



Choline chloride/urea as an effective plasticizer for production of cellulose films



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ABSTRACT

Recently, choline chloride/urea (ChCl/urea), a typical deep eutectic solvent (DES), has been found to possess various applications in organic synthesis, electrochemistry, and nanomaterial preparation. Herein we reported the first attempt to plasticize regenerated cellulose film (RCF) using ChCl/urea as an effective plasticizer. Meanwhile, RCFs plasticized with glycerol and sorbitol were also prepared for comparison. The plasticized RCFs were investigated by Fourier transform infrared (FT-IR) spectroscopy, wide-angle X-ray diffraction (XRD), atomic force microscopy (AFM), and mechanical testing. Transparent and soft RCFs could be successfully prepared in the presence of ChCl/urea, and high elongation at break (34.88%) suggested a significant plasticizing efficiency. No new crystal and phase separation occurred to ChCl/urea plasticized RCFs. The thermal stability of ChCl/urea plasticized RCF was lowered. These results indicated that ChCl/urea was an effective plasticizer for producing cellulose films.

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1. Introduction

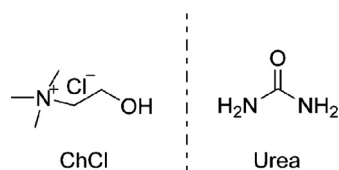
In recent years, DESs, which have similar properties to ionic liquids (ILs) but are much cheaper and more “green” than ILs, have attracted considerable attention (Abbott, Boothby, Capper, Davies, & Rasheed, 2004). A DES is generally composed of two or three cheap and safe components that are capable of self-association through hydrogen bond interactions, forming a eutectic mixture with a melting point lower than that of each individual component. DESs are generally formed by mixing a quaternary ammonium or phosphonium salt with a hydrogen bond donor agent, for instances, acids, alcohols, amines or carbohydrates (Abbott, Capper, Davies, Rasheed, & Tambyrajah, 2003; Choi et al., 2011; Kareem, Mjalli, Hashim, & AlNashef, 2010). Most of DESs have the solvent characteristics similar to ILs, such as low volatility, wide liquid range, water-compatibility, non-flammability, nontoxicity, biocompatibility, and biodegradability. Furthermore, they show the ability to customize their physical properties by choosing the right constituents in terms of chemical nature, relative composition or water content (Choi et al., 2011).

ChCl/urea is the most widely investigated DES. The chemical structures of ChCl and urea were shown in Scheme 1. Abbott et al. (Abbott et al., 2003) first found that the mixture of ChCl and urea showed a deep eutectic effect at a molar ratio of ChCl to urea of 1:2, and its melting point (12 °C) is much lower than that of individual component. ChCl/urea has exhibited excellent performances in various areas such as catalysis (Ilgen et al., 2009; Singh, Lobo, & Shankarling, 2010; Sonawane, Phadtare, Borse, Jagtap, & Shankarling, 2010), organic synthesis (Azizi, Batebi, Bagherpour, & Ghafari, 2012), electrochemistry (Steichen, Thomassey, Siebentritt, & Dale, 2011; Yang, Guo, Birbilis, Wu, & Ding, 2011; Yue, Jia, Yao, Sun, & Jing, 2012), nanoparticle preparation (Chirea et al., 2011; Dong, Hsu, Wong, & Lu, 2010; Liao, Jiang, Zhou, Chen, & Sun, 2008), and carbon material production (Carriazo, Gutiérrez, Ferrer, & Monte, 2010).

Recently, Abbott et al. (Abbott, Ballantyne, Conde, Ryder, & Wise, 2012) found that ChCl/urea could significantly plasticize corn starch to produce a soft and flexible plastic with mechanical properties similar to oil-derived plastics. Ramesh et al. (Ramesh, Shanti, & Morris, 2012) reported that the addition of ChCl/urea into corn starch could enhance the room temperature ionic conductivity by increasing the amorphous elastomeric phase in corn starch (CS): lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) matrix. That was, the presence of ChCl/urea led to the breakage of hydrogen bond in the hydroxyl functional group (–OH) in CS: LiTFSI

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Scheme 1. Chemical structures of ChCl and urea, respectively.

polymer backbone. Furthermore, flexible agarose films were also successfully prepared with ChCl/urea (Shamsuri & Daik, 2012). The pristine agarose film with ChCl/urea was rather smooth and exhibited higher optical transparency as compared with that one without plasticizer. Therefore, ChCl/urea would be a novel plasticizer for biopolymers. In this work, we made the first attempt to investigate the plasticization of ChCl/urea for cellulose film.

Cellulose, the most abundant polysaccharide on the earth, is an ideal alternative to petroleum-based polymers for various applications (Lucia & Rojas, 2007), such as fiber, film, and food packaging (Turner, Spear, Holbrey, & Rogers, 2004; Qi, Chang, & Zhang, 2009). Among these research activities, cellulose-based films have received ever increasing interest. Although some works have been carried out to prepare cellulose-based biodegradable films, the stiff characteristic due to the extensive hydrogen bonds among cellulose chains is still a key problem that restricts their uses in a wide range of applications (Huq et al., 2012; Takegawa, Murakami, Kaneko, & Kadokawa, 2010). Hence, to enhance film forming performance and obtain soft cellulose film, it is necessary to reduce the strong hydrogen bonds. Plasticization is a very simple but useful method to improve the properties of polymers. The additions of glycerol, sorbitol and glycols as plasticizers have been widely applied for cellulosic materials production (Liu, Pang, Zhang, Wu, & Sun, 2013; Xiao, Zhang, Zhang, Lu, & Zhang, 2003).

Being inspired by the above works, the present work was undertaken to evaluate the potential application of ChCl/urea as an inexpensive and environment-friendly plasticizer for cellulose film. The structure and physical properties of the plasticized films were characterized by FT-IR, XRD, TGA, AFM, and tensile testing. For the first time it was shown that ChCl/urea exhibited good plasticizing effect for cellulose film.

2. Experiments

2.1. Materials

Cotton linter with a particle size of 200 mesh was provided by Ruifeng cellulose Co., Ltd (Shandong, China). The content of α -cellulose was 98 wt% and the ash content was less than 0.1 wt%. The viscosity average degree of polymerization of cotton linter measured in CUEN solution was 780 anhydroglucose units on average. Cotton linter was dried in a vacuum oven for 24 h at 50 °C, and then stored in a desiccator. ChCl (98%) was purchased from Beijing lark technology Co., Ltd (Beijing, China) and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was purchased from Shanghai chengjie chemical Co., Ltd. Sorbitol, glycerol and urea were all analytical reagents and used as received without further purification.

2.2. Preparation of regenerated cellulose films

The fabrication scheme of RCFs with or without plasticizer was illustrated in Fig. S1. In a typical procedure, RCF was prepared as followed. [BMIM]Cl (30.00 g) was first melted in an oil bath at 100 °C for 1 h, and then cotton linter (1.00 g) was dissolved in [BMIM]Cl at 100 °C with magnetic stirring until cotton linter was completely dissolved to give a clear and viscous solution (about 5 h).

Polarized light microscopy (OLYMPUS BX-51) was used to assess the dissolution extent of cotton linter. Then the dissolved cellulose solution was cast on a plastic plate and dipped in deionized water to obtain transparent cellulose gel. The gel was washed with deionized water to remove [BMIM]Cl (AgNO₃ solution as indicator). ChCl/urea (molar ratio of 1:2) solutions with various molar ratios of ChCl/urea to H₂O (from 0.01:1 to 0.06:1) were prepared by adding desired amount urea and ChCl into deionized water. The cellulose gels were soaked into the as-prepared ChCl/urea aqueous solutions for 12 h, followed by drying the gels in an oven at 55 °C for 24 h to obtain ChCl/urea plasticized cellulose films. The corresponding cellulose films were named as ChCl/urea_{0.01}, ChCl/urea_{0.02}, ChCl/urea_{0.04}, and ChCl/urea_{0.06} (0.01, 0.02, 0.04, and 0.06 represent the molar ratio of ChCl/urea to H₂O) according to the concentrations of ChCl/urea in the soaking solutions. The reference sample without ChCl/urea was also prepared in the similar way mentioned above. Meanwhile, cellulose films with glycerol, sorbitol, urea, and ChCl alone were also prepared for comparison and coded as G_{0.01}, G_{0.04}, S_{0.01}, S_{0.04}, Urea_{0.04}, and ChCl_{0.04}, respectively, according to the concentrations of substance in the soaking solutions (G represents glycerol and S represents sorbitol; 0.01 and 0.04 represent the molar ratio of plasticizer to H₂O of 0.01:1 and 0.04:1). The contents of plasticizers in cellulose films were calculated as follow. After being weighed, plasticized cellulose films were dialyzed for one week to completely remove plasticizer, which was followed by drying at 105 °C for 4 h. Plasticizer content (c_p) was calculated from the difference between initial (m_i) and final (m_f) weights of cellulose films, using the following formula: $c_p = (m_i - m_f)/m_i$. Before characterization, all films were kept in a conditioning room (50% relative humidity and 24 °C) for 24 h. What's more, those cellulose films were stored for two months in order to identify the stability of plasticizers in films.

2.3. Characterizations

2.3.1. AFM analysis

In AFM scanning, two to four locations on each sample were tested. Topographic (height) and phase images were recorded under ambient air condition. All of the images were recorded in tapping mode in air using silicon cantilevers with a resonance frequency between 250 and 300 kHz.

2.3.2. Thermal analysis

TGA of film was performed on a simultaneous thermal analyzer (Pyris Diamond TG/DSC-200, US). A total of 5.0–10.0 mg of sample was placed in an aluminum pan, and heated from ambient temperature to 600 °C at a rate of 10 °C min⁻¹ in a nitrogen atmosphere with a flush rate of 25 mL min⁻¹.

2.3.3. XRD analysis

XRD plots of film specimens were created with a Bruker D8 advance diffractometer equipped with a Cu K α source monochromatized by a Ni filter ($\lambda = 0.15418$ nm). The equatorial profiles of the diffraction patterns were captured in an increment of 0.04° for 2θ values and the diffraction angle was ranged from 5° to 50°. The sealed tube X-ray generator system was operated at an acceleration voltage of 45 kV and a current of 25 mA. All samples were tested without being grinded.

2.3.4. FT-IR spectra

ATR-FTIR spectra were recorded on a Vector 33 infrared spectrum instrument (Bruker Corporation, Germany). The scan range was 500–4000 cm⁻¹, and the resolution rate was 1 cm⁻¹.

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