LWT - Food Science and Technology 74 (2016) 311–318

Contents lists available at ScienceDirect

LWT - Food Science and Technology

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

Elaboration and characterization of corn starch films incorporating silver nanoparticles obtained using short glucan chains

Na Ji, Chengzhen Liu, Shuangling Zhang, Liu Xiong, Qingjie Sun*

College of Food Science and Engineering, Qingdao Agricultural University, 700 Changcheng Road, Chengyang District, Qingdao, Shandong Province, 266109, China

ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form
28 July 2016
Accepted 29 July 2016
Available online 30 July 2016

Keywords:
Nanocomposite
Antibacterial activity
Gram-negative bacteria
Thermal stability

ABSTRACT

Nanocomposites are being used as a new type of packaging that has good biodegradability and antibacterial ability and that has wide applicability in the preservation and storage field. Transmission electron microscopy results demonstrated that the AgNPs were spherical in shape with the diameter of 2–6 nm for 48 h reaction time. The mechanical properties of composite films increased after the incorporation of AgNPs. Differential scanning calorimetric and thermogravimetric analysis results showed that the thermal stability of silver–starch composite film was increased through incorporation with AgNPs. The composite films exhibited strong antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*, and the composite films were more effective against Gram-negative bacteria (*E. coli*).

1. Introduction

Renewable and abundantly available biopolymers are the most viable alternative for the production of green materials in the near future (Shankar, Reddy, Rhim, & Kim, 2015). Starch isolated from industrial crops has attracted considerable attention as a biodegradable thermoplastic polymer (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006). The application of starch-based films in packaging is promising because of their environmental appeal, low cost, and flexibility (Savadekar & Mhaske, 2012). Over the past decade, a large number of studies have focused on starch or starch-based films (Kampeerapappun, Aht-ong, Pentrakoon, & Srikulkit, 2007; Maran, Sivakumar, Sridhar, & Thirugnanasambandham, 2013). However, poor mechanical properties represent the main limitation of such biopolymer-based films. In order to overcome their shortcomings, starch films have been blended with nanoparticles, such as cellulose nanoparticles (Aila-Suárez et al., 2013), starch nanocrystals (Li et al., 2015), and taro starch nanoparticles (Dai, Qiu, Xiong, & Sun, 2015). Furthermore, starch films are sensitive to contamination with bacteria (Abreu et al., 2015). A number of research studies have reported that to overcome this problem, adding chitosan (Liu, Adhikari, Guo, & Adhikari, 2013a) and other antimicrobial agents (Kuorwel, Cran, Sonneveld, Miltz, & Bigger, 2013) could improve the antibacterial properties of starch film. Thus, there are considerable interests in combining biodegradable materials with inorganic nanofillers to achieve designed functional properties (Chevirona, Gouanvéa, & Espuchea, 2014). Metal nanoparticle–incorporated polymers have attracted great attention because of their widened scope of application (White, Budarin, Moir, & Clark, 2011). Silver nanoparticles (AgNPs) are one of the most commonly explored and used nanoparticles owing to some functionalities such as ultraviolet (UV) protection (Yuen et al., 2013) and antibacterial activity (Shukla, Singh, Reddy, & Jha, 2012). There is rapidly growing interest in the research community to make AgNPs synthesis a sustainable process by using naturally occurring, biodegradable stabilizers and reducing agents (Lokanathan, Ahsan Uddin, Rojas, & Laine, 2014). One can find numerous reports on AgNPs synthesis using stabilizers of natural polymers such as cellulose (Lokanathan et al., 2014), and starch (Gao, Wei, Yan, & Xu, 2011). Polyhydroxyl macromolecules present interesting dynamic supramolecular associations facilitated by inter- and intramolecular hydrogen bonding resulting in molecular level capsules, which can act as templates for nanoparticle growth (Raveendran, Fu, & Wallen, 2003). Starch, a linear polymer formed by α-1-4 glycosidic bonds between D-glucose units, is essentially composed of two main polysaccharides, amylose and amylopectin (Liu, Wang, Li, & Duan, 2015). It also presents interesting dynamic supramolecular associations facilitated by inter- and intra-molecular

* Corresponding author.
E-mail address: phdsun@163.com (Q. Sun).

http://dx.doi.org/10.1016/j.lwt.2016.07.065
0023-6438/

hydrogen bonding resulting in a helical structure, which can act as nanoreactors for the growth of nanoparticles (Imberty, Chanzy, Perez, Buleon, & Tran, 1988). Valodkar, Modi, Pal, and Thakore (2011) also prepared AgNPs by adding aqueous solutions of sucrose, soluble starch, and waxy corn starch to aqueous solutions of silver nitrate. Several approaches have been shown by using starches and starch derivatives as templates for AgNPs synthesis (Huang & Yang, 2004; Sanoe, Channarong, & Ekasith, 2009). Although various starches and starch derivatives have been used as stabilizers for AgNPs, the use of short glucan chains for this purpose has not been reported. Amylopectin mainly consists of short α-l, 4-glucan chains (short glucan chains) linked to each other by α-l, 6 linkages (Cai & Shi, 2010). For decades, AgNPs have been widely used as antimicrobial agents in a number of areas, including chitosan film (Rhim, Hong, Park, & Ng, 2006), cellulose membrane (Jung, Kim, Kim, & Jin, 2009), and food packaging purposes (Tankhiwale & Bajpai, 2009).

Corn starch is widely used in processed foods, pharmaceuticals, textile, and paper products, among other applications, owing to its unique functional properties, lack of odor, low cost, and availability (Xu et al., 2012). In the current work, a new method has been developed to synthesize well-stabilized AgNPs of small size, with short glucan chains reacted as a stabilizing agent. In addition, corn starch films reinforced with AgNPs and their mechanical, optical, thermal, and antimicrobial properties have also been examined. This work will conduce to the development of antimicrobial starch films that have better antibacterial activity and thermal properties; these can be widely used in the preservation and storage field.

2. Materials and methods

2.1. Materials

Waxy rice starch (approximately 1% amylose and 99% amylopectin) and normal corn starch (with an amylose content of approximately 26.33%) were obtained from the Zhucheng Xingmao Corn Development Co. Ltd. (Shangdong, China). Pullulanase (E.C.3.2.1.41, 6.17×10^{-4} kat/g, where ASPU is defined as the amount of enzyme that liberates 1.0 mg glucose from starch in 1 min at pH 4.4 and 60 °C) was supplied by Novozymes (China) Investment Co. Ltd. (Beijing, China). Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$) and glycerol were from Sigma–Aldrich (St. Louis, MO. USA). All other chemicals used in the present study were of analytical grade.

2.2. Synthesis of silver nanoparticles

Short glucan chains was prepared using the method described by Sun, Li, Dai, Ji, and Xiong (2014a), with some modifications. Waxy rice starch (15 g, db) was dispersed into 100 mL of 0.2 moL/L disodium hydrogen phosphate and 0.1 moL/L citric acid buffer solution (pH 5.0). The starch slurry was cooked in boiling water with vigorous stirring for 30 min to fully gelatinize the starch. The temperature of the cooked waxy rice starch was adjusted to 58 °C and pullulanase (3.09×10^{-6} of dry starch) was added. After an 8 h incubation period at 58 °C, isoamylolysis was stopped by heating at 100 °C for 30 min to inactivate the pullulanase and the slurry was centrifuged. The solutions were then freeze-dried to obtain short glucan chains.

In a typical synthesis, 0.5 g/100 g dispersions of short glucan chains were sonicated for 15 min prior to use in the AgNP synthesis procedure. All synthesis experiments were carried out at room temperature. Aqueous $AgNO_3$ solution (200 μL, 10 mM) was added to 2 mL of the short glucan chains dispersion (0.5 g/100 g) and mixed mechanically. Then, 2 mL (20 mM) of aqueous $NaBH_4$ (freshly prepared) was added to the resulting dispersion and stirred continuously for 30 s. The dispersion was allowed to react for 48 h and was centrifuged at 2498*g* for 30 min. The supernatant was resuspended in Milli-Q water and centrifuged at 2498*g* for 30 min. This procedure was carried out twice and the supernatants were then freeze-dried.

2.3. Preparation of the composite films

The method of preparation was adapted from Sun, Xi, Li, and Xiong (2014b), with some modifications. The corn starch (5 g) and glycerol (2 g) were added into 100 mL distilled water to form starch-plasticizer dispersions. The solutions were heated at 100 °C with continuous agitation for 30 min to allow full gelatinization of the corn starch. The starch paste was then cooled to 70 °C, and 50 mL of AgNP stock solution was added into the dispersions. The different amounts of AgNPs were 0, 10, 20, 30, and 40 mg, which corresponded to 0, 2, 4, 6, and 8 mg/g starch, respectively. After introducing the AgNP solution, these dispersions were further stirred for 30 min at 30 rpm. Then, the composite solutions were degassed under a vacuum (0.1 MPa) for 15 min and cooled to room temperature. The mixture (about 65 g) was then spread evenly over Petri dishes (15 cm diameter) and dried for over 8 h at 45 °C. All of the dried starch films were preserved in a humidity chamber (25 °C, RH = 75%) for further testing.

2.4. Ultraviolet–visible absorption spectroscopy (UV–vis)

After the resulting dispersion containing AgNPs was diluted (1 mL/6 mL) using Milli-Q water, the spectra of mixed solutions were recorded at different time intervals using a UV–vis spectrophotometer (Shimadzu-2600, Kyoto, Japan) from 300 to 700 nm.

2.5. Transmission electron microscopy (TEM)

Transmission electron micrograph were taken with a 7650 transmission electron microscope (Hitachi, Tokyo, Japan) with an acceleration voltage of 80 kV. The TEM samples of AgNPs were prepared by pipetting 10 μL of the dispersion at different reaction times onto carbon grids. This was followed by the removal of excess liquid by touching the edge of the drop with Whatman filter paper after incubation for 2 min and allowing it to dry in air. Size analysis of the film dispersion was prepared by placing a droplet of the aqueous dispersion onto Formwar coated grids. Then, the colloidal droplets were dried either directly at room temperature for 10 min or after using a paper towel to obtain a thinner deposit. For each analysis, low electron beam intensity was used and a short exposure time was employed to avoid any evolution of the samples during their exposure to the electron beam.

2.6. Thickness measurements

The thickness of the films was determined using a Palmer digital micrometer (Comecta, Barcelona, Spain) to the nearest 0.001 mm. The reported thickness values were the mean of 10 measurements taken for each film sample. The measurements were carried out in three replicates for each film sample and the average values were presented.

2.7. Mechanical properties

A TA. XT Plus Texture Analyzer (Lloyd Instruments, London, UK) was used to determine the film's tensile strength (TS), elongation at break (E%), and Young's modulus (YM). Film specimens were tested as suggested by Mehyar, Al-Ismail, Han, and Chee (2012), with some