Preparation and characterization of cellulose laurate ester by catalyzed transesterification

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ABSTRACT

The preparation of cellulose laurate was investigated through transesterification in 1-allyl-3-methylimidazolium chloride (AmimCl)/dimethyl sulfoxide (DMSO) cosolvent system by using vinyl laurate as an acylation reagent and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as an effective catalyst. The effects of reaction temperature, reaction time and the molar ratio of vinyl laurate to anhydride glucose unit (AGU) were investigated. The degree of substitution (DS) ranged from 1.47 to 2.74 under the selected conditions and the reaction order of three hydroxyl groups was C-6 > C-3 > C-2. The chemical structure cellulose laurate were explored by Fourier transform infrared (FT-IR) spectroscopy, ^{1}H-nuclear magnetic resonance (NMR), ^{13}C NMR, heteronuclear single quantum correlation (HSQC) and X-ray diffraction (XRD) to confirm the occurrence of transesterification. The improved thermal stability of cellulose laurate was proved by the thermogravimetric analysis (TGA). The tensile analysis and the contact angle measurement confirmed the ductile behavior and the hydrophobicity of the films made from cellulose laurate.

1. Introduction

With the increase of the environmental awareness, cellulose has been popular in the application of making kinds of materials due to its economic advantages. As the most abundant natural polymer, it has many attractive properties such as renewability, biodegradability and biocompatibility. However, there are some drawbacks because cellulose can not be dissolved in water or common organic solvents due to its strong inter- and intra-hydrogen bonds. The lack of thermal plasticity also makes it hardly to be melted for compression molding. Through chemical modification, the physicochemical properties of cellulose can be significantly changed and more easily applied (Chen, Cho, Kim, Nam, & Lee, 2012).

Cellulose esters are important cellulose derivatives with excellent properties. It has been widely used in many different areas such as filtration, coating, pharmacy, and so on (Edgar et al., 2001). In general, cellulose esters can be obtained by acylation in heterogeneous or homogeneous system, among which the reaction in homogenous solution can get more uniform pattern and control the degree of substitution (DS) (Heinze & Liebert, 2001). For the last few decades, many attempts have been made to develop novel solvent systems to dissolve cellulose, including dimethyl sulfoxide/tetrabutylammonium fluoride (DMSO/TBAF) (Ciacco, Liebert, Frollini, & Heinze, 2003), N,N-dimethylacetamide/lithium chloride (DMAC/LiCl) (Ass, Ciacco, & Frollini, 2006), N-methylmorpholine (NMMO) (Fink, Weigel, Purz, & Ganster, 2011) and NaOH/urea (Cai & Zhang, 2005). However, these solvent systems are either expensive or applied in hard conditions. Extensive use of this solvents would not only do harm to the environment but also violate the economic feasibility.

Ionic liquids (ILs), made up of cations and anions, are promising solvents for dissolving cellulose. ILs have got constant attention since being developed due to their low vapor pressure and recyclability (Liebert, 2009; Wu et al., 2004; Zakrzewska, Bogel-Łukasik, & Bogel-Łukasik, 2010). Moreover, ILs were fine reaction media to produce cellulose derivatives such as carboxylic acid esters, inorganic esters, and so on (Gericke, Liebert, Seoud, & Heinze, 2011). The properties of ILs could be tailored by changing cations and anions, which is also attractive. However, in spite of these fascinating properties, ILs also have some disadvantages: long time to dissolve cellulose and the high viscosity of the solution, which is a hindrance for the following cellulose modification. Lately, IL/dimethyl sulfoxide (DMSO) cosolvent system has been developed to solve these problems and also been applied for broadly dissolving lignocelluloses (Casarano, Pires, & El Seoud, 2014; Chen et al., 2015; Jogunola et al., 2016; Lee et al., 2015; Xu, Zhang, Zhao, & Wang, 2013). It has been found that the cosolvent system are more effective for dissolving cellulose than neat ILs (Rinaldi, 2011). The addition of aprotic

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polar solvents like DMSO could not only reduce the viscosity of the dissolved solution and accelerate the mass transfer rate, but also reduce the steric hindrance (Lee et al., 2015).

Nowadays, most of plastic packing films are usually burned or sent to landfill after use, which causes environmental pollution (Yang, Fukuzumi, Saito, Isogai, & Zhang, 2011). Many green packaging films with biodegradability and proper mechanical properties have been made from natural materials such as starch, chitosan and hemicelluloses (Avella et al., 2005; Chen and Qi et al., 2016). Cellulose laurate, one of long chain cellulose esters, is regarded as biodegradable bioplastic due to the O-glucosidic bond of cellulose and the enzymatically labile ester bond. It can be used to form plastic films without any plasticizer compared to the other biopolymers (Thiebaud, Borredon, Baziard, & Senocq, 1997). According to the previous reports, cellulose laurate is usually produced through esterification by using lauroyl chloride or lauric acid as acylation reagent (Crépy, Chaveriat, Banoub, Martin, & Joly, 2009; Crépy, Miri, Joly, Martin, & Lefebvre, 2011; Huang, Wu, Yu, & Lu, 2015), which could provide acidic environment and always cause the degradation of cellulose. Comparatively, transesterification using related vinyl esters to synthesize cellulose esters is a rather mild and effective reaction (Chen, Xu, Wang, Cao, & Sun, 2016; Schenzel, Hufendiek, Barner-Kowollik, & Meier, 2014). In transesterification, a catalyst is needed to motivate the reaction. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) has been reported as an effective nucleophilic catalyst (Birman, Li, & Han, 2007; Ghosh, 2004; Ji, Qian, & Chen, 2013; Seebach, Thaler, Blaser, & Ko, 1991). In the present study, the preparation of cellulose laurate esters was investigated by transesterification using DBU as catalyst and vinyl laurate as acylation reagent in AmimCl/DMSO cosolvent system. As a harmless acylation reagent, the use of vinyl laurate can significantly reduce the harm to the environment caused by lauroyl chloride and lauric acid. Compared to the catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) used in the transesterification (Schenzel et al., 2014), DBU applied in the protocol are more effective to synthesize long chain cellulose esters with higher DS.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (MCC, DP 280) was purchased from Sinopharm Chemical Reagent Company (Shanghai, China). DMSO and DBU were purchased from Sigma-Aldrich Co. (Guangzhou, China). Vinyl laurate was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). 1-Allyl-3-methylimidazolium chloride (AmimCl) with purity of 99% was supplied by Cheng-Jie Chemical Co., Ltd. (Shanghai, China). Other chemicals were all analytical-grade reagents and used as received without further purification.

2.2. Synthesis of cellulose ester via transesterification

The transesterification reaction was carried out in AmimCl/DMSO. MCC (0.2 g) was suspended in 5 g DMSO (50% wt of AmimCl) in a three-neck flask equipped with a magnetic stirrer. The suspension was agitated until the cellulose was dispersed thoroughly. Then 10 g AmimCl was added to the mixture and heated to a certain temperature (70–120 °C) in an oil bath. After the cellulose was dissolved, different amounts of vinyl laurate and 0.3 mL DBU were introduced into the solution for transesterification with agitation. After the required time, the solution was poured into 500 mL ethanol. The precipitates were centrifuged, washed thoroughly with ethanol and dried in the vacuum oven for 24 h.

2.3. Film preparation

The synthesized cellulose laurate (0.3 g) were dissolved in chloroform (10 mL) at room temperature with magnetic stirring. Then the transparent solution was cast into a polytetrafluoroethylene dish to form wet films. The films were put at ambient temperature for 24 h to evaporate chloroform, then dried in an oven at 50 °C for 5 h in order to further remove chloroform thoroughly, and stored in a plastic bag for characterization.

2.4. Characterization

2.4.1. FT-IR

The FT-IR spectra of MCC and cellulose laurate were recorded on a Bruker spectrophotometer (Bruker, Karlsruhe, Germany) in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. All of the samples and KBr were previously dried at 105 °C in an oven for more than 8 h to remove the moisture. The sample and KBr were mixed together with a ratio of 1:100 (w/w), finely ground and pressed into a disc for the measurement.

2.4.2. XRD

X-ray diffraction of modified samples and raw materials were performed on a D8 Advance instrument (Bruker AXS, Germany) with Nickel-filtered Cu Kα radiation (wave length = 0.154 nm) in the diffraction angle 2θ ranging from 5 to 60°.

2.4.3. TGA/DTG

The thermal stability of the modified samples and raw materials were characterized by using TGA/DTG on a QG500 thermogravimetric analyzer (TA Instruments, New Castle, PA, USA). The device was flushed with nitrogen continually. The samples about 9–10 mg were heated from 30 to 600 °C at a rate of 10 °C/min.

2.4.4. NMR analysis

The ^{1}H NMR, ^{13}C NMR and HSQC spectra of the modified cellulose laurate were recorded from 40 mg samples in 0.5 mL chloroform-d$_6$ on a Bruker Advance III 600 M (Bruker, Germany) with a 5 mm multinuclear probe according to the reported method (Zhang, Chen, Liu, Zhang, & Sun, 2015).

2.4.5. Determination of DS

The DS of cellulose laurate can be estimated from the ^{1}H NMR by the calculation with the peak intensity of the corresponding resonances through the following Eq. (1) based on the reported method (Satgé, Granet, Verneuil, Branland, & Krausz, 2004):

$$DS = 10 \times \frac{I_{(CH_3,H)}}{\left(3 \times I_{(AGU,H)} + I_{(CH_3,H)}\right)} \tag{1}$$

where $I_{(CH_3,H)}$ is the integration of the resonances assigned to methyl protons of methyl group, 10 and 3 are the amounts of protons in the glucose ring and methyl group, respectively, and $I_{(AGU,H)}$ is the integration of the resonances assigned to protons of the glucose ring.

2.4.6. Tensile analysis

The tensile strength of cellulose laurate films was determined at rectangular specimens (30 mm × 10 mm) on a Universal Testing Machine 5565 (Instron, Norwood, MA, USA) fitted with a 100 N load cell at 23 °C with 50% relative humidity (RH).

2.4.7. Contact angle

Contact angles of the film surfaces for water droplets were determined at 23 °C and 50% RH on a contact angle machine (dataphysics,