



Water-soluble cellulose acetate from waste cotton fabrics and the aqueous processing of all-cellulose composites



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ABSTRACT

The objective of this study is to explore the possibility of using waste cotton fabrics (WCFs) as low cost feedstock for the production of value-added products. Our previous study (Tian et al., 2014) demonstrated that acidic ionic liquids (ILs) can be highly efficient catalysts for controllable synthesis of cellulose acetate (CA) due to their dual function of swelling and catalyzing. In this study, an optimized “quasi-homogeneous” process which required a small amount of acidic ILs as catalyst was developed to synthesize water-soluble CA from WCFs. The process was optimized by varying the amounts of ILs and the reaction time. The highest conversion of water-soluble CA from WCFs reached 90.8%. The structure of the obtained water-soluble CA was characterized and compared with the original WCFs. Moreover, we demonstrate for the first time that fully bio-based and transparent all-cellulose composites can be fabricated by simple aqueous blending of the obtained water-soluble CA and two kinds of nanocelluloses (cellulose nanocrystals and cellulose nanofibrils), which is attractive for the applications in disposable packaging materials, sheet coating and binders, etc.

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1. Introduction

As the most abundant non-food biomass on earth, cellulose is widely considered an alternative sustainable source of chemicals and energy. The production of cellulose derivatives has attracted much attention due to its abundance in nature, biodegradability and lower environmental impact comparing to polymers obtained from fossil sources (Das, Ali, & Hazarika, 2014). Among them water-soluble cellulose derivatives are highly attractive and widely used in various industrial applications, such as film forming, thickening, lubricating, stabilizing and water-binding (Karlsson, Schuster, Stading, & Rigdahl, 2015).

Most water-soluble cellulose derivatives belong to cellulose ethers (e.g. carboxymethyl cellulose and hydroxypropyl cellulose). Nowadays, commercial cellulose esters such as cellulose acetate (CA) are water insoluble and not suitable in aqueous processing applications. It has been reported that with a degree of substitution (DS) from 0.5 to 1, CA is water-soluble (Gomez-Bujedo, Fleury, & Vignon, 2004). Despite its potential applications, the manufacture of this product is confined in a laboratory scale. The primary reason is that its preparation involves two time-consuming and

environmental-unfriendly steps: sulfuric acid or pyridine catalyzed acetylation of cellulose followed by hydrolysis of the fully substituted CA in an aqueous mineral acid medium (Buchanan, Edgar, & Wilson, 1991). Although sulfuric acid or pyridine show good catalytic activity for the production of cellulose esters, there are a number of drawbacks associated with this procedure, e.g., it drives side reactions and causes considerable corrosion or poisonous. Furthermore, it is impossible to synthesize partially substituted cellulose esters in a one-step process using these heterogeneous catalysts (Yang, Xie, & Liu, 2014). To pave the way for the exploitation of water-soluble CA, a more efficient and environmentally friendly preparation method which avoids the use of strong acid catalysts and back-hydrolysis processes is desired.

Homogeneous derivatization of cellulose in various solvents, e.g. ionic liquids (ILs), provides a feasible approach to synthesis cellulose esters with controllable DS values (Lv, Chen, Shao, Zhang, & Zhao, 2015; Tomé et al., 2011; Wu et al., 2004). Water-soluble cellulose esters can be prepared directly using ILs as reaction medium (Cao, Li, Zhang, Zhang, & He, 2008; Dorn, Pfeifer, Schluffer, & Heinze, 2010). However, a very dilute solution typically 2.5–8 wt% of cellulose in ILs as demonstrated by recent publications (Schenzel, Hufendiek, Barner-Kowollik, & Meier, 2014; Yang et al., 2014) was required in these studies due to the extensive intra- and intermolecular hydrogen bonds in cellulose and the intrinsic high viscosity of ILs. It resulted in a relatively high cost of homogeneous

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derivatization and restricted its large-scale application since ILs is expensive at present.

Recently, we reported a “quasi-homogeneous” process using a small amount of acidic ILs (as low as 3–9 mol% relative to cellulose) as catalyst to synthesize CA with controllable DS values. The dual-function of swelling and catalyzing of acidic ILs played an important role in producing such a “quasi-homogeneous” acetylation system and controlling the DS value of CA (Tian, Han, Lu, Zhang, & Yuan, 2014). The relationship between DS values of the obtained CA and its solubility in various solvents has been elucidated. It was found that CA with DS in the range 0.6–1.25 exhibited good water solubility. However, the effect of ILs concentration and reaction time on the conversion of water-soluble CA through this “quasi-homogeneous” method is unclear until now. Meanwhile, the chemical structure of the obtained water-soluble CA still needs further characterization. Furthermore, the properties (e.g. film-forming) of the prepared water-soluble CA need to be investigated and improved to fulfill the requirement of practical applications.

Therefore, the main focus of this study is to investigate the effect of reaction conditions (molar ratio of ILs/cellulose and reaction time) on the yield of water-soluble CA using acidic ILs as catalyst. In order to develop a more economic attractive method, waste cotton fabrics (WCFs) were used as a cheap cellulose source. In China, huge amount of cellulosic wastes is produced as textile wastes in thousands of plants. They have virtually no use, leading to serious environmental pollutions. In our previous studies, we have developed a series of methods to recycle WCFs (Han, Zhang, Wu, & Lu, 2015; He, Zhang, Zhang, Tian, & Lu, 2014; Sun, Lu, Zhang, Tian, & Zhang, 2013; Sun, Lu, Liu, Zhang, & Zhang, 2014; Zhang, Zhang, Tian, Zhou, & Lu, 2013). Here, we demonstrate for the first time that high conversion (up to 90.8%) of transparent water-soluble CA from WCFs can be achieved through this optimized, facile and environmental-friendly approach. Furthermore, two kinds of nanocelluloses, cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF), are incorporated into the water-soluble CA matrix via a simple aqueous processing approach to prepare transparent, flexible and mechanically robust all-cellulose composites. These properties make it attractive in the applications of disposable packaging materials, sheet coating, binders and flexible electronic devices.

2. Methods

2.1. Materials

Waste cotton fabrics (WCFs) with high cellulose content (≥ 98 wt%) were collected from tailoring workshops and used as cellulose source for preparing cellulose acetate and cellulose nanocrystals (CNC). WCFs were subjected to cutting and shredding processes and after that used without further purification or bleaching. Never-dried bamboo bleached fibers were used as cellulose source for preparing cellulose nanofibrils (CNF). Acidic ILs [Hmim]HSO₄ was purchased from Chengjie Co., Ltd. (Shanghai, China). Analytical grade acetic anhydride, ethanol, sodium hydroxide and sulfuric acid were supplied by Kelong Chemical Regent Co., Ltd. (Chengdu, China).

2.2. Synthesis of water-soluble CA

The acetylation of cellulose was carried out under atmosphere pressure using [Hmim]HSO₄ as catalyst. In a typical reaction, 3.24 g [0.02 mol of anhydroglucose units (AGU), assuming the sample was pure cellulose] of loosened WCFs, 20.4 g (0.2 mol) of acetic anhydride, and 0.1–0.4 molar equivalents of ILs with respect to per mole of AGU were mixed and heated at 100 °C for 1–5 h. The reacted

mixture was poured into 100 mL of ethanol and stirred for 30 min. The solid consisting of CA and unreacted cellulose was filtered and washed with ethanol three times and then dried in a vacuum oven at 60 °C for 24 h. In order to extract water-soluble CA, the sample was then refluxed for 24 h by the Soxhlet extraction method using deionized water as the solvent. The filtrate was then dried in a vacuum oven at 60 °C for 24 h to obtain the water-soluble CA product.

2.3. Preparation of CNC

CNC was prepared by controlled acid hydrolysis of WCFs according to our previous studies (Wang et al., 2016; Zhang, Wu, Lu, & Zhou, 2015). WCFs (22.86 g) were mixed with preheated sulfuric acid solution (64 wt%, 400 mL) at 45 °C for 45 min. The reaction was quenched by the dilution with deionized water. The hydrolysis product was washed twice by centrifugation at 5000 rpm for 5 min, and was dialyzed to remove residual acid for several days until the dialyzate appeared neutral. The solid content of CNC suspension was measured 3 times and the average value was 0.55 wt%.

2.4. Preparation of CNF

CNF was prepared by high shear homogenization of the bleached bamboo pulp according to our previous studies (Xiong et al., 2014). The bamboo pulp was dispersed in distilled water at a solid concentration of 1 wt%. A horn-type ultrasonic generator (JY99-IIDN, Scientz, China) was used to treat the suspension (500 mL) at an output power of 1200 W for 30 min. The suspension was then diluted to the concentration of 0.5 wt% with distilled water. Finally, a high shear homogenizer (IKA T18, Germany) was used to isolate CNF at a rotation speed of 20000 rpm for 1 h.

2.5. Preparation of CA/CNC and CA/CNF composites

The aqueous suspension of nanocelluloses containing different ratios of CNC and CNF was added into the as-prepared CA aqueous solution (2.0 wt%) and homogenized using a high shear mixer (IKA T18, Germany). The mixed suspension was filled into a 90 mm diameter glass Petri dish and allowed to evaporate over 48 h at ambient temperature to produce CA/CNC and CA/CNF composites. The thickness of each film sample was kept constantly at 50 ± 10 μm . The samples were coded as CA/CNC-5, CA/CNC-10, CA/CNC-20 and CA/CNF-5, CA/CNF-10, CA/CNF-20 according to the solid content of CNC and CNF in the composites at 5 wt%, 10 wt% and 20 wt%, respectively.

2.6. Characterization

2.6.1. FTIR analysis

Fourier transform infrared spectra (FTIR) of the water-soluble CA and original WCFs were measured by means of a Nicolet 560 spectrophotometer (USA), taking over 20 scans for each sample with a resolution of 2 cm^{-1} , ranging from 400 to 4000 cm^{-1} . All the samples were dried in vacuum oven at 60 °C for 24 h before testing.

2.6.2. XRD analysis

X-ray diffraction (XRD) patterns were collected on a Philips Analytical X'Pert X-diffractometer (Philips Co., Netherlands), using Cu-K α radiation ($\lambda = 0.1540\text{ nm}$) at an accelerating voltage of 40 kV and the current of 40 mA. The data were collected from $2\theta = 5$ – 60° with a step interval of 0.03° .

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