Food Chemistry 197 (2016) 250–256

Contents lists available at ScienceDirect

Food Chemistry

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

Green and biodegradable composite films with novel antimicrobial performance based on cellulose

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ARTICLE INFO

Article history:
Received 18 May 2015
Received in revised form 18 September 2015
Accepted 24 October 2015
Available online 11 November 2015

Keywords:
Cellulose
Chitosan
Antimicrobial
Food packaging

ABSTRACT

In order to obtain a safe and biodegradable material with antimicrobial properties from cellulose for food packaging, we presented a facile way to graft chitosan onto the oxidized cellulose films. The obtained films had a high transparent property of above 80% transmittance, excellent barrier properties against oxygen and antimicrobial properties against *Escherichia coli* and *Staphylococcus aureus*. The antimicrobial properties, mechanical properties, and water vapor permeability of composites are essential characteristics in determining their applicability as food-packaging materials. Moreover, using a sausage model, it was shown that the composites exhibited better performance than traditional polyethylene packaging material and demonstrated good potential as food packaging materials. The results presented a new insight into the development of green materials for food packaging.

1. Introduction

Food packaging materials with proper mechanical strength, barrier properties against water, water vapor, thermal stability, recyclability, and biodegradability as well as functional properties such as antimicrobial activities are highly desirable for food safety and extending the shelf-life of packaged foods. Currently, the materials used in packaging industries are dominated by petroleum based plastic materials such as polypropylene (PP), polyethylene (PE) or polystyrene (PS) (Fabra, López-Rubio, & Lagaron, 2014). The usage of these kinds of materials not only consumes non-renewable petrochemicals, but also results in environmental pollution (Benbettaïeb, Karbowiak, Brachais, & Debeaufort, 2016; Rochman et al., 2013). Furthermore, the plastic compounds and additives could migrate from packaging materials and have potential risks to food safety and human health (Bang et al., 2012; Guart, Bono-Blay, Borrell, & Lacorte, 2014; Guart et al., 2013). Therefore, research works have been focused on the development of biodegradable packaging materials using biopolymers to substitute petroleum based plastic packaging materials. A variety of biopolymers such as starch, agar, carrageenan, and gelatin have been used for this purpose (Rhim, Park, & Ha, 2013). However, their poor antibacterial, mechanical and processing properties with high production costs have been the main limitation in using the biopolymer films for food packaging application (Kanmani & Rhim, 2014).

Cellulose, the most abundant biopolymer which can be extracted from wood, cotton, leaves and many other sources, is a natural linear organic compound consisting of d-glucopyranose units connected by β-1,4-glycosidic bonds (Johar, Ahmad, & Dufresne, 2012; Khan et al., 2012; Sheltami, Abdullah, Ahmad, Dufresne, & Kargarzadeh, 2012). Cellulose is environmental friendly and biodegradable, it has been successfully used as a packaging material for food preservation (Ghaderi, Mousavi, Yousefi, & Labbafi, 2014; Lu, Xiao, Zhang, & Gong, 2014). However, pristine cellulose lacks intrinsic antimicrobial properties which is useful for instance in the development of antimicrobial materials. Examples of such materials include cellulose nanocomposites with antimicrobial properties by the incorporation of inorganic nanoparticles (Jia, Mei, Cheng, Zhou, & Zhang, 2012; Martins et al., 2012; Yang, Xie, Deng, Bian, & Hong, 2012) or by adequate grafting of reactive groups onto cellulose nanofibers (Barbiroli et al., 2012; Rouabhia et al., 2014). Several techniques have also been reported to immobilize cationic antibacterial groups onto cellulose film surfaces, including tethering antimicrobial polymers onto cellulose film surface via chemical coupling reactions, surface initiated polymerization of monomers having antibacterial moieties, and synthesis of surface-tethered antimicrobial polymer brush via post-polymerization modifications, and self-assembled polyelectrolytes on the cellulose matrix (Abkenar & Malek, 2012; Dong, Qian, Zhao, He, & Xiao, 2014; Gomes, Mano, Queiroz, &

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http://dx.doi.org/10.1016/j.foodchem.2015.10.127
0308-8146/

Gouveia, 2013; Teli & Sheikh, 2012). A major challenge for these methods was that the reaction processes were complex and multi-step.

We have put an intensive research work on the cellulose dissolving and preparation of functional materials from the dissolved solution (Liu, Yan, Tao, Yu, & Liu, 2012; Liu, Yu, Wu, Li, & Li, 2014; Wu, Zhang, Li, & Liu, 2014). In this work, we presented a facile way to prepare highly transparent antimicrobial films by grafting chitosan onto the oxidized cellulose matrix. This work was inspired by the chemical structure and novel antibacterial properties of chitosan. Chitosan is an ammonium salt, and the amino group in chitosan could link with aldehyde group in cellulose matrix though the Schiff base reaction. The obtained composite films had integrated the merits of cellulose and chitosan, they were characterized with the preservation of sausage and obvious antibacterial performance was observed. The results added new insight into the potential of this processing method for the development of biodegradable food packaging applications.

2. Experimental

2.1. Chemicals

Native cellulose (Cotton linter, α-cellulose ⩾95%) was supplied by Hubei Chemical Fiber Co. Ltd. (Xiangfan, China), and its viscosity-average molecular weight (M_η) was about 1.07×10^5, which was determined in cadoxen at 25 °C. Sodium periodate, chitosan and other chemicals with analytical grade were purchased from Shanghai Aladdin Industrial Inc. Deionized water was used for the experiments.

2.2. Preparation of regenerated cellulose (RC) films and composite films

The native cellulose was dissolved by the freezing-thawing method (Liu et al., 2014). Briefly, powder-like filter paper (Native cellulose) was dispersed into aqueous lithium hydroxide/urea solution (8.7 wt%/12.0 wt%), and then put it in a refrigerator for 12 h, after frozen, took it out and thawed at room temperature to obtain a transparent cellulose solution (4 wt%). The resultant cellulose solution was subjected to centrifugation at 7000 rpm and 4 °C for 8 min to eliminate some bubbles in the viscous solution. The viscous bubble-free solution was cast on a glass plate and the thickness of the solution was controlled to be about 1 mm, and then immersed it into coagulation bath containing 5 v% H_2SO_4 to regenerate for 10 min. The regenerated cellulose films (RC) were washed with deionized water and then immersed into Na_5IO_6 solution (5 wt%) for 0.5, 1, 2 and 3 h to obtain oxidized cellulose (OC) films. The OC films were immersed into 2.5 wt% chitosan solution for 3 h, then washed with deionized water and dried at ambient conditions to obtain OC/CS composite films. The process was presented in Scheme 1. The composite films prepared from cellulose with different oxidation time were named for CS-0.5, CS-1, CS-2, CS-3, respectively.

2.3. Determination of oxidation degree

The oxidation degree (OD) of the cellulose films was determined according to the reported method based on the Schiff base reaction between aldehyde groups and hydroxylamine hydrochloride (Cheng et al., 2014). The oxidation degree was calculated through the following equation:

$$\mathrm{OD}\,(\%) = \frac{161(V_2 - V_1)}{c_{(HCl)} \times 10^{-3}} \times 100 \tag{1}$$

where V_1 is the amount of hydrochloric acid for sample titration in mL, V_2 is the amount of hydrochloric acid for control titration in mL, $C_{(HCl)}$ is the concentration of hydrochloric acid in mol/L, and 161 is the average molecular weight when glucose units were translated into 50% dialdehyde.

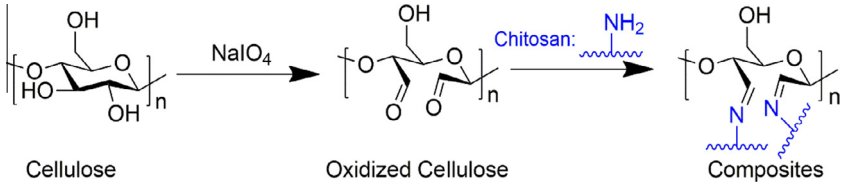
2.4. Characterization

The Fourier-transform infrared (FT-IR) spectra of the samples were characterized with FT-IR spectrometer (Nicolet Nexus 470). The samples were ground into powders, and mixed with KBr and pressed to form a sample disk for the tests. The optical transmittance of the films was carried out on an UV–Visible spectrometer (Shimadzu UV-1700) from 300 to 800 nm using air as a reference, the thickness of the cellulose, and composite films was about 33 μm. The surface morphology of the samples was characterized by scanning electron microscopy (SEM) (Hitachi S4800, Japan). X-ray photoelectron spectroscopy (XPS) was performed by using an axis ultra DLD apparatus (Kratos, UK). The mechanical properties of the films were characterized with a tensile tester (CMT 6503, Shenzhen SANS Test machine Co. Ltd., China) according to ASTM/D638-91 with a speed of 2 mm min^{-1}. Thermogravimetric analysis (TGA) was carried out on a Pyris TGA linked to a Pyris diamond TA Lab System (Perkin-Elmer Co., USA) at a heating rate of 10 °C min^{-1} from 40 to 700 °C under nitrogen atmospheres. The swelling ratio (Q) of the films was characterized by a gravimetric method (Li, Wu, Liang, Li, & Liu, 2014). A known amount of dried film was immersed in distilled water at room temperature. The weight of the film was directly measured after gently wipe off the water on the surface at different times. The swelling ratio (Q) was calculated using the following equation:

$$Q = \frac{W_h - W_d}{W_d} \tag{2}$$

where W_h was the weight of the swollen film and W_d was the weight of the dried sample. Three replicates for each sample were performed to obtain an average value of Q.

The water vapor transmission rate (WVTR) of the films was calculated in accordance with ASTM E96-00 standard test method (ASTM, 2010). Saturated aqueous solutions with different salts were used to establish different relative humidity (RH) inside the test chamber and weighing bottles were used in the test. Certain amount of anhydrous $CaCl_2$ was added to the weighing bottle to maintain 0% RH in the bottle, the test film was placed over the mouth of the weighing bottle and then, molten paraffin was



Scheme 1. The process for the preparation chitosan grafted cellulose composites through the oxidization of regenerated cellulose.