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

Jie Cao¹, Xunwen Sun¹, Canhui Lu¹, Zehang Zhou¹, Xinxing Zhang^{1*} and Guiping Yuan^{2*}

¹State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

²Analytic and Testing Center of Sichuan University, Chengdu 610065, China

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.

*Corresponding author: Xinxing Zhang and Guiping Yuan
E-mail address: xxzwwh@scu.edu.cn, ygp_04@163.com
Tel: +86-28-85460607 Fax: +86-28-85402465

Key words: water-soluble cellulose acetate; waste cotton fabrics; ionic liquids; all-cellulose composites; aqueous processing

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 et al., 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 et al., 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 et al., 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 et al., 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 (Wu et al., 2004; Tomé et al., 2011; Lv et al., 2015). Water-soluble cellulose esters can be prepared directly using ILs as reaction medium (Dorn et al., 2010; Cao et al., 2008). However, a very dilute solution typically 2.5–8 wt% of cellulose in ILs as demonstrated by recent publications (Schenzel et al., 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 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 et al., 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 et al., 2015; Sun et al., 2013; Sun et al., 2014; Zhang et al., 2013; He et al., 2014). 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 ([Zhang et al., 2015](#); [Wang et al., 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.

2.4. 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 $50 \pm 10 \mu\text{m}$. 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.

2.5. Characterization

2.5.1. 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.

2.5.2. 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° .

2.5.3. Thermal property analysis

Thermogravimetric analysis (TGA) was performed under nitrogen purge (flow rate about 100 mL/min) using a TA-2000 analyzer (TA Instrument, USA). The scanning rate of $10^\circ\text{C}/\text{min}$ and temperature range of 40 - 600°C were used. Samples of about 5 mg were placed in an open alumina crucible. All the samples were vacuum oven dried at 60°C for 24 h before testing.

Curves of differential scanning calorimetry (DSC) analysis for the samples were recorded on a NETZSH 204 DSC differential scanning calorimeter (Germany) under a flowing N_2 with sample weight 5 mg. The thermal properties of all samples were measured by heating from ambient temperature to 250°C at a heating rate of $10^\circ\text{C}/\text{min}$.

2.5.4. Morphological investigation

Transmission electron microscopy (TEM) was carried out using a transmission electron microscope (JEOL JEM-100CX, Japan) to observe the morphology of CNC.

The morphology of CNF was investigated by scanning electron microscope (SEM, JEOL JSM-5600, Japan) with an accelerating voltage of 20 kV. The sample was previously sputter coated with gold to prevent charging on the surface.

An Olympus BH-2 optical microscope (Japan) with $10\times$ objective lens was used to observe the dispersion of nanocelluloses (CNC and CNF) in CA matrix with the assistance of two polarized light filters. Samples were viewed under white light conditions.

2.5.5. UV-vis transmittance measurements

The optical transmittances of the film composites were measured from 350 to 900 nm using a Shimadzu UVmini-1240 spectrophotometer (Japan) and correlated based on the sample thicknesses using the Lambert–Beer's law.

2.5.6. Mechanical properties

The stress-strain properties were measured according to ASTM D 412-80 specification using dumb-bell test pieces by an Instron 5567 Universal Testing Machine (USA) at a crosshead speed of 50 mm/min. At least five measurements for each sample were made in order to eliminate experimental error. All the samples were dried in a vacuum oven at 60 °C to reach a constant weight before testing.

2.5.7. ^1H NMR analysis

The molecular structure of water-soluble CA was determined by ^1H nuclear magnetic resonance (NMR) spectroscopy (Bruker AV II-600 MHz, at ambient temperature). The water-soluble CA was dissolved in deuterium oxide and purified by 0.2 μm size of filter membrane. The DS value of CA was calculated by Eq. (1):

$$DS = (7 \times I_{\text{acetyl}}) / (3 \times I_{\text{H,AGU}}) \quad (1)$$

where I_{acetyl} is the peak integral of methyl protons of acetyl moiety, and $I_{\text{H,AGU}}$ is the peak integral of all protons of AGUs (Goodlett, Dougherty, & Patton, 1971).

2.5.8. GPC analysis

Gel permeation chromatography (GPC) studies were carried out to determine the molecular weights of water-soluble CA using a Viscotek Model 270 GPC with RI detector at room temperature. Shodex KF 803, 804, and 805 columns were used, eluted at 1 mL/min flow rate with 0.1 M aqueous NaCl and NaN_3 (2/10000, w/w) solution. The column effluent was monitored using a refractive index detector. Sample preparation: 10 mg of CA was dissolved in 5 mL of ultrapure water.

3. Results and discussion

3.1. Synthesis of water-soluble CA from WCFs

The essence of our designed strategy for extracting water-soluble CA from WCFs and the aqueous processing of all-cellulose composites is schematically depicted in Fig. 1. Our previous study (Tian et al., 2014) revealed that the DS values had a significant effect on the solubility of CA and it could be easily regulated by changing the amount of ILs catalyst and the time of acetylation. In order to realize high conversion of water-soluble CA from WCFs, it is essential to investigate the influence of ILs amount and reaction time on the conversion of products. Fig. 2 and Table S1 show the conversion of water-soluble CA with four ILs concentrations multiply five reaction time. It is worth noting that there is no water-soluble CA without ILs catalyst, because most of cellulose is not reacted. The conversion of water-soluble CA increases significantly with the increase of ILs amount when the reaction time is 1 h. While the conversion of water-soluble CA first increases with the increase of ILs amount and then decreases rapidly when the reaction time is 2 h. The same changes take place when the reaction time is 3, 4 and 5 h. This situation can be ascribed to the increase of DS values and the consequently decrease of solubility in

water. Our previous study (Tian et al., 2014) demonstrated that only the CA with a DS ranging from 0.60 to 1.25 was soluble in water. It is worth noting that the conversion of water-soluble CA increases progressively with increasing reaction time from 1 to 3 h and decreases as the DS values exceed the soluble range (0.60–1.25) when the amount of ILs is 0.2 molar per molar of AGU. Prolonging the reaction time has a favorable effect on the diffusion and absorption of reactants which lead to higher DS values. The optimum condition for acetylation reaction is using 0.2 molar equivalents of ILs per molar of AGU and reacting for 3 h. A very high conversion (90.8 %) of water-soluble CA was obtained.

The efficiency of derivatization reactions of cellulose is highly dependent on the accessibility of the reactants to the AGU unit (Wan Daud & Djuned, 2015). We have used sulfonated biochar as a solid acidic catalyst to catalyze the acetylation reaction of WCFs as a contrast experiment in Fig. S1. However, the conversion of the obtained CA was only 11.1%. The extensive intra- and intermolecular hydrogen bonds in cellulose make the reactants difficult to reach the hydroxyl groups of cellulose. On the other hand, the dual function of swelling and catalyzing of acidic ILs for the acetylation of cellulose makes it possible to destroy the hydrogen bonds of cellulose and increase the reaction accessibility of hydroxyl groups. As a result, this “quasi-homogeneous” process using acidic ILs as catalysts exhibited good catalytic activity for the acetylation of cellulose. The amount of the ILs used in our study is approximately 0.5 wt% of the homogeneous esterification, making it very attractive for large-scale applications.

3.2. Characterization of water-soluble CA

Although high conversion of water-soluble CA from WCFs was realized in this study, we know little about the structure of this new waste-derived material. Therefore, various characterizations were carried out to investigate its structure with the comparison of original WCFs. The FTIR spectra of original WCFs and the obtained water-soluble CA are given in Fig. 3(a). Compared with the spectrum of underivatized cellulose, the

spectrum of the water-soluble CA provides obvious evidence of acetylation by the presence of three important ester bonds at 1752 (C=O ester), 1369 (C–H bond in –OCOCH₃ group) and 1235 cm^{–1} (–CO– stretching band of acetyl group) (Das et al., 2014). In addition, decreased peak intensity at 3412 cm^{–1} which originates from OH stretching in the spectrum of water-soluble CA also indicates the partial acetylation. The obtained CA has a molecular weight $M_w \sim 87678$ as shown in Table S2. The degree of polymerization value was calculated to be 409 (Gomez-Bujedo et al., 2004).

XRD analysis was conducted to investigate the crystalline structural changes of the WCF cellulose after acetylation. Fig. 3(b) shows the XRD patterns of original WCFs and the water-soluble CA. The underivatized cellulose exhibits characteristic of cellulose crystal I structure with four diffraction peaks localized at 14.5°, 16.1°, 22.6° and 33.6°, which are assigned to the diffraction planes of 101, 101, 002 and 040, respectively (Matsumura et al., 2000). The water-soluble CA presents a decrease in diffraction intensity and broadening of diffraction peaks, indicating a decrease in the degree of crystallinity after acetylation. This reduction in crystallinity compared with the original WCFs could be ascribed to the substitution of the hydroxyl groups by acetyl groups with greater volume, which broke the inter- and intramolecular hydrogen bonds of cellulose (Ashore et al., 2014).

The TGA curves of original WCFs and the obtained water-soluble CA are shown in Fig. 3(c). The TGA curves of both original WCFs and water-soluble CA exhibit a single weight loss step with a maximum decomposition temperature at about 352 and 251 °C, respectively. Meanwhile, the onset temperature of degradation of the water-soluble CA (210 °C) is lower than that of the underivatized cellulose (251 °C). This reduction in thermal stability is generally attributed to the decrease of crystallinity after acetylation, but could also be associated to the high lability of the ester linkages introduced to the cellulose structure (Tomé et al., 2011). This behavior is consistent with the acetylation of cellulose reported by other researchers (Tomé et al., 2011; Cao et al., 2007).

The thermal properties of original WCFs and the obtained water-soluble CA were further analyzed by DSC measurements and the results are shown in Fig. 3(d). The diagram of underivatized cellulose does not display the glass transition temperature and molten peak until it decomposed at standard heating scan, which is in accordance with the literature (Zhang et al., 2014). However, the DSC diagram of the obtained water-soluble CA in this study shows an endothermic peak located at about 186 °C, which can be assigned to the fusion of the acetylated cellulose (Wan Daud & Djuned, 2015). Because of the strong hydrogen bonding and stable crystal structure, the underivatized cellulose could not melt but just decomposed under high temperature. The introduction of acetyl groups after acetylation could weaken the hydrogen bonds and improve the movement of molecular chain of cellulose, resulting in the melting of the acetylated cellulose (Zhang et al., 2014).

¹H NMR analysis was conducted to evaluate the distribution of acetyl among the three hydroxyl groups of the AGU. Fig. 4 shows the ¹H NMR spectra of the water-soluble CA with a DS value of 1.25. The three hydroxyl groups at C₂, C₃ and C₆ positions exhibit different reaction activities with an order C₆ -OH > C₂ -OH > C₃ -OH during this quasi-homogeneous cellulose acetylation system according to our previous work (Tian et al., 2014). From the spectra, we can find that there is only a single broad peak at 2.02 ppm of chemical shift, which refers to the fact that the hydroxyl groups at C₆ position are mainly substituted by acetyl groups and the single substitution of cellulose acetate are obtained (Kamide & Okajima, 1981). In addition, it's interesting that two peaks at 7.33 ppm and 8.54 ppm are observed while there were no peaks at the same chemical shifts in our previous work (Tian et al., 2014). Meanwhile, there are three peaks around 2 ppm with high DS (2.67 and 3.02) of CA in our previous work while only one peak at 2.02 ppm in this study. Therefore, the two peaks at 7.33 ppm and 8.54 ppm might be the protons of hydroxyl groups at C₂ and C₃ positions. The results indicate that water-soluble CA with low DS and good water-solubility was prepared successfully by the optimized reaction conditions.

According to the discussion above, a plausible mechanism for the synthesis of water-soluble CA through

quasi-homogeneous acetylation reaction can be proposed. As shown in Fig. 1, cellulose were swelled by acidic ILs, and the strong inter- and intramolecular hydrogen bonds of cellulose were destroyed. The space between the stacked sheets of cellulose molecules increased so that the acetic anhydride could diffuse in (Torr et al., 2012). Then the crystallinity and crystal size of cellulose decreased and the hydroxyl groups were exposed. Meanwhile, H^+ was ionized by ILs and activated the carbonyl group of acetic anhydride, drawing electrons away from the carbonyl carbon to cellulose and making it more positively charged and thus more reactive with acetic anhydride (Biswas et al., 2005). The hydroxyl groups at C₆ position were mainly acetylated due to their higher activity.

3.3. Aqueous processing of all-cellulose composites

Over the last few years, blending of polymers especially renewable, biodegradable and low cost lignocellulosic materials to improve their chemical and physical properties has received increasing attention (Stefanescu et al., 2012; Ashore et al., 2014). The water-soluble characteristic of the CA prepared from WCFs makes it very suitable for aqueous processing of cellulose-derived composites. As a demonstration, two kinds of nanocelluloses (CNC and CNF) which typically preserved as an aqueous suspension were incorporated into the water-soluble CA matrix for the improvement of its mechanical properties. Fully bio-based and biodegradable composites can be fabricated by simple aqueous blending and followed by film casting.

The morphology of CNC was analyzed by TEM and the morphology of CNF was analyzed by SEM, respectively. As shown in Fig. 5(a), the rod-like CNC is 10–20 nm in width and 100–250 nm in length and the aspect ratio is about 10–20. The CNC suspension has a good stability because there are sulfate groups grafted on its surface during acid hydrolysis and creating a strong electrostatic repulsion (Xiong et al., 2012). The SEM morphology of the obtained CNF is shown in Fig. 5(b), which appears as an inter-connected web structure. The diameter of CNF is 20 ± 10 nm while the length is estimated more than 1000 nm, which leads to a higher aspect ratio than CNC.

The dispersion of CNC and CNF in CA matrix could be revealed by polarized light microscopy (PLM) analysis due to the crystalline structure of nanocelluloses. The PLM micrographs of CA/CNC and CA/CNF composites with the filler content of 20 wt% are shown in Fig. 5(c) and (d), respectively. Distinct light domains could be observed in these figures, which could be ascribed to the strong birefringence of CNC and CNF under the polarized light. It is worth noting that the light domains dispersed evenly in the PLM micrographs, indicating good dispersion of CNC and CNF in CA matrix. The good interfacial adhesion between cellulose nanofibers and water-soluble CA is expected since they have similar molecular structure and hydrophilic nature.

UV-vis transmittance measurements were carried out to evaluate the transparency of the prepared CA/CNC and CA/CNF composites. Fig. 6 shows the UV-vis transmittance of approximately 50 μm thick films of neat CA, CA/CNC-20 and CA/CNF-20 composites. The transmittance at 900 nm is about 56% for the neat CA, while it is about 75% and 81% for the CA/CNC-20 and CA/CNF-20 composites, respectively. It should be noted that no bleaching process was involved in this study. The good transparency of the water-soluble CA from WCFs could be ascribed to the fact that the dyestuffs in WCFs are generally insoluble in water and were detached from CA during water extraction. However, there is still a small amount of residual small molecular dyes which would reduce the transmittance of CA. So, the transmittance of water-soluble CA produced from WCFs is not very high. Furthermore, the introduction of CNC and CNF leads to the higher light transmittance of CA membrane. This result could be ascribed to the densely packing of cellulose nanofibers in CA matrix. As a result, the interstices between the fibers are small enough to avoid light scattering (Nogi et al., 2009) and the composite becomes transparent. Such a high transparency of the prepared composites is very attractive for packaging applications.

The effect of nanocelluloses (CNC and CNF) content on the mechanical properties of water-soluble CA film was investigated and the results are shown in Fig. 7. The neat CA film is very weak, which shows a maximum tensile strength of 2.4 MPa and Young's modulus of 0.6 GPa. The incorporation of nanocelluloses significantly

improves the tensile strength and Young's modulus of the CA film. With addition of 20 wt% nanocelluloses, the tensile strength of CA/CNC-20 and CA/CNF-20 composites is 9.4 and 16.3 MPa, which is about 3.9 and 6.8 times of neat CA film, respectively. Meanwhile, the Young's modulus of CA/CNC-20 and CA/CNF-20 composites is 3.2 and 3.7 GPa, which is about 5.3 and 6.2 times of neat CA film, respectively. The results indicate that CNF has a better reinforcing efficiency than that of CNC, which could be ascribed to the higher aspect ratio of CNF than CNC as shown in Fig. 5. However, the elongation at break decreases with the increase of nanocelluloses loading due to the high rigidity of nanocelluloses. We compared the tensile strength of the prepared all-cellulose composites with other bio-based and oil-based composites as shown in Table S3. The results show that CA/CNF-20 has a higher tensile strength than that of most thermoplastic starch-based composites and low density polyethylene-based composites, while basically same with that of chitosan-based composites. The enhanced mechanical property of the composites makes it more promising for practical application of this waste-derived all cellulose composites.

In view of the importance of thermal stability for the practical application of packaging materials, the thermal decomposition of the CA/CNC-20 and CA/CNF-20 composites was investigated by TGA analysis and compared with the neat CA. As shown in Fig. 8, the degradation temperature of the films was found to follow the order: CA/CNF-20 > CA/CNC-20 > CA. This result indicates that the incorporation of nanocelluloses can improve the thermal stability of water-soluble CA. Although CNC has a higher degree of crystallinity than CNF because of the removal of amorphous region, the thermal stability of CNC is poorer than that of CNF. This is because the sulfate groups introduced on cellulose chains catalyzed the thermal degradation of cellulose. (Roman & Winter, 2004)

Conclusion

Harmless disposal and value-added utilization of WCFs is highly attractive for ecological and economic benefits. In this study, we developed a facile, green and efficient approach to prepare water-soluble CA from WCFs

with very high conversion (up to 90.8 %). Acidic ILs played a dual role of swelling and catalyzing, which makes it possible to control the DS values and solubility of the obtained CA at one-step synthesis without dissolution of cellulose. The highest conversion was obtained by using 0.2 molar equivalents of ILs per molar of AGU and reacted for 3 h. Furthermore, transparent, flexible and mechanically robust all cellulose composites were prepared by simple aqueous blending of the obtained water-soluble CA and nanocelluloses. The utilization of inexpensive waste-derived cellulose to fabricate bio-based and biodegradable high performance composites has great potential for large-scale applications and may be extended to the exploiting of other biomass wastes (e.g. straw).

Acknowledgments

The authors thank the National Science Foundation of China (51203105 and 51473100) and State Key Laboratory of Polymer Materials Engineering (Grant No. sklpme2015-2-02) for financial support.

References

- Ashore, A., Babaei, M., Jonoobi, M., & Hamzeh, Y. (2014). Solvent-free acetylation of cellulose nanofibers for improving compatibility and dispersion. *Carbohydrate Polymers*, 102, 369-375.
- Biswas, A., Shogren, R. L., & Willett, J. L. (2005). Solvent-free process to esterify polysaccharides. *Biomacromolecules*, 6, 1843-1845.
- Buchanan, C. M., Edgar, K. J., & Wilson, A. K. (1991). Preparation and characterization of cellulose monoacetates: the relationship between structure and water solubility. *Macromolecules*, 24, 3060-3064.
- Cao, Y., Li, H. Q., Zhang, Y., Zhang, J., & He, J. S. (2008). Synthesis of cellulose acetates with low degree of substituent and their water solubility. *Chemical Journal of Chinese Universities*, 29, 2115-2117.
- Cao, Y., Wu, J., Meng, T., Zhang, J., He, J. S., Li, H. Q., & Zhang, Y. (2007). Acetone-soluble cellulose acetates

328 prepared by one-step homogeneous acetylation of cornhusk cellulose in an ionic liquid
329 1-allyl-3-methylimidazolium chloride (AmimCl). *Carbohydrate Polymers*, 69, 665-672.

330 Das, A. M., Ali, A. A., & Hazarika, M. P. (2014). Synthesis and characterization of cellulose acetate from rice
331 husk: Eco-friendly condition. *Carbohydrate Polymers*, 112, 342-349.

332 Dorn, S., Pfeifer, A., Schlufte, K., & Heinze, T. (2010). Synthesis of water-soluble cellulose esters applying
333 carboxylic acid imidazolides. *Polymer Bulletin*, 64, 845-854.

334 Gomez-Bujedo, S., Fleury, E., & Vignon, M. R. (2004). Preparation of Cellouronic Acids and Partially Acetylated
335 Cellouronic Acids by TEMPO/NaClO Oxidation of Water-Soluble Cellulose Acetate. *Biomacromolecules*, 5,
336 565-571.

337 Goodlett, V. W., Dougherty, J. T., & Patton, H. W. (1971). Characterization of cellulose acetates by nuclear
338 magnetic resonance. *Journal of Polymer Science Part A-1: Polymer Chemistry*, 9, 155-161.

339 Han, Y. Y., Zhang, X. X., Wu, X. D., & Lu, C. H. (2015). Flame Retardant, Heat Insulating Cellulose Aerogels
340 from Waste Cotton Fabrics by in Situ Formation of Magnesium Hydroxide Nanoparticles in Cellulose Gel
341 Nanostructures. *ACS Sustainable Chemistry & Engineering*, 3, 1853-1859.

342 He, X., Zhang, X. X., Zhang, W., Tian, D., & Lu, C. H. (2014). Mechanochemically activated waste-derived
343 cellulose as a novel functional additive to enhance melt processability and mechanical properties of poly(vinyl
344 alcohol). *Journal of Vinyl and Additive Technology*, 20, 177-184.

345 Kamide, K., & Okajima, K. (1981). Determination of distribution of O-acetyl group in trihydric alcohol units of
346 cellulose acetate by carbon-13 nuclear magnetic resonance analysis. *Polymer Journal*, 13, 127-133.

347 Karlsson, K., Schuster, E., Stading, M., & Rigdahl, M. (2015). Foaming behavior of water-soluble cellulose

348 derivatives: hydroxypropyl methylcellulose and ethyl hydroxyethyl cellulose. *Cellulose*, 22, 2651-2664.

349 Lv, Y. X., Chen, Y. L., Shao, Z. Q., Zhang, R. X., & Zhao, L. B. (2015). Homogeneous tritylation of cellulose in
350 1-allyl-3-methylimidazolium chloride and subsequent acetylation: The influence of base. *Carbohydrate*
351 *Polymers*, 117, 818-824.

352 Matsumura, H., Sugiyama, J., & Glasser, W. G. (2000). Cellulosic nanocomposites I. Thermally deformable
353 cellulose hexanoates from heterogeneous reaction. *Journal of Applied Polymer Science*, 78, 2242-2253.

354 Nogi, M., Iwamoto, S., Nakagaito, A. N., & Yano, H. (2009). Optically transparent nanofiber paper. *Advanced*
355 *Materials*, 21, 1595-1598.

356 Roman, M., & Winter, W. T. (2004). Effect of sulfate groups from sulfuric acid hydrolysis on the thermal
357 degradation behavior of bacterial cellulose. *Biomacromolecules*, 5, 1671-1677.

358 Schenzel, A., Hufendiek, A., Barner-Kowollik, C., & Meier, M. A. R. (2014). Catalytic transesterification of
359 cellulose in ionic liquids: sustainable access to cellulose esters. *Green Chemistry*, 16, 3266-3271.

360 Stefanescu, C., Daly, W. H., & Negulescu, I. I. (2012). Biocomposite films prepared from ionic liquid solutions of
361 chitosan and cellulose. *Carbohydrate Polymers*, 87, 435-443.

362 Sun, X. W., Lu, C. H., Liu, Y., Zhang, W., & Zhang, X. X. (2014). Melt-processed poly(vinyl alcohol) composites
363 filled with microcrystalline cellulose from waste cotton fabrics. *Carbohydrate Polymers*, 101, 642-649.

364 Sun, X. W., Lu, C. H., Zhang, W., Tian, D., & Zhang, X. X. (2013). Acetone-soluble cellulose acetate extracted
365 from waste blended fabrics via ionic liquid catalyzed acetylation. *Carbohydrate Polymers*, 98, 405-411.

366 Tian, D., Han, Y. Y., Lu, C. H., Zhang, X. X., & Yuan, G. P. (2014). Acidic ionic liquid as “quasi-homogeneous”

367 catalyst for controllable synthesis of cellulose acetate. *Carbohydrate Polymers*, 113, 83-90.

368 Tomé, L. C., Freire, M. G., Rebelo, L. P. N., Silvestre, A. J. D., Neto, C. P., Marrucho, I. M., & Freire, C. S. R.

369 (2011). Surface hydrophobization of bacterial and vegetable cellulose fibers using ionic liquids as solvent media

370 and catalysts. *Green Chemistry*, 13, 2464-2470.

371 Torr, K. M., Love, K. T., C, etinkol, Ö. P., Donaldson, L. A., George, A., Holmes, B. M., et al. (2012). The impact

372 of ionic liquid pretreatment on the chemistry and enzymatic digestibility of *Pinus radiata* compression wood.

373 *Green Chemistry*, 14, 778-787.

374 Wan Daud, W. R., & Djuned, F. M. (2015). Cellulose acetate from oil palm empty fruit bunch via a one step

375 heterogeneous acetylation. *Carbohydrate Polymers*, 132, 252-260.

376 Wang, S. M., Zhang, X. X., Wu, X. D., & Lu, C. H. (2016). Tailoring percolating conductive networks of natural

377 rubber composites for flexible strain sensors via a cellulose nanocrystal template assembly. *Soft Matter*; DOI:

378 10.1039/c5sm01958c.

379 Wu, J., Zhang, J., Zhang, H., He, J. S., Ren, Q., & Guo, M. L. (2004). Homogeneous Acetylation of Cellulose in a

380 New Ionic Liquid. *Biomacromolecules*, 5, 266-268.

381 Xiong, R., Han, Y. Y., Wang, Y. R., Zhang, W., Zhang, X. X., & Lu, C. H. (2014). Flexible, highly transparent and

382 iridescent all-cellulose hybrid nanopaper with enhanced mechanical strength and writable surface. *Carbohydrate*

383 *Polymers*, 113, 264-271.

384 Xiong, R., Zhang, X. X., Tian, D., Zhou, Z. H., & Lu, C. H. (2012). Comparing microcrystalline with spherical

385 nanocrystalline cellulose from waste cotton fabrics. *Cellulose*, 19, 1189-1198.

386 Yang, Y. L., Xie, H. B., & Liu, E. H. (2014). Acylation of cellulose in reversible ionic liquids. *Green Chemistry*, 16,

387 3018-3023.

388 Zhang, X. X., Wu, X. D., Lu, C. H., & Zhou, Z. H. (2015). Dialysis-Free and in Situ Doping Synthesis of
389 Polypyrrole@Cellulose Nanowhiskers Nanohybrid for Preparation of Conductive Nanocomposites with
390 Enhanced Properties. *ACS Sustainable Chemistry & Engineering*, 3, 675-682.

391 Zhang, X. X., Zhang, W., Tian, D., Zhou, Z. H., & Lu, C. H. (2013). A new application of ionic liquids for
392 heterogeneously catalyzed acetylation of cellulose under solvent-free conditions. *RSC Advances*, 3, 7722-7725.

393 Zhang, Y. J., Gan, T., Luo, Y. W., Zhao, X. H., Hu, H. Y., & Huang, Z. Q. (2014). A green and efficient method
394 for preparing acetylated cassava stillage residue and the production of all-plant fibre composites. *Carbohydrate*
395 *Polymers*, 102, 139-144.

396

Fig. 1 Schematic illustration of extracting water-soluble CA from WCFs and the aqueous processing of all-cellulose composites.

Fig. 2 The conversion of water-soluble CA from WCFs with four IL concentrations multiply five reaction time.

Fig. 3 (a) FTIR spectra of water soluble CA and original WCFs, (b) XRD patterns of water soluble CA and original WCFs, (c) TGA curves of water soluble CA and original WCFs, (d) DSC curves of water soluble CA and original WCFs.

Fig. 4 ^1H NMR spectra of the prepared water-soluble CA.

Fig. 5 (a) TEM image of CNC, (b) SEM image of CNF, (c) PLM image of CA/CNC-20 composite, (d) PLM image of CA/CNF-20 composite.

Fig. 6 Digital camera picture of water-soluble CA (a), CA/CNC-20 composite (b), CA/CNF-20 composite (c), UV-vis transmittance of approximately 50 μm thick CA, CA/CNC-20 and CA/CNF-20 composites (d).

Fig. 7 Tensile strength, **Young's modulus and elongation at break** of CA composites with different amounts of CNC and CNF.

Fig. 8 TGA curves of CA, CA/CNC-20 and CA/CNF-20 composites.

413

414

415

416

417

418

419

420

421

422

423

424

425

426

427

428