



Preparation and characterization of regenerated cellulose from ionic liquid using different methods



Zhengkui Liu^a, Xiaofu Sun^a, Mingyang Hao^a, Chengyi Huang^a,
Zhimin Xue^b, Tiancheng Mu^{a,*}

^a Department of Chemistry, Renmin University of China, Beijing 100872, China

^b College of Materials Science and Technology, Beijing Forestry University, Beijing 100083, China

ARTICLE INFO

Article history:

Received 27 August 2014

Accepted 21 September 2014

Available online 30 September 2014

Keywords:

Cellulose

Ionic liquid

Compressed carbon dioxide

Anti-solvent

Biomass treatment

ABSTRACT

In this study, regenerated cellulose was prepared from ionic liquid 1-butyl-3-methylimidazolium acetate ([Bmim]Ac) solution using anti-solvent compressed CO₂ of different pressures. And other anti-solvents like water, ethanol and acetonitrile were also employed to regenerate cellulose to provide comparisons. The two-dimensional nuclear magnetic resonance (2D NMR), namely heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond coherence (HMBC), and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) indicated that carboxylate zwitterions [Bmim⁺-COO⁻] formed through the chemical reactions between CO₂ and [Bmim]Ac. Besides, FTIR, wide-angle X-ray diffraction (XRD), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to provide structure characterization of native and regenerated cellulose using different anti-solvents. The results show that the crystallinity of cellulose decreases during the dissolution and regeneration process. And a crystal transformation of cellulose I to cellulose II was verified. The stability of the regenerated cellulose is lower than that of native cellulose. A higher compressed CO₂ pressure results in a smoother surface, a thicker shape and a more homogeneous texture of regenerated cellulose.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Biomass is an important and renewable energy material on Earth, among which cellulose is the most widespread natural polymer which exists as a useful industrial raw material because it is cheap, chemically stable, nonpoisonous, environmentally friendly, and modifiable (Miller, 2013; Ragauskas et al., 2006). Preparation of valuable products of different kinds from biomass, especially from cellulose, via technically feasible ways has been explored all along (Hama et al., 2014; Qu et al., 2014; Vo, Widyaya, Jae, Kim, & Lee, 2014). But cellulose has strong inter- and intra-molecular hydrogen bonds, which cause it hard to dissolve in common molecular solvents and thus difficult for the subsequent dispositions because dissolution is prerequisite before translating into other desired products in many cases. So in spite of enormous annual production, the difficulty of dissolving would limit its utilization to quite a narrow scope.

The ability of disrupting the interchain hydrogen bonds of cellulose determines the dissolution efficiency of a solvent. Some solvent systems have already been developed to dissolve cellulose, such as thiourea/H₂O or NaOH/urea system, NaOH/CS₂ system, alkali/H₂O system, LiOH/urea/H₂O system, molten salt hydrate system, like LiSCN·2H₂O and LiClO₄·3H₂O, and some other systems like *N*-methylmorpholine-*N*-oxide (NMMO), dimethyl sulfoxide (DMSO)/tetrabutyl ammonium fluoride (TBAF), LiCl/1,3-dimethyl-2-imidazolidinone (DMI), LiCl/*N*-methyl-2-pyrrolidine (NMP) and LiCl/*N,N*-dimethylacetamide (DMAc) (Klemm, Heublein, Fink, & Bohn, 2005; Xu, Wang, & Wang, 2010). But these systems always have difficulty in solvent separation and cause environmental pollution. Besides, ionic liquid (IL) can dissolve cellulose to a satisfying concentration (Pinkert, Marsh, Pang, & Staiger, 2009; Swatloski, Spear, Holbrey, & Rogers, 2002). IL is a kind of organic salts with a melting point at or below room temperature which is being considered to have a wide variety of applications in organic synthesis, synthesis of nanomaterials, catalysis, separation analysis and electrochemistry (Petkovic, Seddon, Rebelo, & Pereira, 2011). ILs are composed of only ions that makes most of them own a series of particular physicochemical properties, such as negligible vapor

* Corresponding author. Tel.: +86 1062514925; fax: +86 1062516444.

E-mail addresses: tcmu@chem.ruc.edu.cn, tcmu@ruc.edu.cn (T. Mu).

pressure, outstanding solvation ability, wide temperature for liquid, high thermal stability, designability and wide electrochemical window. Famous for “task-specific” and “tailor-making”, ILs are viewed as green solvents and environmentally friendly alternatives for conventional volatile organic solvents by virtue of tailored physical and chemical prosperities by different matches of cations and anions and modifying the functional groups on cations or anions. IL was first used to dissolve cellulose by Swatloski et al. (2002) and after that several ILs with higher dissolving capacity were found (Andanson et al., 2014; Zhang, Wu, Zhang, & He, 2005; Zhao et al., 2008) among which 1-butyl-3-methylimidazolium acetate ([Bmim]Ac) was reported to possess excellent ability to dissolve cellulose (Xu et al., 2010).

It is fairly important that biomass products of various types are separated efficiently but cellulose/IL solution possesses the disadvantage of difficulty in separating and purifying. At present, anti-solvent method performs remarkably in cellulose separation from ILs. For example, ethanol or water, as an anti-solvent, is loaded into the cellulose/IL solution (Xu et al., 2010). Since ethanol and water are miscible with IL but not with cellulose, the solubility of cellulose in IL is significantly lessened and thus we acquire regenerated cellulose. By using conventional anti-solvents, after the cellulose precipitates, molecular solvent and IL are mixed together as a phase thus leaving a troublesome problem of how to separate them due to the strong interactions between IL and anti-solvents. So it is requisite to develop an energy saving, environmentally benign and effective method to regenerate cellulose from IL.

Compressed CO₂, as a cheap, safe, environmentally benign, non flammable medium, has continuously adjusted physical properties from gas-like to liquid-like by changing temperature and pressure, which can be easily recycled after use (Eckert, Knutson, & Debenedetti, 1996; Zhang & Han, 2012). Considerable amount of CO₂ can be absorbed into ILs but cellulose is not soluble in compressed CO₂, which acts as a gas anti-solvent here (Blanchard, Hancu, Beckman, & Brennecke, 1999). Besides, formation of carboxylate zwitterion from [Bmim]Ac and CO₂ contributes to the coagulation of cellulose from [Bmim]Ac (Gurau et al., 2011). Therefore, dissolved cellulose will precipitate from ILs by using compressed CO₂ and a noteworthy benefit is that CO₂ can be easily separated from ILs by depressurization without new problems in separation process, which solves the big problem of the separation of IL and anti-solvent and the issue of recycling.

In our current work, we studied the regeneration of cellulose from [Bmim]Ac using compressed CO₂ as a gas anti-solvent. Because of its outstanding dissolving ability, [Bmim]Ac was used as the solvent of cellulose. Compressed CO₂ of different pressure was loaded into the cellulose solution to receive regenerated cellulose. Besides, water, ethanol and acetonitrile were also used to precipitate cellulose to provide comparisons. Rogers et al. have proposed the method of using compressed CO₂ to regenerate chitin from 1-ethyl-3-methylimidazolium acetate (EmimAc) (Barber et al., 2013), and our previous work gave a further exploration of the systems (Sun, Chi, & Mu, 2014a; Sun, Xue, & Mu, 2014b). And in this work, we probed into the regeneration mechanism and structure characterization of regenerated cellulose using different anti-solvents, compressed CO₂ of different pressure included. Yields of regenerated cellulose were measured. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR–FTIR) and two dimensional nuclear magnetic resonance (2D NMR), namely heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond coherence (HMBC) were employed to confirm the regeneration mechanism. Beside, Fourier transform infrared spectroscopy (FTIR) and wide-angle X-ray diffraction (XRD) provided structure characterization, and thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to give thermal

analysis. Finally, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were applied to morphology observation.

2. Materials and methods

2.1. Materials

The linter cellulose was purchased from Hubei Golden Ring Co., Ltd. (Xiangyang, Hubei Province, China). The cellulose samples were teared into small pieces and dried in a vacuum oven at 80 °C for around 10 h before use. CO₂ (99.999%) was obtained from Beijing Beiwen Gas Chemical Industry Co., Ltd. [Bmim]Ac (99.9 wt%) was received from Lanzhou Greenchem. ILs, LICP, CAS, China (Lanzhou, China). After drying it at 40 °C in a vacuum oven for 48 h, the water content of IL was less than 1000 ppm determined by Karl–Fischer titration. Deionized water was employed throughout the experiments.

2.2. Dissolution of linter cellulose in [Bmim]Ac

Cellulose fragments were added into [Bmim]Ac with portions of 0.2 wt% of ionic liquid every time under continuous stirring at about 100 °C until the concentration of cellulose achieved 10.0 wt% of the IL. Finally, a homogeneous and plained solution was obtained.

2.3. Regeneration of cellulose from [Bmim]Ac using compressed carbon dioxide and other anti-solvents

The cellulose samples dissolved in [Bmim]Ac were put in high-pressure cells with a volume of about 8 ml, respectively, at 25 °C in a water bath with a constant temperature controller (± 0.1 °C). Then CO₂ was loaded into the cells after the air in the cells were removed until presupposed pressure was achieved. After 3 h CO₂ was released and aerogels were obtained. Ethanol was used to wash away the IL, and the regenerated cellulose retained, from which we can calculate the yields. In addition, we put the cellulose solutions into water, ethanol and acetonitrile and obtained gels directly and immediately. After further washing with ethanol to remove IL, we got regenerated cellulose.

2.4. Characterization of the regenerated and native cellulose

2.4.1. Yields

Yields were calculated using an electronic analytical balance (Mettler Toledo ML204/actual scale interval = 0.1 mg). Masses of each cellulose sample before dissolution and after regeneration were weighed, respectively.

2.4.2. ATR–FTIR and 2D NMR spectroscopy measurement

Pure and dried ionic liquid [Bmim]Ac of 5 ml was put into the high-pressure cell at 25 °C in a water bath with a constant temperature controller (± 0.1 °C). Then CO₂ was loaded into the cells after the air in the cells were removed until presupposed pressure 6.6 MPa was achieved. After keeping for 3 h, redundant CO₂ was released and the pressure reached the normal pressure (0.1 MPa). ATR–FTIR spectroscopy was implemented to investigate structure changes in the liquid phase and our ATR–FTIR measurements were performed on a Prestige-21 FTIR spectrometer (Shimadzu, Japan, DTGS detector) using a single reflection ATR cell (a ZnSe ATR–8200H cell, 584 mm² surfaces, 45° incident angles) over the range of 2000–1100 cm⁻¹ with a resolution of 4 cm⁻¹ and 40 total scans. Besides, 2D NMR (HSQC and HMBC) spectra were acquired with a Bruker Advance 600 MHz spectrometer using a co-axial capillary containing D₂O as a lock solution.

Download English Version:

<https://daneshyari.com/en/article/7789493>

Download Persian Version:

<https://daneshyari.com/article/7789493>

[Daneshyari.com](https://daneshyari.com)