



Hydrophilic modification of cellulose nanocrystals improves the physicochemical properties of cassava starch-based nanocomposite films



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ABSTRACT

Carboxymethyl cellulose nanocrystals (N-CMCs) were produced by carboxymethylation of cellulose nanocrystals (CNCs) that derived from sweet potato residue. Transmission electron microscopy showed that the N-CMCs which had a porous surface structure were more loosely packed and slightly larger with a uniform diameter ranging from 30 nm to 50 nm. N-CMCs with low viscosity (<25 mPa s) and nano-sized scale were used as reinforcement for preparing cassava starch-based films. Effect of N-CMCs varying 0.2 g/100 mL – 0.5 g/100 mL was studied on physicochemical properties of N-CMCs/cassava starch films. N-CMCs/cassava starch film with 0.4 g/100 mL N-CMCs exhibited a 554% increase in tensile strength, 41% increase in elongation at break, and 123% increase in water solubility compared with the CNCs/cassava starch film. Moreover, the water vapor permeability and moisture absorption of the N-CMCs/cassava starch film decreased by 42.7% and 15.9%, respectively. Better mechanical properties, water barrier properties and water solubility was achieved for the N-CMCs/cassava starch film than for the CNC/cassava starch film, indicating N-CMCs after carboxymethylation were beneficial for reinforcement of cassava starch-based films. The moisture absorption abilities of both cassava starch nanocomposite films were comparable. The results may be applied to the development of water-soluble and biodegradable edible films for food packaging.

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1. Introduction

Natural and biodegradable polymers have been extensively studied to develop edible films for packaging. Among various biopolymers, starch is considered as one of the most promising candidates for preparing edible films owing to its availability, low cost, renewability and biodegradability (Rhim, Park, & Ha, 2013). Starch films generally possess good barrier properties against oxygen, carbon dioxide and lipids. However, they have inferior mechanical and moisture barrier properties compared to conventional films made from synthetic polymers (Miri et al., 2015), thereby limiting their industrial applications. In general, these shortcomings can be enhanced by adopting several approaches such as chemical modification of starch via cross-linking (Ramaraj, 2007) and addition of functional additives with or without simple modification (Chang,

Jian, Zheng, Yu, & Ma, 2010; Ghanbarzadeh, Almasi, & Entezami, 2011). Adding functional additives to starch polymers for preparing starch-based edible films is an effective way to improve the material properties (Kaushik, Singh, & Verma, 2010; Müller, Laurindo, & Yamashita, 2009; Magdalena and Caisa, 2016). Numerous studies have shown that adding various nanofillers represents an effective to improve the properties of starch-based nanocomposite films, such as nanoclay (Souza et al., 2012), carbon nanotubes (Castrejón-Parga et al., 2014), nanorod-rich zinc oxide (Nafchi, Alias, Mahmud, & Robal, 2012), carboxymethyl chitosan (Duan, Sun, Wang, & Yang, 2011), cellulose nanocrystals (CNCs) (Lu, Weng, & Cao, 2005), and cellulose nanofiber (Azeredo et al., 2009), and therefore, broadens their fields of application. In order to produce economical biodegradable and edible films, the polymer matrix and reinforcement should be derived from renewable and abundant resources. In this context, CNCs are attractive reinforcement to fabricate starch-based edible films with improved water vapor barrier and increased mechanical properties (Rhim et al., 2013).

CNCs are highly crystalline and nontoxic nanoparticles that can

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be obtained from various cellulose sources by controlled sulfuric or hydrochloric acid hydrolysis. However, CNCs particles could easily aggregated via van der Waals forces and hydrogen bonding interaction during drying because of its high surface area and numerous active hydroxyl groups. Moreover, the degree of irreversible aggregation is greater at higher temperatures (Ahola, Myllytie, Österberg, Teerinen, & Laine, 2008). Aggregated CNCs are difficult to disperse via physical methods, thereby limiting their applications. CNCs can be hydrophobically modified to improve its re-dispersion. Hydrophobic modification of the CNCs surface has attracted great attention because hydrophobically modified CNCs are more compatible with water-insoluble polymers like polyolefins (Fortunati et al., 2012; Goussé, Chanzy, Cerrada, & Fleury, 2004). However, hydrophobic modification still has its drawbacks. For example, thoroughly mixing hydrophobic material with hydrophilic CNCs in the reaction process is difficult because of significant difference in their polarity, thereby producing a nonhomogeneous reaction product. In addition, hydrophobic modification by grafting polymerization presents several problems, including strict reaction conditions, low grafting efficiency and complex grafting homopolymers (Lee et al., 2011; Morandi, Heath, & Thielemans, 2009). However, studies have shown that CNCs by hydrophilic modification contain a mass of hydrophilic groups such as hydroxyl and carbonyl groups and are potentially miscible with starch, due to the formation of hydrogen bonds (Rodríguez-González et al., 2012). Therefore, a simple and efficient method is needed to improve the re-dispersion of CNCs by hydrophilic modification for reinforcing starch-based edible films.

Starches from different plant sources, such as potato, corn, sweet potato, cassava, pea and banana, have been used as film-forming matrices (Huan, Yu, & Ma, 2006; da Silva, Pereira & Druzian, 2012; Kibar & Us, 2013). Among these starches, the use of cassava starch as edible film-forming matrix is promising and offers several advantages, such as availability, low cost, high amylopectin and high viscosity, which leads to good film-forming properties. In this work, CNCs were prepared from the residues after starch extraction of sweet potato. The CNCs were then carboxymethylated to obtain carboxymethyl cellulose nanocrystals (N-CMCs). The N-CMCs were used as reinforcement in the preparation of cassava starch-based nanocomposite edible films. Effects of N-CMCs reinforcement on the physicochemical properties of the nanocomposite films were investigated.

2. Materials and methods

2.1. Materials

Sweet potato residue and cassava starch were supplied by Sichuan Guangyou Shuye Co., Ltd. (Sichuan, China) and Yunlong Technology Co., Ltd. (Guangxi, China), respectively. Isopropyl alcohol, sodium hydroxide, monochloroacetic acid, potassium carbonate, magnesium nitrate, anhydrous calcium chloride, calcium nitrate, calcium sulfate, and glycerol were purchased from Kelong Chemical Reagent Factory (Chengdu, China). All reagents were of analytical grade.

2.2. Production of CNCs

CNCs were prepared from the residues after starch extraction of sweet potato according to the method of Lu, Gui, Zheng, and Liu (2013). In order to prepare the cellulose nanocrystals, the raw cellulose was micronized to pass through a 180-mesh screen, and the micropowder of cellulose was set as microcrystalline cellulose. The microcrystalline cellulose was dispersed in 65% sulfuric acid solution (10 mL/g) into a flask, and then placed in an ultrasonic

equipment. Hydrolysis was performed at 55 °C with the ultrasonic power of 120 W for 120 min. To avoid the increase in the temperature of solution, ice was put in the reactor during the process of sonication. Suspensions were diluted five-fold to stop the hydrolysis reaction. The suspension was centrifuged at 11,000 rpm for 15 min to separate the nanocrystals in the suspension. The nanocrystals were washed with distilled water and centrifuged at 11,000 rpm for 15 min. The process was repeated three times. Then, the suspension was submitted to neutralizing with 2 g/100 mL sodium hydroxide until the pH of the suspension reached a constant value of 7.0. To further decentralize and reduce the size of the cellulose nanocrystals, the suspension of cellulose nanocrystals was processed through a highpressure homogenizer with a pair of Z-shaped interaction chambers under an operating pressure of 300 MPa before vacuum drying at 45 °C for 24 h.

2.3. Production of N-CMCs

The resulting CNCs were subjected to carboxymethylation reaction to obtain N-CMCs via a slurry method (Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim, & Emam, 2010). Briefly, 1 g of CNCs were soaked in 45 mL of isopropyl alcohol for 30 min at the temperature of 25 °C while stirring. 2 mL of sodium hydroxide solution (48 g/100 mL) was added dropwise to the mixture for approximately 10 min. After continuous stirring for 60 min at 25 °C, 1.42 g of monochloroacetic acid was dissolved in 15 mL of isopropyl alcohol and added to the solution aforementioned. The whole reaction system would be heated up to 50 °C and kept for 50 min. Subsequently, 1 mL of sodium hydroxide solution (48 g/100 mL) was added dropwise. The mixture was continuously stirred and incubated for 90 min at 60 °C. After carboxymethylation, the mixture was filtered, suspended in 150 mL of aqueous methanol (80 mL/100 mL), and neutralized with acetic acid (90 mL/100 mL). The resulting product (N-CMCs) was washed thrice with aqueous ethanol (70 mL/100 mL) and once with absolute methanol before vacuum drying at 45 °C for 24 h. The degree of substitution of the N-CMCs which measured according to the ASTM D1439-03 was 1.343.

2.4. Preparation of nanocomposite films reinforced with N-CMCs

The nanocomposite films were prepared using the conventional solution casting method following the method of Oun and Rhim (2015) with minor modification. Cassava starch (5.0 g) and N-CMCs (varying from 0 g to 0.5 g) were well mixed in 100 mL of distilled water. The mixture was heated to 80 °C under constant stirring for 10 min, after which glycerol (1.5 g) was added to the mixture. The mixture was stirred for 20 min to obtain a film-forming solution. The film-forming solution was degassed in vacuum below 0.09 MPa for 20 min. When the degassed solution was cooled to 70 °C, the cassava starch-based films reinforced with N-CMCs (named as N-CMCs/cassava starch films) were cast by pouring 10 mL of the solution onto plastic Petri dishes (internal diameter, 60 mm) and dried at 60 °C for 2 h. The cassava starch films which was without any reinforcement and the cassava starch-based films reinforced with CNCs (named as CNCs/cassava starch films) were also prepared for comparison. The thickness of the film was measured using a digital micrometer (0.001 mm accuracy; Mitutoyo Manufacturing Co. Ltd., Japan) and controlled at approximately 0.06 mm. Reported values of thickness were the mean of five measurements for each film sample. All of the produced films were removed from the dishes and stored at 50% relative humidity and 23 ± 1 °C for 15 d before testing.

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