Food Hydrocolloids 44 (2015) 309–319

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Characterization of tara gum edible films incorporated with bulk chitosan and chitosan nanoparticles: A comparative study

John Antoniou, Fei Liu, Hamid Majeed, Fang Zhong*

Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Food Science and Technology, Jiangnan University, Wuxi 214122, PR China

ARTICLE INFO

Article history:
Received 29 April 2014
Accepted 9 September 2014
Available online 28 September 2014

Keywords:
Antimicrobial edible films
Galactomannan
Tara gum
Chitosan nanoparticles
Characterization

ABSTRACT

Tara gum films were successfully produced with the inclusion of bulk chitosan or chitosan nanoparticles at various concentrations. The composites films were compared in terms of antimicrobial activity, thermomechanical, physicochemical and barrier properties. The thermal stability of the films was studied using thermogravimetric analysis (TGA). Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) measurements were used to study the interactions and compatibility between the polysaccharides with in the films. The microstructure of the films was analyzed using atomic force microscopy (AFM) and scanning electron microscopy (SEM). Incorporation of chitosan nanoparticles improved mechanical, physicochemical and barrier properties. Tensile strength was increased by 35.73 MPa while the elongation was decreased by 7.21%. Water solubility and water vapor permeability (WVP) were reduced by 74.3% and 22.7%, respectively. The compact structure of the chitosan nanoparticles reduced the free volume of the polymer matrix more than bulk chitosan by obstructing the diffusion of water and thereby decreasing the moisture content of the films. Additionally, the microstructure of the films showed that the nanoparticles were distributed homogenously with in the structure and increased the roughness of the surface. However, tara gum films with bulk chitosan exhibited better antimicrobial activity. Incorporation of chitosan nanoparticles produced films less effective against *Escherichia coli* compared to *Staphylococcus aureus*, and their antimicrobial activity was reduced at high concentrations probably due to agglomeration.

1. Introduction

Natural galactomannans are an alternative material that can be used for the production of edible films/coatings based on their edibility and biodegradability (Cerqueira, Bourbon, et al., 2011). Galactomannans are reserve polysaccharides composed of linear chains of (1 → 4)-β-D-mannopyranosyl residues having single side chain units of (1 → 6)-α-D-galactopyranosyl (Dey, 1978). Among the most commercial galactomannans is tara gum (TG) which is the ground endosperm of the seeds of tara tree (*Cesalpinia spinosa*). Galactose substitution in TG occurs on approximately every third mannose unit. TG functions mainly as a good thickener and stabilizer but due to the lower galactose substitution compared to fenugreek and guar gum it can also produce a stronger film (Embuscado & Huber, 2009). However, relatively poor mechanical and water vapor barrier properties of those films result in a major limitation of their industrial use. Over recent years, in order to overcome these drawbacks of biodegradable films, different types of nano-fillers have being introduced. By adding appropriate nanoparticles, it is possible to produce materials with improved mechanical reinforcement, higher thermal stability and barrier properties, and lower moisture sensitivity (Chivrac, Pollet, & Avérous, 2009; Sorrentino, Gorrasi, & Vittoria, 2007).

In view of maintaining the edibility of the films much attention has been focused on polysaccharide nano-fillers. The most common polysaccharides used for nanoparticle production in edible films are cellulose, starch and chitosan. Cellulose nanoparticles such as microcrystalline cellulose, nano-fibrils cellulose and cellulose whiskers, have been used for reinforcing hydroxypropyl methyl cellulose based films (Bilbao-Sáinz, Avena-Bustillos, Wood, Williams, & McHugh, 2010; Bilbao-Sainz, Bras, Williams, Sénechal, & Orts, 2011). Likewise, Azeredo et al. (2010) and Chang, Jian, Zheng, Yu, and Ma (2010) improved the mechanical and water vapor barrier properties of chitosan and glycerol-plasticized starch films respectively with the addition of cellulose nanostructures in the polymer matrix. Similar results have been reported for starch-

* Corresponding author. Tel.: +86 510 85328307.
E-mail address: fzhong@jiangnan.edu.cn (F. Zhong).

http://dx.doi.org/10.1016/j.foodhyd.2014.09.023
0268-005X/

based nanoparticles. Angellier, Molina-Boisseau, Dole, and Dufresne (2006) and Kristo and Biliaderis (2007) have shown the reinforcing effect of waxy maize starch nano-crystals in glycerol-plasticized starch and sorbitol-plasticized pullulan films. Spray dried and vacuum freeze dried starch nanoparticles have also been successfully incorporated into starch films (Shi, Wang, Li, & Adhikari, 2013a, 2013b).

Among the polysaccharides that produce nano-fillers with attractive features is chitosan. Chitosan nanoparticles can be produced based on ionic gelation as a result of inter- and intra-molecular cross-linking of chitosan's protonated amino groups by multivalent polyanions. Sodium tripolyphosphate (TPP) is a very popular polyanion because it is non-toxic and forms gels with desirable properties (De Moura et al., 2009). Chitosan nanoparticles have been successfully used as fillers to improve mechanical and barrier properties as well as the thermo-stability of films, decrease solubility and produce more compact and dense materials (Chang, Jian, Yu, & Ma, 2010a; De Moura, Avena-Bustillos, McHugh, Krochta, & Mattoso, 2008; De Moura et al., 2009). Additionally, chitosan compared to other bio-based food packaging materials has the advantage of antibacterial activity (Dutta, Tripathi, Mehrotra, & Dutta, 2009; Lei et al., 2014). The antimicrobial activity of chitosan has been observed against a wide variety of microorganisms including fungi, algae, and bacteria (Huang et al., 2012; Rabea, Badawy, Stevens, Smagghe, & Steurbaut, 2003). The broad antimicrobial properties of chitosan nanoparticles have also been reported and has been attributed to their high surface area and charge density (Qi, Xu, Jiang, Hu, & Zou, 2004; Xing, Chen, Liu, Cha, & Park, 2009). However, a direct comparison of the antimicrobial activity between bulk chitosan and chitosan nanoparticles within films has not been reported.

In this study, chitosan nanoparticles (CSNPs) and bulk chitosan (CS) were incorporated in glycerol-plasticized TG films. The aim of the study was to compare the effect of bulk CS and CSNPs on TG films in terms of thermomechanical, physicochemical, morphological and barrier properties. Additionally, the antimicrobial activity of the composite films was examined against *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive), two of the most currently observed food-borne bacteria. The structural changes of TG film were examined by FTIR and XRD analysis.

2. Materials and methods

2.1. Materials

Tara gum was obtained from Dymatic Chemicals Co., Ltd. (Guangdong, China) with molecular weight ~1000 kDa which was determined by gel permeation chromatography (GPC) (Tosoh Corp., HLC-8320GPC, Japan). Chitosan of molecular mass 100 kDa and DD of 90% derived from crab shells was obtained from Golden-Shell Biochemical Co., Ltd. (Hangzhou, China). Sodium tripolyphosphate was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). *E. coli* HB2151 and *S. aureus* ATCC 25923 were purchased by Distance Biotechnology Co., Ltd. (Hangzhou, China) and Haibo Biotechnology Co., Ltd. (Qingdao, China), respectively. Other reagents were all commercially available and used as received. Distilled water was used in all experiments.

2.2. Preparation of chitosan nanoparticles (CSNPs)

CSNPs were obtained according to the procedure first reported by Calvo, Remunan-Lopez, Vila-Jato, and Alonso (1997) with modifications. The formation is based on the ionic gelation of CS with TPP anions. In an acidic environment CS is solubilized by protonation of the amino groups, rendering the polymer positively charged. CS (1.5 mg/mL) was dissolved in aqueous solution containing acetic acid at concentration 3 times that of CS solution. TPP was obtained in aqueous solution at a concentration of 2.0 mg/mL. The TPP solution was added drop-wise to the CS solution under vigorous magnetic stirring at room temperature and the formation of CSNPs started spontaneously via the TPP-initiated ionic gelation mechanism. The final solution was ultra-sonicated (VCX 500, Sonics and Materials Inc., USA) for 0.5 min in order to break any aggregations and reduce particle size.

2.3. Characterization of CSNPs

2.3.1. Measurement of particle size and ζ-potential of CSNPs

The measurements of particle size, polydispersity index (PDI) and ζ-potential of nanoparticles were performed using a Zetasizer Nano-ZS (Malvern Instruments, Worcestershire, UK) on the basis of dynamic light scattering (DLS) techniques.

2.3.2. Transmission electron microscopy (TEM)

The morphology of CS and CSNPs was examined by a high-performance digital imaging TEM (JEOL 2100, Hitachi High-Technologies Corp., Tokyo, Japan). One drop of the suspended solution was spread onto a carbon-coated copper grid and stained with 2% (w/v) phosphotungstic acid. After drying at room temperature the samples were placed for TEM analysis using accelerating voltage of 100 kV.

2.4. Preparation of edible films

The TG composite solutions were prepared using the method described by Pinheiro et al. (2011) and Martins et al. (2012) with modifications. CSNPs and CS solutions (150 mL) were prepared at different concentrations 0, 5, 10, 15% w/w on dry basis of the weight of TG. 1% w/v TG was dissolved in each solution at 45 °C for 2 h until a homogeneous solution was obtained. 20% w/v glycerol was added as a plasticizer in the solution in order to make the final films less brittle and easier to handle. The acetic acid concentration was the same for all solutions (0.42% v/v). Film-forming solutions were then centrifuged at 3000 *g* for 10 min to remove un-dissolved matter and air bubbles. 75 mL of solutions were poured into square plastic petri dishes (10 × 10 cm) and dried at 35 °C for 24 h. The obtained films were conditioned at 53 ± 1% RH and 25 ± 1 °C for at least 3 days in a controlled environmental chamber (Shanghai, China).

2.5. Film characterization

2.5.1. Film thickness

Film thickness was measured with a digital micrometer (Shanghai, China) to the nearest 0.001 mm. Ten thickness measurements were taken on each testing sample in different points and the mean values were used in mechanical and permeability calculations.

2.5.2. Mechanical properties

A texture analyzer (Stable Micro Systems, Surrey, UK) was used in order to measure mechanical properties according to ASTM D882 (ASTM, 2001) with some modifications. The films were initially cut into strips (2 × 8 cm) after their equilibration at 53 ± 1% RH for 72 h. The initial grip separation and crosshead speed used were set at 50 mm and 0.5 mm/s, respectively. Tensile strength (TS) and elongation (*E*%) were calculated from the plot of stress (tensile force/initial cross-sectional area) versus strain (extension as a fraction of the original length) using the following Equations (1) and (2):