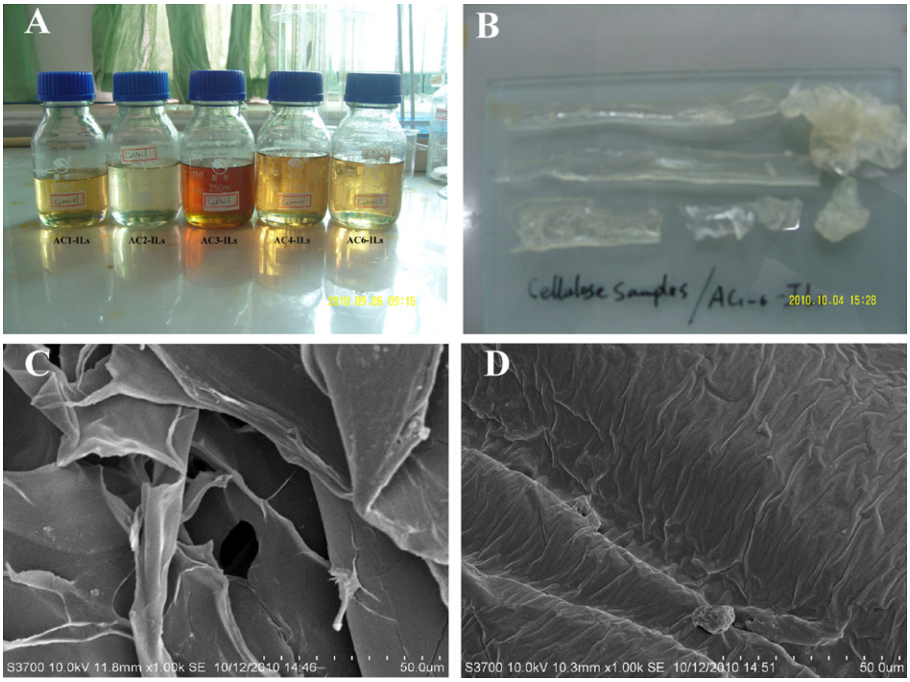

Fig. 8. Image of 1-allyl-3-alkylimidazolium chloride (A), the regenerated cellulose samples (B), and SEM image of the regenerated cellulose samples dried by vacuum freeze-dry method (C) (×1000) and air-dry method (D) (×1000), respectively.

In contrast to this finding, cellulose exhibited better solubility in AHIMCl at a lower temperature of 60 °C.

The pretreatment of cellulose by aqueous 20% (w/w) NaOH or EDA solution can change the physical structure of the rigid crystalline region of cellulose, probably contributing to the easier dissolution of cellulose in ionic liquids (Pérez & Samain, 2010; Wang, Keshwani, Redding, & Cheng, 2010). Fig. 4D shows that compared with fibrous pulp, the MCC–NaOH samples had higher solubility in AEIMCl at 100 °C. This probably resulted from the attack of these reagents on cellulose, which could have led to the increase of cation and chloride anions of the ionic liquid in accessibility to the crystalline or amorphous regions of the cellulose sample. This facilitates the attack on the hydrogen bonds within or across cellulose chains. Remarkably, the pulp samples without any pretreatment also dissolved well in AEIMCl and AHIMCl. The AHIMCl had significantly better dissolving efficiency in the pulp samples than AEIMCl (Fig. 4D). The Pulp–EDA samples showed significantly higher solubility in AEIMCl and AHIMCl than the Pulp–NaOH samples. The better dissolving efficiency of the Pulp–EDA samples by AHIMCl and compared with that of AEIMCl was observed.

Fig. 5 shows the mechanism of cellulose processing by 1-allyl-3-alkylimidazolium chloride ionic liquids. The synthesized ionic liquids have special chemical structures, including a small chloride anion and another large molecule of 1-allyl-3-alkylimidazolium cation. Similar to other ionic liquids (e.g., BMIMCl and EMIMAc) (Lee, Doherty, Linhardt, & Dordick, 2009; Swatloski et al., 2002), both anions and cations are considered involved in the dissolution process (Pinkert, Kenneth, Marsh, & Mark, 2009). The oxygen and hydrogen atoms of the cellulose form electron donor–electron acceptor complexes with the charged species of the ionic liquids. 1-Allyl-3-alkylimidazolium cation can easily connect to oxygen in the inter- and intramolecular H-bonds between cellulose chains, whereas the chloride anions connect to the hydrogen atom. This process breaks the inter- and intramolecular H-bonds of cellulose chains, leading to the dissolution of the cellulose in ionic liquids (Pinkert et al., 2009; Zhang et al., 2005).

3.3. XRD analysis

XRD has been used extensively for the investigation of the super molecular order (crystalline) of cellulose and their derivatives (Liu et al., 2008). Fig. 6A shows the XRD curves of the MCC, MCC–NaOH, and the regenerated MCC–NaOH samples from AMIMCl and AHIMCl. The distinct diffracted intensity of the MCC at 2θ values was less intense and shifted to a lower 2θ value of 21.91° after the treatment of 20% aqueous NaOH solution at 5 °C for 72 h. These results indicate that the crystal form of cellulose (I) of the MCC samples changed to cellulose (II) of the MCC–NaOH sample, showing the decrease in the crystallographic index of the MCC. The more distinct decrease in diffracted intensity was observed from the regenerated MCC–NaOH samples from AMIMCl and AHIMCl, where the diffraction angles of 14.91°, 16.45°, 20.58°, and 34.65° nearly disappeared. Only weak diffracted intensities of the regenerated MCC–NaOH samples from AMIMCl and AHIMCl were respectively observed at 2θ value of 21.38° and 21.87°. Fig. 6B shows that the 0 0 2 plane apparent crystallite size of the MCC, MCC–NaOH, and the regenerated MCC–NaOH samples from AMIMCl and AHIMCl was respectively 6.2466–2.0088, 0.5338, and 0.5226 nm. This suggests that unlike in the treatment of aqueous NaOH, the 1-allyl-3-alkylimidazolium chloride ionic liquids severely damaged the crystal structure of cellulose.

3.4. TGA analysis

The TGA curves are shown in Fig. 7 for the AAIMCl ionic liquids and the regenerated cellulose samples. In the thermal degradation process of the ionic liquids, their starting decomposition temperature nearly occurred at 195 °C, which is relatively lower than that of 300–400 °C for most ionic liquids (e.g. $[BMIM]PF_6$, $[EMIM]BF_4$) (Pinkert et al., 2009; Ngo, Compte, Hargens, & McEwen, 2000). This finding indicates the relatively poor thermal stability of 1-allyl-3-alkylimidazolium chloride ionic liquids. The weight losses of AMIMCl, AEIMCl, APIMCl, ABIMCl, and AHIMCl in an N_2 atmosphere occurring in the range of room temperature (30 °C) to 192.5 °C varied from 9.41%, 2.83%, 8.43%, 2.86%, and 16.95%, respectively, due to the elimination of smaller residual molecules. The greatest decomposition temperature (T_d) of the abovementioned ionic liquids varied from 274.3 °C to 283.1 °C. The combined weight loss from 192.5 °C to T_d was 63.16%, 56.06%, 58.27%, 58.9%, and 59.98%, respectively, for AMIMCl, AEIMCl, APIMCl, ABIMCl, and AHIMCl (Fig. 7A). In the rapid decomposition process from 192.5 °C to T_d, the anions decompose through dealkylation, whereas the cations primarily undergo alkyl migration and elimination reactions (Baranyai, Deacon, MacFarlane, Pringle, & Scott, 2004; Hao, Peng, Hu, Li, & Zhai, 2010). Based on the above data, AMIMCl and AHIMCl had relatively poor thermal stability due to the lower overall symmetry of the cation asymmetry structures than AEIMCl, APIMCl, and ABIMCl.

The regenerated MCC–NaOH samples from AMIMCl and AHIMCl at 100 °C had weight losses of 29.03% and 12.85%, respectively, at a range of room temperature to 150 °C. The weight losses of the regenerated MCC–NaOH samples were higher than 5.86% of the MCC (Fig. 7B). The regenerated MCC–NaOH samples from AMIMCl and AHIMCl had lower decomposition temperatures (T_d) of 257.7 and 274.4 °C, respectively, than that of the MCC and MCC–NaOH samples. This finding indicates that the damage in the crystal structure and the part breakage of cellulose chains resulted in the poor thermal stability of cellulose samples.

3.5. Morphology analysis

Fig. 8A shows that 1-allyl-3-alkylimidazolium chloride had were of a flaxen color, except for the brownish red APIMCl. When cooled to room temperature, all the new ionic liquids were liquid, whereas [C_4mim]Cl formed a crystalline solid (Cao et al., 2009). The cellulose regenerated from 1-allyl-3-alkylimidazolium chloride showed perfect diaphanous membrane-forming properties (Fig. 8B). Many fragments of cellulose membrane were apparent (Fig. 8C and D) but no fibers were observed. The surface of the cellulose membrane was slippery and diaphanous. This verified the reconstruction of cellulose chains as well as the completed dissolution of cellulose. Unlike in the vacuum freeze-dry method for cellulose membrane, in the air-dried method, the cellulose membrane maintains the entire membrane property.

4. Conclusions

In this study, 1-allyl-3-alkylimidazolium chloride ionic liquids were synthesized and characterized by increasing the carbon atoms ($n \leq 6$) of alkyl chains on the cationic 3-imidazole ring. The cellulose samples of pulp as well as the pulp and MCC pretreated by aqueous 20% (w/w) NaOH or EDA solution showed reasonable solubility in AMIMCl, AEIMCl, and AHIMCl. AEIMCl was more capable of dissolving cellulose at high dissolution temperature of 100 or 120 °C, whereas AHIMCl showed perfect dissolution of cellulose at low dissolution temperature of 60 °C. AMIMCl showed good dissolution of cellulose within 60–100 °C. The AHIMCl seemed to dissolve pulp and the treated pulp more efficiently than did AEIMCl. The cellulose samples treated by AMIMCl and AHIMCl had poor crystal structures and thermal stabilities compared with those treated by 20% (w/w) NaOH solution.

Acknowledgements

We gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (No. 31000285), the Fundamental Research Funds for the Central Universities, South China University of Technology, PR China (No. 2009ZM0106), and the Pulp & Paper Engineering State Key Laboratory, South China University of Technology, PR China (No. 200914).

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