Carbohydrate Polymers 155 (2017) 525–534

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Acylation of cellulose nanocrystals with acids/trifluoroacetic anhydride and properties of films from esters of CNCs

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ARTICLE INFO

Article history:
Received 14 June 2016
Received in revised form 17 August 2016
Accepted 3 September 2016
Available online 5 September 2016

Keywords:
Cellulose nanocrystals (CNCs)
Long chain fatty acids
Esters of CNCs (ECNCs)
Tensile property
Transmittance
Barrier properties

ABSTRACT

To eliminate the effect of humidity on nanopapers from nanocellulose, esters of CNCs (ECNCs) were synthesized via acylation of cellulose nanocrystals (CNCs) with fatty acids and Trifluoroacetic anhydride (TFAA). The structure information of ECNCs was confirmed via FTIR, degree of substitution (DS) determination, and XRD, respectively. With the increase of DS, the ECNCs could be dissolved in dichloromethane, which provided a ready way for fabrication of ECNCs films via casting/evaporation method. The tensile property, transmittance, hydrophobicity, thermal property and oxygen permeability of films were tested with universal tensile tester, UV–vis spectrophotometer, Contact angle tester, Simultaneous thermal analyzer and Oxygen permeability tester, respectively. With the increase of DS, the contact angles of ECNCs increased, and the water uptake decreased. The enhancement of hydrophobicity promised the preservation of tensile parameters for films after water absorbing. The hydrophobicity, high transmittance, and high oxygen barrier property make films have potential application in packaging filed.

1. Introduction

Cellulose, as one of the most abundant biopolymers in nature, has many advantages for its application, such as low cost, availability, and renewability (Yu, Chen, & Wang, 2015). Due to the reactivity of hydroxyls on cellulose molecules, cellulose derivatives, including esters, ethers, and other products, were extensively synthesized and investigated.

Nanocellulose, as one kind of important derivatives of cellulose, could be divided into two forms, cellulose nanocrystals/whiskers (CNCs) (Azizi Samir, Alloin, & Dufresne, 2005), and nanofibrillated cellulose (NFC) (Isogai, Saito, & Fukuzumi, 2011). The difference between CNCs and NFC was the length of final products, rather than their diameter. And the diameter of CNCs and NFC was confirmed in the nm range. The difference was believed due to the processing procedure applied. The applications of CNCs and NFC were extensively investigated. Nanopapers from CNCs/NFC have kept increasing during the last years due to the improved mechanical strength, barrier properties, transparency and biodegradability. Nanopaper has potential applications in packaging (Liu, Walther, Ikkala, Belova, & Berglund, 2011) and flexible electronic devices (Fujisaki et al., 2014; Sun, Wu, Ren, & Lei, 2015).

NFC is typically isolated using high-intensity mechanical fibrillation of coarse lignocellulosic fibers accompanying with chemical or enzymatic pretreatment (Paakko et al., 2007; Saito et al., 2009; Qing et al., 2013). The typically entangled networks of nanoscale cellulose fibrils made NFC have high aspect ratio and a large specific surface area. Thus, NFC has been shown to have interesting and useful properties. Numerous attempts have been devoted to develop green and high-quality NFC products with applications including barrier and transparent films, engineering polymeric composites, and functional aerogels (Capadona et al., 2007; Okahisa, Yoshida, Miyaguchi & Yano, 2009; Aulin, Johansson, Wågberg, & Lindström, 2010; Olsson et al., 2010).

As compared to the producing of NFC, the most common way for fabrication of CNCs was hydrolysising cellulose via organic/inorganic acids. The preparation of CNCs from various sources have been extensively developed and summarized in literature (Bettaieb, Khiari, Dufresne, Mhenni, & Belgacem, 2015). Furthermore, CNCs has been widely used as a reinforcing material for composite materials. And the incorporation of CNCs as reinforcing agents or as fillers in polymer composites have received more and more increased attention (Pereda, Kissi, & Dufresne, 2014; Bettaieb, Khiari, Belgacem et al., 2015; Park, Um, Lee, & Dufresne, 2014; Castro, Frollini, Ruvolo-Filho, & Dufresne, 2015). It is essential

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http://dx.doi.org/10.1016/j.carbpol.2016.09.010
0144-8617/

to disperse uniformly CNCs in polymers matrix for the preparation of polymers-based nanocomposites. On the one hand, due to the hydrophilic nature of CNCs, CNCs without further surface modifications could meet the requirements of uniform dispersion in matrix for some hydrophilic polymers (Peresin, Habibi, Zoppe, Pawlak, & Rojas, 2010; Lu et al., 2015). On the other hand, the surface modification of CNCs was required for the fabrication of hydrophobic nanocomposites (Kiziltas, Kiziltas, Bollin, & Gardner, 2015; Hua, Lin, Chang, & Huang, 2015). Several possible methods for modifying CNCs surface were reported by many authors (Ljungberg, Bonini, Bortolussi, Boisson, Heux, Cavaillé, 2005; Samir et al., 2004; Eichhorn, 2011; Goffin, Habibi, Raquez, & Dubois, 2012). Modification of hydroxyls presented at the surface of nanocellulose through esterification is widely used. Acetylation of nanocellulose with a mixture acetic anhydride and acetic acid was the most widely studied. Esterification of CNCs with organic fatty acid chlorides, having aliphatic chains of different lengths, has been reported also (Junior de Menezes, G. Siqueira, Antonio Curvelo, & Dufresne, 2009; Lee, Blaker, & Bismarck, 2009; Lee et al., 2011).

Cellulose nanopaper, made from CNCs and/or CNF, had attained great interest due to its transparency, excellent gas barrier properties, high strength, large surface area, and biodegradability,and a lot of results about the fabrication and properties of nanopaper were reported (Kumar et al., 2014; Diaz et al., 2014). However, the most important shortage of nanopaper was deficient in moisture resistance. For instance, under high moisture condition, the strength, water vapor transition rate, and oxygen permeability of nanopaper were affected hardly (Lindström et al., 2012). The efforts for improvement the comprehensive properties of nanopaper have been carried out by many authors (Sehaqui, Zimmermann, & Tingaut, 2014; Rodionova, Hoff, Lenes, Eriksen, & Gregersen, 2013). However, there has no information about nano films and/or nanopaper from ECNCs.

The present paper focused on fabrication high transparence, oxygen barrier and self-standing nano films from ECNCs. In order to prepare the films, the acylation of CNCs extracted from microcrystal cellulose with fatty acids and TFAA was carried out. Furthermore, ECNCs films were fabricated via casting/evaporation method with dichloromethane as solvent. The properties of ECNCs films, such as tensile property, thermal stability, light transmittance, and oxygen barrier property were investigated systematically. ECNCs films have potential application in the packaging filed and other fields.

2. Experimental

2.1. Materials

Microcrystal cellulose (MCC) (OurChem, DP = 235) powder was used for preparation of CNCs. Special grade trifluoroacetic anhydride (TFAA) and fatty acids (Capric acid, Lauric acid, and Stearic acid) were used for the acylation of cellulose. Reagent grade sulfuric acid, chloroform, dichloroform, and other reagents were used as supplied from Sinopharm Chemical Reagent Co.,Ltd, China without being further purified.

2.2. Fabrication of CNCs

CNCs were prepared by acid hydrolysis of MCC according to previously described method (Lin & Dufresne, 2013, 2014). In short, MCC powders were mixed with 65 wt% H_2SO_4 solution at a MCC concentration of 20 wt% in a 500 mL flask. The suspensions were then continuously stirred at 100 rpm under 45 °C. After 30 min of hydrolysis, the suspensions were washed by successive centrifugations in distilled water until neutrality was achieved. At last, the CNCs precipitate was ultrasonically homogenized in an aqueous solution and then the obtained CNCs suspension was freeze-dried. The scanning electron microscopy image for CNCs particles was shown in Fig. S1.

2.3. Esterification of CNCs

Esters of CNCs (ECNCs) were synthesized following method described by Huang (Huang, 2012). TFAA and long chain acid (molar ratio of fatty acid to TFAA was 1.1:1.0, Capric acid, Lauric acid, and Stearic acid, respectively) were mixed together in a 250 mL three-neck flask equipped with a condenser and stirred mildly at 50 °C for 20 min to form the mixed acid anhydride. Pre-dried CNCs powder (molar ratio of TFAA to AGU was 1:1) was added to this solution and stirred mildly at 50 °C for 5 h. The reaction mixtures were poured into an excess amount of ethanol, and the precipitates were filtered and washed with methanol (50 mL per gram of CNCs) three times at 60 °C. Finally, the polymers were dried at 50 °C for 24 h under vacuum to yield products. The ECNCs from lauric acid in different molar ratio of acid to AGU was labeled as CNCs-L1, CNCs-L2, and CNCs-L3 for 1.1:1, 2.2:1, and 3.3:1, respectively. And CNCs-C1, CNCs-C2, CNCs-C3, CNCs-S1, CNCs-S2, and CNCs-S3 were defined in the same manner of CNCs-Ls. The scanning electron microscopy image for CNCs-S3 particles was shown in Fig. S2. After modification, the particles of CNCs-S3 are easily aggregated. However, the aggregated particles are formed by smaller particles in nanometer size.

2.4. Fabrications of ECNCs films (typical method)

ECNCs films were manufactured by casting/evaporation technique using dichloromethane as solvent with method described in our previous work with some modification (Huang, Wu, Yu, & Lu, 2015). CNCs-S3 powder (1.50 g) was dissolved in 15.0 mL dichloromethane under Ultrasonic for ~15 min. Then the solution was cast into a Petri dish (Φ10.5 mm) and the solvent was evaporated at ambient temperature for 24 h. In order to evaporate dichloromethane completely, the disk was removed to oven at 50 °C under vacuum for another 4 h. The thickness of the sample was ca. 120 μm (average value for ten measurements). For CNCs-C1, CNCs-L1, and CNCs-S1, which possessed lower DS, could only disperse rather than dissolve in dichloromethane. They were difficult to obtain uniform transparent films. (as shown in Figs. S4 and S5).

2.5. Measurements and characterization

2.5.1. Degree of substitution (DS)

The degree of substitution (DS) was determined according to the method proposed by Kim et al. (Kim, Nishiyama, & Kuga, 2002) The ECNCs and CNCs (100 mg, solid content of 2%) were placed in conical flasks. Consequently, 40 mL of 75% ethanol was added and the flasks were kept at 50 °C for 30 min. Finally, 40 mL of NaOH (0.5 M) solution was added to the mixture and heated to 50 °C for 15 min. The mixture was kept at room temperature for 48 h under constant stirring. The excess of NaOH was titrated with HCl (0.5 M) until a pH of 7 was obtained.

2.5.2. Fourier transform infrared spectrometry (FTIR)

FTIR spectra for all samples were measured on a Perkin-Elmer Spectrum 100 using the KBr pellet technique for all samples, in order to determine the changes in functional groups in the materials. The samples for FTIR were mixed with KBr. The FTIR analysis was carried out using 50 scans with a resolution of 4 cm^{-1}, in transmittance mode within the range of 4000–400 cm^{-1}.