Carbohydrate Polymers 117 (2015) 286–296

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Tunicate cellulose nanocrystals: Preparation, neat films and nanocomposite films with glucomannans

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ARTICLE INFO

Article history:
Received 21 February 2014
Received in revised form 4 May 2014
Accepted 12 September 2014
Available online 22 September 2014

Keywords:
Tunicate cellulose
Ciona intestinalis
Nanocrystals
Konjac glucomannan
Spruce glucomannan
Nanocomposite films

ABSTRACT

Cellulose nanocrystals (CNs) were prepared from tunicate by enzymatic hydrolysis (ECN), TEMPO-mediated oxidation (TCN) and acid hydrolysis (ACN). They were cast alone or blended with glucomannan (GM) from konjac or spruce to prepare films. Different CNs were obtained with a yield of ECN > TCN > ACN with corresponding order of decreased M_w but increased crystallinity. The CNs' diameters were on the nanometre scale, with lengths of ECN > TCN > ACN. For CN-films, TCN and ACN fibrils were stretched and parallel to each other due to surface charges. For CN–GM films, both components interacted strongly with each other, resulting in changes of crystallinity, specific surface area, fibril diameter and contact angle compared with CN films. The composite films had good thermal, optical and mechanical properties; the last ones are apparently better than similar films reported in the literature. This is the first systematic study of different tunicate CN–GM nanocomposite films and the first ever for spruce GM.

1. Introduction

In recent years, renewable, sustainable and environmentally friendly materials have gained much attention for science and technology development. Among all natural polymers, cellulose is considered to be one of the most promising materials due to its abundant availability in nature and its excellent renewability. Its inherent fibrous and crystal structure makes cellulose attractive for various potential material applications, such as films or composites, due to its high strength, stiffness, transparency and protective barrier. Specifically, cellulose is a good candidate for substituting synthetic polymers for food applications, such as packaging and other food contact surfaces (Sorrentino, Gorrasi, & Vittoria, 2007). Because cellulose is nontoxic and biodegradable, it is particularly advantageous for these applications. For example, cellulose-based edible films have been tested for packaging fresh beans and strawberries (Ayranci & Tunç, 1997). Regenerated cellulose films are biodegradable in soil (Zhang et al., 1996). However, the primary issues remain concerning cellulose applications: processing, performance and cost (Sorrentino et al., 2007). Distinctly, cellulose has very low film formation processability due to its poor dissolution and suspension properties in water. To prepare high performance films or biocomposites, good dispersion in an aqueous solution during processing and strong interactions in the final structures are important. For decades, the degradation of cellulose into nanoscale particles, termed cellulose nanocrystals (CNs), has been an effective means of modifying cellulose. After size reduction, with or without the introduction of surface charge, a CN can be suspended in aqueous solution, improving its processability. In addition, due to its nanometre-size after dispersion, markedly improved mechanical, thermal, barrier and other physio-chemical properties can be obtained for CN fibril films and composites compared to untreated cellulose. In the literature, there are many synonyms used to describe the CNs used in this study, including cellulose microcrystals, whiskers, nanoparticles, microcrystallites, nanofibres, or nanowires. A detailed description of CNs and the field in general may be found in numerous reviews (Azizi Samir, Alloin, & Dufresne, 2005; de Souza Lima & Borsali, 2004; Fleming, Gray, & Matthews, 2001; Habibi, Lucia, & Rojas, 2010; Klemm, Heublein, Fink, & Bohn, 2005; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Peng, Dhar, Liu, & Tam, 2011) and textbook (Kimura & Itoh, 2007).

Abbreviations: TC, tunicate cellulose; CN, cellulose nanocrystal; ECN, CN from enzymatic hydrolysis; TCN, CN from TEMPO-mediated oxidation; ACN, CN from acid hydrolysis; GM, glucomannan; KGM, konjac glucomannan; SGM, spruce glucomannan; EKG20, composite film with ECN and 20% KGM; TKG20, composite film with TCN and 20% KGM; AKG20, composite film with ACN and 20% KGM; CSG10, composite film with regenerated TC and 10% SGM; ESG20, composite film with ECN and 20% SGM; TSG20, composite film with TCN and 20% SGM; ASG20, composite film with ACN and 20% SGM; CKG10, composite film with regenerated TC and 10% KGM.

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http://dx.doi.org/10.1016/j.carbpol.2014.09.020
0144-8617/

CNs are prepared by various physical and chemical methods, among which acid hydrolysis is the most common (Anglès & Dufresne, 2000; Chang, Wang, Hung, & Perng, 2010; Jiang & Hsieh, 2013). Other methods include mechanical refining (Jiang & Hsieh, 2013), TEMPO-mediated oxidation (Habibi, Chanzy, & Vignon, 2006; Okita, Fujisawa, Saito, & Isogai, 2010a) and enzymatic hydrolysis-assisted mechanical treatment (Henriksson, Henriksson, Berglund, & Lindström, 2007), and these methods produce a suspension of rod-like whiskers whose dimensions depend on the pretreatment method and cellulose origin (de Souza Lima & Borsali, 2004). In principle, the acid hydrolysis can not only remove the amorphous part and shorten the length of the cellulose fibrils, but also introduce charged sulfate groups to the cellulose surface, and increase thus the dispersion ability of the CN in water (Revol, Bradford, Giasson, Marchessault, & Gray, 1992). However, it has also disadvantages, such as that the sulfate moieties at the CN surfaces are labile which can be readily removed with mild alkaline treatment (Habibi et al., 2006). The TEMPO-mediated oxidation converts the hydroxyl groups at the surface of the cellulose into charged carboxyl groups without the liability problem as the sulfate groups (Okita, Saito, & Isogai, 2010b). However, both methods are based on chemical reactions. An enzymatic hydrolysis is a totally bio-based treatment, which has advantages from the environmental point of view when compared with the chemical methods (Henriksson et al., 2007). To our best knowledge, it is rare that all these three methods were used and comprehensively compared in one study.

Among all natural cellulose sources, tunicate is the only animal species that produces cellulose in the outer tissues, termed tunic, from which a purified fraction termed tunicin can be obtained (Hirose, Kimura, Itoh, & Nishikawa, 1999). Similar to plant cellulose, tunicate cellulose (TC) in the tunic aggregates in the form of microfibrils composed of a nearly pure cellulose I_β allomorph (Kimura, Ohshima, Hirose, Nishikawa, & Itoh, 2001). TC has a very large aspect ratio (length = 100 nm to several micrometres and width = 15–30 nm); thus, the aspect ratio is between 3 and 67 (Peng et al., 2011). TC also has a high specific surface area (150–170 m^2/g), a high crystallinity (95%) and a reactive surface due to the presence of hydroxyl groups, which are important for its excellent mechanical properties (Šturcová, Davies, & Eichhorn, 2005). Therefore, TC is an excellent candidate for CN preparation and for film or composite film applications. For example, a tunicin whisker/plasticised starch nanocomposite material has been developed (Anglès & Dufresne, 2000, 2001).

When producing CN-based biodegradable films, synthetic plasticisers are commonly used to further improve their chemical or physical properties, but it was found that for a low molecular weight plasticiser, the plasticiser was easily lost during utilisation, leading to contamination. A better method to achieve this goal is the incorporation of high molecular weight synthetic or natural polymers with cellulose to improve plasticity. Epoxy polymer (Ruiz, Cavaillé, Dufresne, Graillat, & Gérard, 2001), chitosan (Fernandes et al., 2010), starch (Teixeira et al., 2009), xylan (Stevanic, Bergström, Gatenholm, Berglund, & Salmén, 2012), latex (Favier et al., 1995) and PHA latex (Dufresne, Kellerhals, & Witholt, 1999) have been tested. In some cases, the role of CNs is simply to serve as a filler in films (Veigel, Müller, Keckes, Obersriebnig, & Gindl-Altmutter, 2011). A structural analogue to cellulose, glucomannan (GM), is another biopolymer consisting of β-1,4 linked mannose and glucose residues. Due to its low isolation cost, renewability and biodegradability, GM is an attractive candidate to replace traditional artificial polymers (Persson, Nordin, Zacchi, & Jonsson, 2007). Konjac is a well-known source for GM and konjac glucomannan (KGM) has commonly a weight average molecular weight of 1.088×10^6 (Li & Xie, 2006) and a mannose to glucose ratio of 1.51:1 (Yuan, Wu, Zhao, Wu, & Li, 2003). Spruce is another GM-rich source. There are two types of GMs in spruce depending on the galactose content. The spruce glucomannan (SGM) used in this study is the galactose-poor GM and has lower weight average molecular weight (1.0×10^4) and higher mannose to glucose ratio (3.75:1) compared with the KGM (Zhang, Li, Lindström, Stepan, & Gatenholm, 2013). Generally, all mannan-based polysaccharides will interact well with cellulose (Whitney, Brigham, Darke, Reid, & Gidley, 1998), allowing for the production of good composite films from CN and GM blends. In the literature, spruce galactoglucomannan, the galactose-rich GM, and KGM have been used to produce composite films with woody cellulose nanowhiskers (Mikkonen et al., 2010).

The aim of this study was to investigate the performance characteristics, such as high optical and thermal stability, mechanical strength and barrier function, of biodegradable and edible film materials constructed from tunicate CNs with or without the addition of GM to further modify film microstructure and physical properties. Three different preparations of tunicate CNs, enzymatic treatment, TEMPO-mediated oxidation and acid hydrolysis, were applied, and two GMs, KGM and SGM, were included in the study. To our knowledge, this is specifically the first study to report the preparation, structure and high mechanical strength of different tunicate CNs in one study and their forming nanocomposite films with GM and the first ever using SGM in the field.

2. Experimental

2.1. Materials

TC was prepared and characterised from *Ciona intestinalis* in our laboratory (Zhao & Li, 2014). Food additive grade KGM (M_w of 1000k) was purchased from Hubei Konson Konjac Gum Co., Ltd, China. SGM (M_w of 10k) was extracted and purified from spruce (*Picea abies*) holocellulose in our laboratory, as described previously (Zhang et al., 2013). After analysis, the two GMs were found also differing in their mannose:glucose ratio (3.75 for SGM and 1.46 for KGM). Endoglucanase (Novozym 476) was purchased from Novozymes AS (Denmark) and used without further purification. All reagents were of analytical grade, and they were obtained from VWR International AB, Stockholm, Sweden.

2.2. Preparation of CNs

2.2.1. Enzymatic hydrolysis

A 0.5% cellulose suspension in phosphate buffer (pH 5) was prepared. After the addition of Novozym 476 (20 FPU/g), the mixture was incubated at 50 °C for 2 h with shaking manually once every 30 min. The Novozym 476 in the reaction system was then denatured at 80 °C for 30 min. Next, the treated cellulose was recovered by vacuum filtration and washed several times with deionised water (Henriksson et al., 2007). Finally, the tunicate CN was dispersed in deionised water to produce a 0.5% suspension, which was then subjected to homogenisation using an IKA T-25 ULTRA-TURRAX Digital Homogeniser at 15000 rpm for 2 min and ultrasonication (Unique Sonicator, 40 kHz) for 1 min in an ice-bath to yield a homogeneous CN suspension, termed ECN.

2.2.2. TEMPO-mediated oxidation

Cellulose (0.5 g) was suspended in water (100 ml) containing TEMPO (0.016 g, 0.1 mmol) and sodium bromide (0.1 g, 1 mmol). The cellulose suspension was stirred continuously at 400–500 rpm. Then, 3.1 ml aqueous NaClO solution (12%, ~1.61 M, made from the commercial NaClO with a commercially described 10–15% available amount of chlorine) was added drop-wise, so the total addition of NaClO was ~5 mmol, equivalent to 10 mmol per gram of cellulose (Okita et al., 2010b). The pH of the reaction system was controlled at 10.0 ± 0.1 via the addition of 0.5 M NaOH. The reaction reached