



Preparation, characterization, and properties of chitosan films with cinnamaldehyde nanoemulsions



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ABSTRACT

Natural aldehydes, such as cinnamaldehyde, can be used to modify the properties of chitosan-based materials by covalent cross-linking the chitosan molecules. Due to the non-polarity and hydrophobicity of cinnamaldehyde, emulsification technique was used to prepare homogeneous cinnamaldehyde-chitosan films. Under optimized conditions, cinnamaldehyde nanoemulsions led to the successful fabrication of uniform and smooth chitosan films. FTIR analysis of the films indicated the formation of chitosan-cinnamaldehyde Schiff base. The cross-linked films strongly absorbed UV–visible light and inhibited the emission of fluorescent light, and may therefore provide good photo-protection. The thickness (26–61 μm) and transparency (clear to turbid) of the chitosan films were modulated by varying the aldehyde/amino group ratio. The mechanical properties and water vapor permeability of the films also depended on the amount of cinnamaldehyde nanoemulsion utilized. Chitosan films showed good antimicrobial activity, but had better antifungal than antibacterial activity.

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1. Introduction

There is increasing interest in the development of sustainable coating materials to protect the quality and safety of fruits, vegetables, fish, and meats (Kalia & Parshad, 2014; Pasha, Saeed, Sultan, Khan, & Rohi, 2014). Biopolymers, such as proteins and polysaccharides, are popular candidates for the fabrication of these coatings because they are non-toxic, biocompatible, biodegradable, and renewable (Arora & Padua, 2010; Rhim & Ng, 2007; Vargas, Pastor, Chiralt, McClements, & Gonzalez-Martinez, 2008). Chitosan is a cationic polysaccharide isolated from natural sources (Croisier & Jérôme, 2013), which has been utilized in the food industry for its film forming properties, antibacterial activity, and

oxygen impermeability (Elsabee & Abdou, 2013). However, films fabricated from pure chitosan tend to be rigid and brittle, and so plasticizers are needed to reduce the frictional forces between the polymer chains and thereby improve their mechanical properties (Aguirre, Borneo, & León, 2013; Thakhiew, Champahom, Devahastin, & Soponronnarit, 2015). Alternatively, the functional groups on chitosan molecules (such as amino and hydroxyl groups) can be chemically modified to enhance the mechanical attributes of chitosan films (Hu, Xin, Hu, Chan, & He, 2013; Yu, Song, Shi, Xu, & Bin, 2011).

A common technique used to chemically modify chitosan films is based on the formation of a Schiff base between amino groups on the chitosan chain and aldehyde groups on cross-linking agents (Schiffman & Schauer, 2007). Schiff-base reactions have been widely applied in the fields of biomedicine, chemistry, and food science, due to mild reaction conditions and high reaction rates (Xin & Yuan, 2012). Essential oils are aromatic oily liquids extracted from certain fruits, vegetables and spices, which can be utilized as natural antioxidant and antimicrobial substances. Previous

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investigations have demonstrated their antimicrobial properties and applications in the preservation of fruits, vegetables and meats (Fernández-Pan, Carrión-Granda, & Maté, 2014; Perdonés, Sánchez-González, Chiralt, & Vargas, 2012; Severino et al., 2015). Cinnamon oil, which is an essential oil extracted from cinnamon bark, has been shown to be particularly effective (Burt, 2004). The main active constituent in cinnamon oil is cinnamaldehyde, which is a hydrophobic aromatic aldehyde that has been approved by the FAO/WHO Expert Committee on Food Additives (JECFA) for use as a food-flavoring agent (Cocchiara, Letizia, Lalko, Lapczynski, & Api, 2005). Cinnamaldehyde is a well-known natural antimicrobial compound that has been shown to be effective against a broad spectrum of food-borne pathogens (Burt, 2004; Holley & Patel, 2005). The aldehyde group in cinnamaldehyde can react with the amino group in chitosan through the Schiff base reaction. Studies have shown that cinnamaldehyde cross-linked chitosan nanoparticles can be prepared using water-in-oil emulsions as templates (Nipun Babu & Kannan, 2012). Imino-chitosan films have also been fabricated using the Schiff-base reaction from cinnamaldehyde, vanillin, piperonal and other natural aldehydes (Marin, Simionescu, & Barboiu, 2012; Marin et al., 2013; Marin et al., 2015). Typically, non-polar aldehydes need to be dissolved within water-miscible organic solvents (such as methanol, ethanol or acetone) before they can be mixed with aqueous chitosan solutions. Then, high reaction efficiency between aldehydes and chitosan can be greatly achieved by the slow water removal. However, the efficiency of chitosan cross-linking would be relatively low without the addition of solvents, due to the poor water-solubility of the non-polar aldehydes used. Our previous study showed that mixing cinnamaldehyde oil with an aqueous chitosan solution did not promote gel formation, but mixing emulsified cinnamaldehyde led to gel formation at pH > 4.6 (Lei et al., 2015). This study also showed that gels formed using emulsified cinnamaldehyde and chitosan had higher antibacterial activities than solutions formed from cinnamaldehyde oil and chitosan.

In the current study, we investigated the possibility of Schiff base cross-linking of chitosan films at low pH by first converting cinnamaldehyde into a water-dispersible oil-in-water nano-emulsion. The film was formed by the vacuum drying method to remove water. Then, physicochemical properties and antimicrobial activity of the films were investigated. The results showed that the cross-linked chitosan films obtained in our study may be appropriate for utilization as antimicrobial coatings for direct application to a variety of foodstuffs.

2. Materials & methods

2.1. Materials

Chitosan (degree of deacetylation of 85%; viscosity of 1% chitosan solution at 20 °C at 1250 mPa s; Mw: 2.78×10^5 Da by dynamic light scattering) was provided by Zhejiang Golden-Shell Pharmaceutical Co. (Zhejiang, China). Cinnamaldehyde ($\geq 95\%$) and potassium bromide (KBr) were purchased from Aladdin Reagent Co. (Shanghai, China). Medium chain triglycerides (MCT, $\geq 95\%$) were obtained from Wuhan Boxing Chemical Co. (Wuhan, China). Agar was supplied from Shanghai Titan Scientific Co., Ltd (Shanghai, China). Mueller Hinton broth (MHB) and Yeast Extract Peptone Dextrose agar (YPD) were purchased from Qingdao Hope Bio-Technology Co., Ltd (Qingdao, China). Tween 80, hydrochloric acid (HCl), sodium hydroxide (NaOH), disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), sodium chloride (NaCl) and ethanol were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Distilled water (electrical resistance $\approx 18.2 \text{ M}\Omega\cdot\text{cm}$) was used to prepare all aqueous

solutions. All the other chemicals were of analytical grade. *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) were obtained from the culture collection in Department of Food Science and Technology, Huazhong Agricultural University (Wuhan, China). *Candida Albicans* HG01 (*C. albicans*) was provided by the College of Bioengineering in Hubei University of Technology (Wuhan, China).

2.2. Formation of chitosan films

2.2.1. Cinnamaldehyde-loaded nanoemulsion preparation

The formation of cinnamaldehyde nanoemulsions was carried out using the spontaneous emulsification method described previously (Tian, Lei, Zhang, & Li, 2015). Briefly, an organic phase (10 wt%) was added dropwise into an aqueous phase (90 wt%) at ambient temperature while continuously stirring at 600 rpm using a magnetic stirrer for 15 min. The organic phase consisted of a mixture of cinnamaldehyde, MCT, and Tween 80, while the aqueous phase consisted of distilled water. The mass ratio of MCT and cinnamaldehyde was 1:1 and the concentration of Tween 80 was 7.5%.

2.2.2. Chitosan solution preparation

Powdered chitosan (2 wt%) was dispersed in 1 wt% acetic acid solution at room temperature, and then agitated overnight. Finally, the solution was centrifuged to remove any air bubbles or other impurities.

2.2.3. Film preparation and cross-linking

Cinnamaldehyde cross-linked chitosan films were prepared by mixing cinnamaldehyde nanoemulsions and chitosan solutions. The mixture was continuously stirred for 30 min to make sure the thorough blending. Then, the air bubbles in the mixture were eliminated by the vacuum treatment. After this process, the pH of the mixed solution was around 4.3. Aliquots (3 mL) of film-forming solution were then cast on Petri dishes (polytetrafluoroethylene, 5.5 cm \times 5.5 cm) and dried for 10 h at 60 °C in a vacuum oven. The films were then peeled from the plates and placed in desiccators containing silica gel before characterization. The preparation of a pure chitosan film (control) was carried out using the same procedure but without including the nanoemulsion. The ratio and concentration of cinnamaldehyde nanoemulsion and chitosan solutions were set based on the ratio of -CHO/-NH₂ molar ratios. Here, -CHO and -NH₂ refer to the carbonyl group on the cinnamaldehyde molecules and the amino groups on the chitosan molecules, respectively. For the sake of convenience, the films are referred to by the abbreviation "CnN" according to their -CHO/-NH₂ molar ratios (*n*). For example, a film that has a molar ratio of 1.5 cinnamaldehyde carbonyl groups to chitosan amino groups is referred to as "C1.5N", while a pure chitosan film is referred to as "CON". Finally, cinnamaldehyde-chitosan films were stored in an amber glass desiccator with P₂O₅ at ambient temperature (around 23 °C) prior to use.

2.3. Characterization of chitosan films

2.3.1. Film thickness

Film thickness (*T*) was measured to the nearest 0.001 mm with a hand-held digital micrometer (QuantuMike Mitutoyo, Japan). The values obtained for each sample at three different locations were averaged.

2.3.2. Optical properties

Transparency: The optical transmittance (*T_m*) of the films was measured using a UV-vis spectroscopy from 200 to 800 nm using air as a reference material (F300s Ultraviolet lamp, Shimadzu, Tokyo). The transmittance was calculated by measuring the

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