



Cellulose acetate fibers prepared from different raw materials with rapid synthesis method



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ABSTRACT

Transesterification is a mild process to prepare cellulose acetate (CA) as compared with the traditional method. In this study, CA fibers were produced from six cellulose raw materials based on a simple and rapid transesterification method. The properties of the CA solutions and the obtained CA fibers were investigated in detail. Results showed that all of the cellulose raw materials were esterified within 15 min, and spinning dopes could be obtained by concentrating the CA solutions via vacuum distillation. The XRD, FT-IR, ^1H , ^{13}C and HSQC NMR analysis confirmed the successful synthesis of CA. The degree of substitution (DS) of the obtained CA was significantly affected by the degree of polymerization (DP) of cellulose raw materials, which further influenced the viscosity of CA solutions as well as the structural, thermal and mechanical properties of the CA fibers.

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1. Introduction

Lignocellulosic biomass has been considered as a promising potential alternative to obtain chemicals, energy and various materials due to its renewable and biodegradable characteristics (Balat & Balat, 2009; Dodds & Gross, 2007; Gandini, 2008). Cellulose is one of the most abundant lignocellulosic resources and widely distributed in plants, some marine animals, fungi, bacteria, algae, invertebrates, and even amoeba (Habibi, Lucia, & Rojas, 2010; Ohlrogge et al., 2009). The physical properties of cellulose can be significantly modified by derivatization, and the production of cellulose derivatives has attracted significant attention (Hu, Chen, Yang, Li, & Wang, 2014). Cellulose acetate (CA) is one of the most important derivatives of cellulose and has been used in many applications (Aoki, Teramoto, & Nishio, 2007). The traditional method to prepare CA is by acetylating the hydroxyl groups in cellulose with acetic acid and acetic anhydride in the presence of sulfuric acid (Fischer et al., 2008). However, special equipment is required due to the acidic environment in the process of acetylation.

Other methods, including *N,N*-carbonyldiimidazole, dialkylcarbodiimide, iminium chlorides, ring-opening esterification and transesterification, have been developed to synthesize CA under heterogeneous or homogeneous conditions (Heinze & Liebert,

2004; Heinze, Liebert, & Koschella, 2006). Transesterification is a relatively mild acetylation method, which uses acetate ester as an innocuous acyl donor, avoiding the formation and introduction of acidic reagents in the acetylation system. The transesterification of cellulose with acetic anhydride or vinyl acetate in dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF) was achieved in good yield (Heinze et al., 2000; Ass, Frollini, & Heinze, 2004). Other solvents, such as *N*-ethyl-pyridinium chloride (Deus, Friebolin, & Siefert, 1991), *N,N*-dimethylacetamide (DMAc)/lithium chloride (LiCl) (Morgado, Rodrigues, Almeida, El Seoud, & Frollini, 2013; Tosh, Saikia, & Dass, 2000), and 1,3-dimethyl-2-imidazolidinone (DMI)/LiCl, were also employed to prepare CA. However, long pretreatment and reaction times are usually required in these systems. Ionic liquids (ILs) have been considered as efficient solvents for the acetylation of cellulose (Abbott, Bell, Handa, & Stoddart, 2005; Wu et al., 2004), but their industrial application is limited due to the lack of economy.

Our group reported a simple and highly efficient transesterification system to synthesize cellulose esters (Cao et al., 2013, 2014). In these studies, microcrystalline cellulose (MCC) was used as raw material and successfully esterified within several minutes under the catalysis of NaOH or KOH in DMSO. The preparation conditions were optimized and the cellulose esters prepared from different vinyl esters, including vinyl acetate, vinyl propionate, vinyl butyrate, vinyl hexanoate, vinyl octanoate, vinyl dextanoate and vinyl laurate, were characterized, which provided a better understanding of this novel reaction system.

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Normally, the raw materials used for CA fibers are cotton linter pulp and dissolving wood pulp. Because the planting area for cotton and wood is limited, it is necessary to expand the scope of the raw materials. In our previous studies (Cao et al., 2013, 2014), the cellulose esters were prepared only from MCC. This study represents an attempt to prepare CA fibers based on the above transesterification method from various cellulose raw materials, such as MCC, cotton linter pulp (CP), wheat straw pulp (WP), bamboo pulp (BP), bleached softwood sulfite dissolving pulp (SP) and bleached hardwood kraft pulp (HP). After the CA was synthesized, the solution was concentrated by vacuum distillation to remove most of the solvent. CA fibers were then produced from the concentrated solution via a wet spinning method using ethanol as a coagulation bath. The properties of the CA solutions were investigated by optical microscopy and viscometry. The chemical structure, morphology, mechanical and thermal properties of the CA fibers were measured by X-ray diffraction (XRD) patterns, Fourier transform infrared (FT-IR) spectroscopy, proton nuclear magnetic resonance (^1H NMR), solution state ^{13}C NMR, heteronuclear singular quantum correlation (HSQC) NMR, scanning electron microscopy (SEM), tensile strength tester and thermogravimetric analyses (TGA). Therefore, the purposes of this article are to prepare CA fiber from varied lignocellulose raw materials using a rapid synthesis method and to clarify the effect of raw materials on the properties of the CA products.

2. Materials and methods

2.1. Raw materials

MCC was acquired from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). CP was purchased from Hubei Chemical Fiber Co. Ltd. (Hubei Province, China). WP and BP were obtained after delignification with sodium chlorite and alkaline treatment with potassium hydroxide from wheat straw (harvested from Shandong Province, China) and bamboo stem (harvested from Sichuan Province, China), respectively (Chen et al., 2015). SP was provided by CHTC Helon Co., LTD. (Shandong Province, China) and HP was kindly supplied by Fibria Celulose S.A. (Aracruz, Brazil). All the above cellulose raw materials were dried at 105°C for 4 hour (h) and kept in a desiccator for further use. DMSO was obtained from Xilong Chemical Co., Ltd. (Guangdong Province, China). Vinyl acetate was purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). Other chemicals, including sodium chlorite, potassium hydroxide and sodium hydroxide, were of analytical grade and used without further purification.

2.2. Synthesis of cellulose acetate

The acetylation of the cellulose raw materials was carried out according to a previous method with a slight change (Cao et al., 2014). Briefly, 25 mmol (anhydroglucose units, 162 g/mol) of dried cellulose material was mixed with 100 ml of DMSO in a three-necked glass flask (250 mL), which was equipped with a mechanical stirrer and a condenser. 5.0 mL of aqueous NaOH solution (10 mol/L) was dropwise added into the mixture at room temperature and stirred for 5 min to activate the cellulose hydroxyl groups. The flask was then transferred into an oil bath heated at 100°C and stirred for another 10 min. Then 150 mmol of vinyl acetate was poured all at once into the mixture under vigorous stirring for 15 minutes (min) to get a cellulose acetate (CA) solution. The schematic acetylation of cellulose is shown in Fig. S1.

2.3. Preparation of CA fibers

The CA solution was then filtered and concentrated by vacuum evaporation at 120°C until 90 mL DMSO was removed. The concentrated solution was then vacuum degassed, transferred into a syringe and extruded through a needle with a diameter of 0.21 mm into an ethanol bath at room temperature. The formed CA fiber was washed with ethanol and water for several time to completely remove the solvent. After being air dried, the fiber was collected by a spool and labeled as CA-MCC, CA-CP, CA-WP, CA-BP, CA-SP, CA-HP, respectively, according to the type of raw materials used.

2.4. Characterizations

The obtained CA solution was observed with an optical microscope. The viscosity of the concentrated CA solution was measured on a Brookfield digital viscometer DV-II+ PRO (Brookfield Instruments, America) using S34 rotor with a speed of 0.5 rpm over the temperature range from 25°C to 80°C .

The viscosity-average DP (DP_v) of the cellulose raw materials was determined by dissolving the cellulose in cupriethylenediamine solution. The limiting viscosity $[\eta]$ of the solution was measured by Ubbelohde viscometer, and the DP_v was calculated from the following equation (Evans & Wallis, 1989):

$$\text{DP}_v^{0.90} = 1.65 \times [\eta] \quad (1)$$

The $[\eta]$ of CA, which was dissolved in dichloromethane/methanol (90/10, ratio by volume) mixed solution, was determined using a Wagner capillary tube viscometer according to ASTM D871–96(2010). The DP_v of CA was calculated from the following equation (Whistler, Wolfrom, Bemiller, & Shaw, 1963):

$$\text{DP}_v = 147 \times [\eta]^{1.2} \quad (2)$$

The XRD patterns of CA fibers were measured on a XRD-6000 instrument (Shimadzu, Japan) with a scattering angle from 5° to 40° 2θ at a scanning speed of $0.2^\circ/\text{min}$. FT-IR spectra of the CA samples were obtained using a Thermo Scientific Nicolet iN10 FT-IR Microscope (Thermo Nicolet Corporation, USA) equipped with a liquid nitrogen cooled MCT detector in the mode of reflection. The spectra were recorded in a range from 4000 to 670 cm^{-1} with 128 scans per sample at a resolution of 4 cm^{-1} .

The ^1H NMR, ^{13}C NMR and HSQC NMR spectra were all recorded on a 400-MHz Bruker AVIII spectrometer (Germany) at 25°C with the signals of the solvent used as internal standards. Before measurement, 40 mg dried CA samples were dissolved in 0.55 mL of DMSO- d_6 with a drop of trifluoroacetic acid- d . The ^1H NMR spectra were obtained with a minimum of 256 scans and the ^{13}C NMR spectra were performed in the pulse FT mode (100.6 MHz) with a minimum of 20,000 scans. The HSQC NMR spectrum was acquired in the HSQCGE experimental mode. The number of collected complex points was 1024 for the ^1H -dimension and the relaxation time was 5 s. The $^1\text{J}_{\text{C-H}}$ used was 150 Hz. The number of scans was 128 for the ^{13}C -dimension with time increments of 256.

The degree of substitution (DS) of CA was calculated by integration of the areas of the ^1H NMR peaks (Ass, Ciacco, & Frollini, 2006; Elomaa et al., 2004; Sun, Lu, Zhang, Tian, & Zhang, 2013) as follows:

$$\text{DS} = \frac{7 \times I(\text{CH}_3, \text{H})}{3 \times I_{(\text{AGU}, \text{H})}} \quad (3)$$

where $I(\text{CH}_3, \text{H})$ is the integration of the resonances assigned to the three methyl protons of acetyl group ($\delta \sim 1.6\text{--}2.3$ ppm) and $I_{(\text{AGU}, \text{H})}$ is the integration of the resonances assigned to the seven protons of glucose ring ($\delta \sim 2.8\text{--}5.5$ ppm, except the residual water signal at around 3.3 ppm).

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