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Dissolution and blending of chitosan using 1,3-dimethylimidazolium chloride and 1-H-3-methylimidazolium chloride binary ionic liquid solvent

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ABSTRACT

A novel, lower viscosity and highly efficient ionic liquid (IL), 1,3-dimethylimidazolium chloride (DMImCl), has been prepared. This IL together with another IL 1-H-3-methylimidazolium chloride (HMImCl) have been developed for the dissolution and regeneration of chitosan, which can be used to prepare chitosan/cellulose blended membranes and fibers. Wide-angle X-ray diffraction (WAXD), Fourier transform IR (FTIR) and thermal gravimetric analysis (TGA) were used to visualize the modifications of the native structures of chitosan during the dissolution and the regeneration processes. No or little ammonium salts came into being in the dissolution process of chitosan. The morphological features and mechanical properties of the blended materials were carried out to evaluate the effect of blending by scanning electron microscope (SEM) and tensile testing, respectively. The resulting chitosan/cellulose blended membranes and fibers not only present brown compact structure but also possess good mechanical properties.

1. Introduction

To date, only limited solvents have been reported to dissolve cellulose and chitin including LiCl/N,N-dimethylacetamide system (Terbojevich, Cosani, Conio, Ciferri, & Bianchi, 1985; Uragami, Ohsumi, & Sugihara, 1981), NaOH/(thio) urea aqueous solution (Cai & Zhang, 2005; Hirano & Midorikawa, 1998; Zhang, Guo, & Du, 2002), some strong acids such as methanesulfonic acid (MSA) (Nishi, Noguchi, Tokura, & Shiota, 1979), and some fluorinated solvents such as hexafluoro-2-propanol (HFIP) (Min et al., 2004). Chitosan is soluble in dilute aqueous solutions of organic and mineral acids (Austin, 1978; Einbu, Naess, Elgsaeter, & Varum, 2004), but an alkaline solution treatment process is necessary to remove the acid after dissolution (Fuji Spinning Co. Ltd., 1984; Mitsubishi Rayon Co. Ltd., 1981). Furthermore, the polyelectrolyte solutions had limited application as transition metal sorbents (Weltrowski, Martel, & Morcellet, 1996) and drug carriers (Nah & Jang, 2002) because bioactive agents may be affected by acetic acid.

Recently, ionic liquids (ILs) were regarded as green solvents to replace the volatile organic compounds (VOCs) in various processing and synthesis industries (Seddon, 1999; Welton, 1999). Pioneer studies by Rogers et al. showed that 1-butyl-3-methylimidazolium chloride (BMImCl) is a powerful solvent for cellulose, up to 25 wt.% of cellulose can be dissolved in BMImCl to form a homogeneous solution (Swatloski, Spear, Holbrey, & Rogers, 2002). Due to ILs have many advantages such as width of liquid range, excellent dissolution ability, freeness from the effect of vapor pressure, ease of recycling and design (Seddon, 1999; Welton, 1999), Rogers work offered a convenient and environmentally friendly platform to the exploitation of these natural polysaccharides. In the following studies, research faculties synthesized a variety of ILs through changing the structure of cations or anions (Feng & Chen, 2008; Liebert & Heinze, 2008), in particular, several low viscous ILs with smaller cation (Phillips et al., 2004; Zhang, Wu, Zhang, & He, 2005) or formate anion (Fukaya, Sugimoto, & Ohno, 2006), which could improve the solubility of polysaccharides. It is generally accepted that low viscous ILs with high solubility of polysaccharides are strongly desirable (Forsyth, MacFarlane, Thomson, & Itzstein, 2002). We had intended to develop low viscous ILs by changing cation. But it is difficult to be finished by traditional method because the low boiling points of volatile halogenoalkanes (bromomethane, chloromethane, chloroethane, 1-chloropropane, etc.) often lead to IL preparations requiring either a sealed tube or an elaborate apparatus.

In this paper, we report a green method for synthesis of dialkyl imidazolium ILs with smaller cation size. 1,3-Dimethylimidazolium chloride (DMImCl) and acidic IL 1-H-3-methylimidazolium chloride (HMImCl) were chosen to dissolve chitosan. The preparation, characterization, and mechanical property of the chitosan and chitosan/cellulose blended membranes and fibers are also described.

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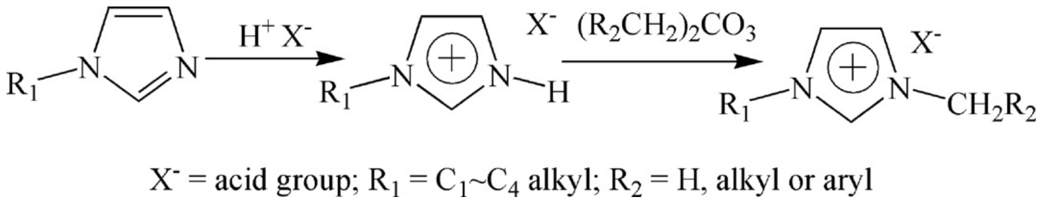

X^- = acid group; $R_1 = C_1$~C_4 alkyl; R_2 = H, alkyl or aryl

Fig. 1. Preparation procedures for ionic liquids.

2. Experimental

2.1. Materials

Microcrystalline cellulose and chitosan (deacetylation degree > 90%) were purchased from Qingdao Shenyan Chemical Industry Co. Ltd. N-Methylimidazole (99%) was obtained from Jiangsu Meihua Chemicals Co. Ltd. (Suzhou, China). Dimethyl carbonate (99%), chloropropylene (98%), 1-chlorobutane (98%) and other reagents were supplied from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2.2. Preparation of ILs

For the DMImCl synthesis, firstly, appropriate amount of HCl (36%) was added dropwise in a round-bottomed flask containing N-methylimidazole in ice bath. After being stirred for several hours, the reaction mixture was evaporated in vacuo. The residue was washed with ethyl acetate, then dried by azeotropic removal of water with a rotatory evaporator according to the literature (Ohno & Yoshizawa, 2002; Zhu, Yang, Tang, & He, 2003) to obtain acidic ionic liquid precursor (AILP) HMImCl. Secondly, HMImCl (2.0 mmol) and dimethyl carbonate (2.0 mmol) were transferred into a stainless steel autoclave (inside volume 3.0 ml) and heated to 170 °C for 20 h. After the reaction, the reactor was cooled to room temperature and opened for analysis of the sample on a NMR spectrometer. ^{1}H NMR spectra of DMImCl and HMImCl are shown as follows:

HMImCl: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ4.12 (3H, s), 7.17 (1H, s), 7.40 (1H, s), 9.75 (1H, s), 15.80 (1H, s). (Yield: 99%).

DMImCl: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ4.10 (6H, s), 7.13 (1H, s), 7.37 (1H, s), 9.69 (1H, s). (Yield: 99%).

Other ILs including BMImCl and 1-allyl-3-methylimidazolium chloride (AMImCl) were prepared according to literature (Dyson et al., 1997). Briefly, mixtures of 1-chlorobutane or chloropropylene (1.2 mol), N-methylimidazole (1.0 mol) and CH_3CN (150 ml) were added to a round-bottomed flask fitted with a reflux condenser with stirring. After 48 h the CH_3CN was removed by distillation and the residue was washed with ethyl acetate (3 × 60 ml) then dried in vacuum at 100 °C for 24 h to give purified ILs. Their ^{1}H NMR spectra are shown as follows:

BMImCl: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ0.95–1.00 (3H, t), 1.34–1.46 (2H, m), 1.87–1.97 (2H, m), 4.15 (3H, s), 7.51 (1 H, s), 7.61 (1H, s), 10.83 (1H, s). (Yield: 97%).

AMImCl: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ4.06 (3H, s), 4.94 (2H, d), 5.4 (1H, d), 5.91–5.97 (1H, m), 7.42 (1H, s), 7.65 (1H, s), 10.44 (1H, s). (Yield: 95%).

2.3. Dissolution of cellulose and chitosan in ILs

To a round-bottomed flask, 2 g of dried ILs and 20 mg of cellulose or chitosan were mixed under nitrogen atmosphere. Then the mixture was stirred for 15 min at each temperature (controlled by an oil bath). If the polysaccharide was not completely dissolved, the temperature was raised by 5 °C. The minimum temperature to give a clear solution was recorded as the dissolution temperature. DMImCl and DMImCl/HMImCl (DMImCl:HMImCl = 9:1) are solvents for cellulose and chitosan, respectively.

2.4. Regeneration of cellulose and chitosan from ILs

For the chitosan membranes preparation, typically, the chitosan DMImCl/HMImCl solution (4 wt.%) was cast onto a glass slide. Then the glass slide was soaked in the methanol bath overnight to remove ILs from membrane. The obtained semi-transparent regenerated gel was finally oven-dried at 60 °C to obtain a pure chitosan membrane. The regenerated blended fibers could also be obtained. Typically, the chitosan DMImCl/HMImCl solution (4 wt.%) was transferred into a syringe, and then the solution was injected into the methanol bath to form fibers. After being soaked overnight to remove ILs, these regenerated fibers were wound on a glass bobbin to prevent recoiling and dried overnight at room temperature.

Preparation procedures for chitosan/cellulose blended membranes or fibers are as follows: firstly, cellulose was dissolved in DMImCl to form one solution, and chitosan was dissolved in DMImCl/HMImCl to form another solution. Secondly, two solutions were mixed to form a homogeneous mixture. Lastly, the resulting mixture was cast onto a glass slide or transferred into a syringe,

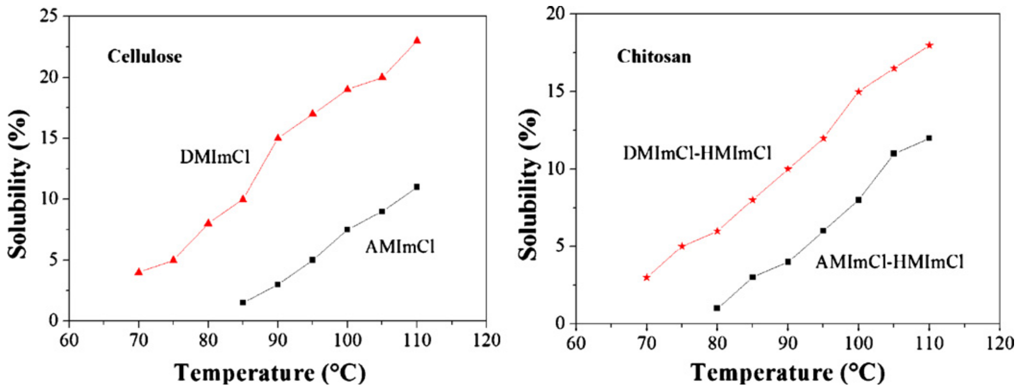

Fig. 2. Temperature dependence of solubility of cellulose and chitosan in ionic liquids.

and the following procedures were the same as the procedures mentioned above.

2.5. Measurements

Due to the absence of the equipment to study the dynamic viscosity, we only measured the ILs kinematic viscosity with an ubbelohde viscometer. Wide-angle X-ray diffraction (WAXD) measurements were conducted using a PW3040/60 X-ray diffractometer with Cu Kα radiation using normal θ–2θ scanning method (k = 0.15418 nm). The Fourier transform IR (FTIR) spectra of the samples were recorded with a Fourier transform IR spectrometer (NEXUS 670, Nicolet, USA) in the range of 400–4000 cm^{-1}. Thermal gravimetric analysis (TGA) measurements were performed on a Netzsch STA 449 at a heating rate of 10 °C/min in nitrogen. The general morphologies were characterized by scanning electron microscope (SEM LEO-1530) at acceleration voltage of 5 kV. Samples were deposited onto double-sided conductive carbon tape, which was then ultimately attached onto the surfaces of SEM brass stubs. These samples were then conductively casted with gold by sputtering for 20 s, so as to minimize charging effects under imaging conditions. The mechanical properties were carried out under tensile mode by electronic universal testing machine (WDS-5) and a tensile rate of 5 mm/min, four parallel measurements were carried out for each sample.

3. Results and discussion

3.1. Dissolution of chitosan and cellulose in ILs

We chose DMImCl as solvent to dissolve polysaccharides due to its optimal effect dissolution, highest yield and easiest preparation. The synthetic process of DMImCl is illustrated in Fig. 1. Various ILs were prepared by reaction of commercially available imidazole derivatives with inorganic acids to form AILPs (Ohno & Yoshizawa, 2002), followed by their alkylation with dialkylcarbonate. ILs comprising varieties of cations (DMIm$^+$, EMIm$^+$, PMIm$^+$, BMIm$^+$, etc.), and anions (Cl^-, Br^-, I^-, $NO_3{}^-$, $BF_4{}^-$, $CH_3CO_2{}^-$, $PF_6{}^-$, $C_2O_4{}^{2-}$, $SO_4{}^{2-}$, etc.) could also be synthesized by this method. Compared with conventional method (Welton, 1999), this synthesis process overcame the defect of using low boiling points of volatile halogenoalkanes, as well as varieties of anions could be designed and the anion exchange was not necessary.

The structure of chitosan is similar to cellulose. But due to the presence of amino groups, its hydrogen bonds are stronger, which makes it notoriously resistant to dissolve and only soluble in dilute aqueous solutions of organic and mineral acids. In our initial experiments, we attempted to dissolve chitosan in AMImCl or BMImCl, but no real dissolution could be achieved. Later we tried a Brønsted acidic IL HMImCl, but chitosan could be dissolved in neither pure HMImCl nor its dilute aqueous solution. Lastly, we employed DMImCl/HMImCl (DMImCl:HMImCl = 9:1) binary ILs and the dissolution proceeded smoothly.

Fig. 2 shows the solubility (wt.%) of cellulose and chitosan in DMImCl and DMImCl/HMImCl, respectively. To dissolve 5 wt.% cellulose, the sample dissolved in AMImCl had to be heated up to 95 °C, whereas the sample dissolved in DMImCl had to be heated up to 75 °C. We also dissolved 5 wt.% chitosan in AMImCl/HMImCl and DMImCl/HMImCl. The former had to be heated up to 90 °C and the latter to 75 °C. These results show that DMImCl dissolved both cellulose and chitosan at lower temperature than AMImCl which has fine ability to disrupt hydrogen bonds (Zhang, Wu, Zhang, & He, 2005), and DMImCl dissolved more cellulose or chitosan than AMImCl at the same temperature. Furthermore, the solubility of polysaccharides decreased in the order of DMImCl > AMImCl > BMImCl, which is in agreement with the trend of viscosity. The dynamic viscosity of DMImCl (55.76 mm^2/S) was lower than AMImCl (458.23 mm^2/S), and BMImCl (5093.37 mm^2/S) at 30 °C. It is worth to notice that lower viscosity would favour the processes such as regeneration of cellulose materials, which would have important application value.

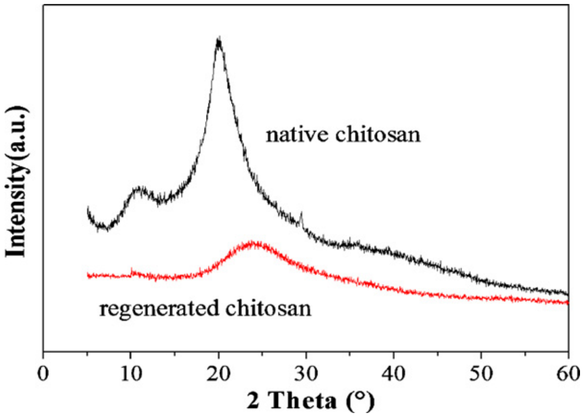

Fig. 3. WAXD profiles of the native and regenerated chitosan.

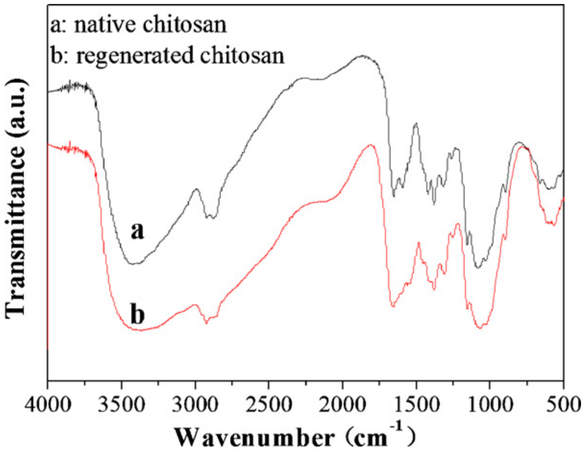

Fig. 4. FTIR spectra of the native and regenerated chitosan.

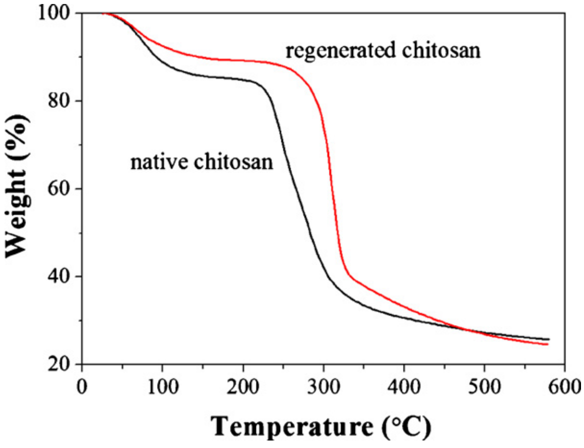

Fig. 5. TGA curves of the native and regenerated chitosan.

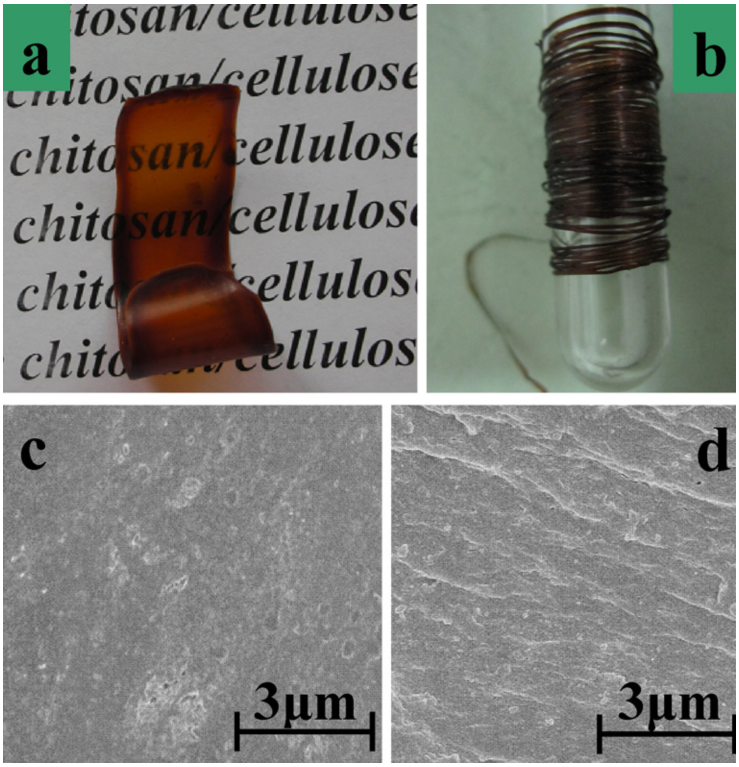

Fig. 6. Digital images of regenerated chitosan/cellulose (1:3, w/w) blended membrane (a), fibers (b), SEM micrographs of the surface of regenerated chitosan/cellulose (1:3, w/w) blended membrane (c), and fibers (d).

3.2. *WAXD profiles analysis*

The chitosan/ILs solutions were found to form gel after being cooled down to room temperature. Thus, it is quite easy to prepare a transparent soft material by casting the as-prepared chitosan/ILs solution onto glass slide and cooling to room temperature. After that, the ILs in the gels could be extracted out by rinsing the chitosan/ILs gels in methanol. The resulting gels were then dried to obtain chitosan membrane.

The WAXD profiles of the native chitosan, as well as the regenerated chitosan precipitates from the DMImCl/HMImCl solutions materials are shown in Fig. 3. The regenerated chitosan shows a broad amorphous halo centered at 25°, but no typical diffraction pattern of native chitosan (with a prominent peak at $2\theta = 10.1^\circ$ and 20.4° which are assigned to (0 2 0) and (1 0 0) reflection, respectively (Tian, Liu, Hu, & Zhao, 2003). This result indicates that during the dissolution process, DMImCl and HMImCl have broken inter- and intra-molecular hydrogen bonds and destroyed the original crystalline form. The native crystal structure of chitosan is barely reconstituted but suffers a remarkable decrease in the crystallinity. Moreover, the coagulation process was so transitory that unfavorable to the chitosan crystallization.

3.3. *FTIR spectra analysis*

The FTIR spectra of native and regenerated chitosan are shown in Fig. 4, the results show that the regenerated and the native chitosan differ little. Stretching vibration absorption peak of N–H and O–H at about 3200–3500 cm^{-1}, and the bending vibration absorption peak of N–H at about 1590 cm^{-1} show some weakened trend. It indicates that the H-bond networks in the native chitosan have been greatly destroyed in the dissolution process by the ILs, and the hydrogen bonds network might not be completely reconstituted during the regeneration process by the coagulants. On the other hand, there was not a variable angle vibration absorption peak of $\mathrm{NH_3}^+$ at 1520 cm^{-1} (Sashiwa, Shigemasa, & Roy, 2000). Together with the fact that dilute aqueous solution of HMImCl could not dissolve chitosan. These results indicate that no or little ammonium salts came into being in our dissolution procees. A plausible explanation is that the addition of HMImCl increased the concentration of Cl^- thus improved the ability to dissolve chitosan. The non-polyelectrolyte solution process would broaden the application of chitosan.

3.4. *Thermal analysis*

Thermal-degradation of the native and regenerated chitosan in a nitrogen atmosphere was measured. From Fig. 5, the thermal stability of regenerated chitosan is slightly superior to that of natural chitosan. The degradation of nature chitosan was ca. 220 °C. In the case of the regenerated chitosan, the onset of degradation was above 258 °C. The results indicate that the dissolution and regeneration processes may homogenize the structures of the native chitosan samples, and are also responsible for the removal of some relatively unstable impurities and low molecular weight compounds.

All results of the WAXD, FTIR and TGA indicate that ILs can dissolve chitosan to get homogeneous mixtures through breaking its hydrogen bonds network. The chitosan membranes and fibers can be easily prepared through a regeneration process. But the hydrogen bonds network and the crystal structure of the regenerated chitosan might not be completely reconstituted. Further investigation on the mechanism of dissolution is currently in progress.

3.5. *Morphologies observation*

However, the chitosan membrane is very brittle, let alone the chitosan fiber. It is well known that blending is a common way

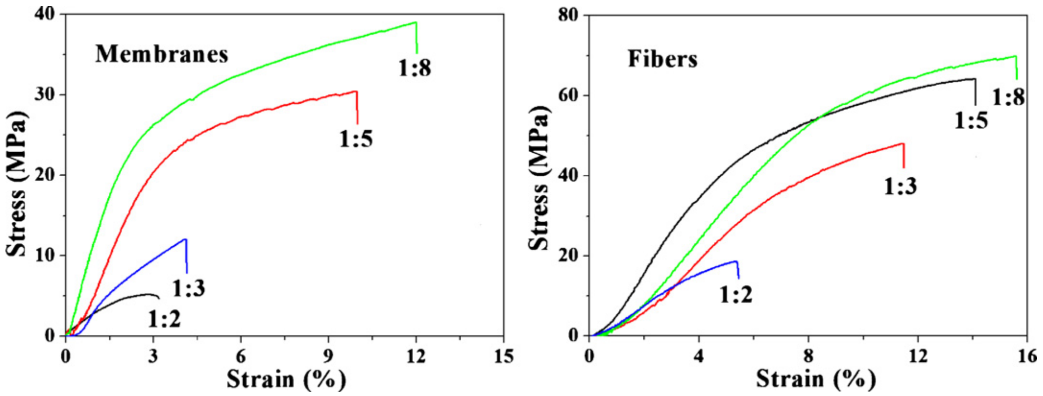

Fig. 7. Stress–strain behavior for chitosan/cellulose blended membranes and fibers with different molar ratio of chitosan to cellulose.

to improve biopolymers mechanical properties. Furthermore, the DMImCl is also an excellent solvent for the cellulose (Fig. 2). Thus, the regenerated blended membranes and fibers could also be obtained easily at the above mentioned conditions in the laboratory. Fig. 6a and b shows the digital images of chitosan/cellulose (1:3, w/w) blended membrane and fibers. The resulting membrane and fibers present brown, indicating that chitosan has blended in cellulose uniformly.

Fig. 6c and d shows the SEM micrographs of the surfaces of the chitosan/cellulose (1:3, w/w) blended membrane and fibers. Together with the digital images of blended membrane and fibers, all display a homogeneous structure, which exhibits a certain level of miscibility of the components. Different from the structure of the cellulose regenerated from NaOH/H_2O (Zhang et al., 2001) or the chitin regenerated from 1-butyl-3-methylimidazolium acetate (BminAc) (Wu, Sasaki, Irie, & Sakurai, 2008), no porous structure was observed in blended membranes and fibers.

3.6. Mechanical properties analysis

The tensile strength of the blended membranes decreases with the molar ratio of chitosan to cellulose as shown in Fig. 7a. Increasing the molar ratio of chitosan to cellulose from 1:8 to 1:2, the tensile strength of the blended membranes decreases from 39.0 to 5.2 kPa. When the molar ratio is more than 1:2, it is difficult to get the stable membrane. On the other hand, the mechanical properties of the blended fibers also became more brittle with increasing the ratio of chitosan. The tensile strength of the blended fiber decreases from 69.9 to 18.6 kPa with the molar ratio of chitosan to cellulose increasing from 1:8 to 1:2 (Fig. 7b).

4. Conclusions

In this study, a novel IL of DMImCl with lower viscosity has been prepared. Due to the strong hydrogen bond acceptability, cellulose and chitosan were solubilized with high concentrations under relatively low temperatures. Different from the traditional method, chitosan was dissolved in ILs seem to a non-polyelectrolyte solution process, which would broaden the application of chitosan. The thermal stability of regenerated chitosan is slightly superior to that of natural chitosan. Furthermore, the chitosan/cellulose blended membranes and fibers can be easily prepared through blending. The resulting brown blended membranes and fibers show good miscibility of the components and mechanical properties. Overall, this method described herein may be valuable to expand chemical modification and applications of chitosan and chitin.

Acknowledgements

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