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Physical and antimicrobial properties of sodium alginate/carboxymethyl cellulose films incorporated with cinnamon essential oil

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ABSTRACT

Antimicrobial sodium alginate/carboxymethyl cellulose (SA/CMC) films were prepared by using glycerol as plasticizer, cinnamon essential oil (CEO) as antimicrobial agent, and Tween® 80 as surfactant. The effects of CEO concentration on the microstructure and physical, barrier, mechanical, and antimicrobial properties of SA/CMC films with Tween® 80 were investigated. It was found that the incorporation of CEO increased the thickness, water vapour permeability, oxygen permeability, and elongation at break of the films and significantly reduced the moisture content and tensile strength. However, water vapour permeability was reduced when 15 g/L CEO was incorporated into the films. The oxygen permeability of films slightly decreased with increasing Tween® 80 concentration. Moreover, SA/CMC films containing CEO exhibited excellent antimicrobial activity for *Escherichia coli* and *Staphylococcus aureus*. With increasing CEO amount to 15 g/L, the inhibitory effects on *Staphylococcus aureus* increased with increasing amounts of Tween® 80. In addition, film-forming solutions with CEO were used as coatings for the preservation of bananas. The results showed that the coatings could extend the shelf life of bananas.

1. Introduction

The synthetic polymeric packaging has been widely used in the food industry for several decades. However, the plastic material wastes have caused serious environmental problems associated to its non-biodegradability (Lopez de Dicastillo, Rodriguez, Guarda, & Galotto, 2016). Recently, the use of packaging material from biopolymers as a substitute for conventional synthetic polymeric packaging has been a hot topic in order to reduce environment pollution (Wu et al., 2015). The bio-films are nontoxic, biodegradable, and renewable. In addition, they can serve as carriers of active compounds such as antimicrobials or antioxidants to against the spoilage and oxidation of food (Acevedo-Fani, Salvia-Trujillo, Rojas-Graü, & Martín-Belloso, 2015).

The most common biopolymers for the formation of food packaging and coatings are proteins, polysaccharides and lipids, and combinations of these, which allow for preparing blends with ameliorated characteristics (Atarés & Chiralt, 2016; Coltelli et al., 2015; de Léis, Nogueira, Kulay, & Tadini, 2017; Zink, Wyrobnik, Prinz, & Schmid, 2016). Sodium alginate (SA) is a linear polysaccharide extracted from marine algae, which consisted of various proportions of α-L-guluronate and β-D-mannuronate connected via 1–4 glycosidic bonds. It is water-soluble, nontoxic, biocompatible, and reproducible (Liu et al., 2013). In particular, SA is easy to form hydrogels or insoluble polymers by the addition of divalent and trivalent ions, specifically Ca^{2+}, which has been widen their application in food and non-food industries (Rhim, 2004).

Carboxymethyl cellulose (CMC) is an anionic polysaccharide derived from celluloses (Yadav, Rhee, Jung, & Park, 2013). It has been considered as a potential edible film or coating material because of it is nontoxic, biocompatible, biodegradable, and has good film-forming property (Oun & Rhim, 2015). SA and CMC are two valuable biopolymers that can be used for the formation of biodegradable films (Ibrahim & El Salmawi, 2012). However, the limitations in antimicrobial properties restrict their better end-use applications. Nowadays, more attentions have been paid to the addition of natural antimicrobial agents into the packaging films or coatings which have no harmful effects on human health, aiming to reduce the application of synthetic antimicrobial agents in the food industry (Alves-Silva et al., 2013).

Essential oils, GRAS (Generally Recognized as Safe) materials, are natural substances with effective antimicrobial activity against various groups of pathogenic microorganisms (Pola et al., 2016). Recently, the use of essential oils to provide antioxidant and antimicrobial properties in edible/biodegradable films is becoming popular (Chen,

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Zhang, & Zhong, 2015; Pereda, Amica, & Marcovich, 2012). Cinnamon essential oil (CEO) from the cinnamon barks is a kind of effective antimicrobial agent with broad-spectrum antimicrobial properties (Arancibia, Giménez, López-Caballero, Gómez-Guillén, & Montero, 2014). Previous reports have shown that eugenol and cinnamaldehyde are the major active component of CEO. These volatile phenolic compounds can damage microbial cells by slowing down their development and, moreover, they are highly capable of neutralizing free radicals (Ayala-Zavala et al., 2013). Thus, the addition of CEO into SA/CMC films provides the possibility of improving antimicrobial activity of the films. Moreover, an effective surfactant is required to form and stabilise emulsions. Ojagh, Rezaei, Razavi, and Hosseini (2010) have tested the effect of adding CEO into chitosan films against Gram-negative and Gram-positive bacteria with the emulsification of Tween® 80. However, there is little information about the effects of CEO on the physical and antimicrobial properties of SA/CMC films by combining with Tween® 80.

The work was undertaken to study the effects of adding CEO in different levels on the properties of SA/CMC-based films by combining with Tween® 80, such as thickness, moisture content, oxygen permeability (OP), water vapour permeability (WVP), mechanical properties, and morphological properties. Antimicrobial activities of these films were also tested against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*). Additionally, bananas were coated with film-forming solutions to estimate the effect of CEO on the fruit preservation.

2. Materials and methods

2.1. Materials

Carboxymethyl cellulose (CMC; Henan Anli Fine Chemical Co. Ltd., China), Sodium alginate (SA; Hebei Subway Biological Technology Co. Ltd., China), CEO (Huamei Natural Spices Oil Refineries, China), Tween 80 and glycerol (Tianjin Guangfu Fine Chemical Research Institution, China), were used to prepare film-forming solutions. *S. aureus* (ATCC25923-3) and *E. coli* (ATCC25922-3) were provided by Qingdao Hope Bio-Technology Co. Ltd., China. Nutrient agars were produced in AoBoXing Bio-tech Co. Ltd., China.

2.2. Preparation of films

The film-forming solutions were obtained by dissolving SA (7.5 g/L, W/V film solution), CMC (2.5 g/L), and glycerol (5 g/L) in 350 mL of distilled water with mechanical stirring (Powerdriven force mixer, HD2010W, Shanghai Sile Instrument Co., LTD., Shanghai, China) at a speed of 500 r/min in a water bath (~60 °C). CEO (5 g/L, 10 g/L, and 15 g/L, W/V film solution) was mixed with Tween® 80 at various concentrations (50 g/kg, 100 g/kg, and 200 g/kg, W/W CEO) and incorporated into the film-forming mixtures. Additional CaCl$_2$ (1.5 g/L) was added to strengthen the film. The final film solution volume reached 400 mL by adding distilled water. The solutions were processed by a centrifuge (Table-top low speed centrifuge, TDL-40B, Shanghai Anting Scientific Instrument Factory, Shanghai, China) at 1500 *g* for 3 min to remove bubbles and then cast onto plexiglass plates (260 mm × 260 mm) in an oven at 60 ± 2 °C for around 36 h. The dried films were peeled and stored in a desiccator at 25 ± 2 °C and 43 ± 2% relative humidity (RH) prior to testing. Sample code and formulation are listed in Table 1.

2.3. Characterization of SA/CMC films

2.3.1. Fourier transform infrared (FT-IR) spectroscopy

A FT-IR spectrometer (Nicolet 6700, Thermo Fisher Scientific Co., Ltd., MA, USA) with attenuated total reflection (ATR) mode was used to record the FT-IR spectra of the films between 4000 and 650 cm^{-1} with 4 cm^{-1} resolution.

Table 1
Code and formulation of SA/CMC and SA/CMC-CEO films.

Film code	SA (g/L)	CMC (g/L)	Glycerol (g/L)	CaCl$_2$ (g/L)	Tween® 80 (g/kg)	CEO (g/L)
control film	7.5	2.5	5.0	1.5	0	0
CEO-1	7.5	2.5	5.0	1.5	50	5
CEO-2	7.5	2.5	5.0	1.5	50	10
CEO-3	7.5	2.5	5.0	1.5	50	15
CEO-4	7.5	2.5	5.0	1.5	100	5
CEO-5	7.5	2.5	5.0	1.5	100	10
CEO-6	7.5	2.5	5.0	1.5	100	15
CEO-7	7.5	2.5	5.0	1.5	200	5
CEO-8	7.5	2.5	5.0	1.5	200	10
CEO-9	7.5	2.5	5.0	1.5	200	15

2.3.2. Scanning electron microscopy (SEM)

The morphologies of the films were examined via SEM (Philips-FEI Co., AMS, The Netherlands) at an accelerating voltage of 5 kV after gold coating.

2.3.3. Film thickness (FT) and moisture content

FT was determined by a micrometer (ID-C112XBS, Mitutoyo Corporation, Tokyo, Japan) at five random locations on the films. Moisture content of films (20 mm × 20 mm) was measured after drying at 103 °C for 24 h. The data was averaged over three samples.

2.3.4. Water vapour permeability (WVP)

WVP of films was carried out by using gravimetric method previously developed (Han & Wang, 2017). Films were cut and sealed to the bottles (7.0 cm in diameter and 3.5 cm in height) filled with 50 g calcium chloride anhydrous. The bottles were then conditioned in a desiccator containing oversaturated solutions of NaCl (75% RH) at 25 °C. The weight of the bottles was measured for 7 days at 12 h intervals. The WVP was evaluated as follows:

$$WVTR = \Delta m/(\Delta t{\cdot}A) \tag{1}$$

$$WVP = WVTR{\cdot}FT/\Delta p \tag{2}$$

where $WVTR$ is water vapour transmission rate, $\Delta m/\Delta t$ is the rate of water gain, A is the exposed area of the film, WVP is water vapour permeability, FT is the film thickness, and Δp is partial water vapor pressure difference across the film.

2.3.5. Oxygen permeability (OP)

OP measurements of the films were determined at 25 °C and 0% RH by a Perme OX2/230 (Labthink, Jinan, China) for three replications. The film was placed on a sample chamber with an open testing area of 50 cm^2. Nitrogen (10 mL/min) flowed in one side of the film and oxygen (60 mL/min) flowed in the other side. OP was calculated as follows:

$$OP = OTR{\cdot}FT/\Delta p \tag{3}$$

where OP is oxygen permeability, OTR is oxygen transmission rate, FT is the film thickness, and Δp is partial pressure of oxygen.

2.3.6. Mechanical properties

Mechanical properties, containing tensile strength (TS) and elongation at break (*E*%), were performed using an auto tensile tester (XLW-PC, PARAM, Jinan, China). A load cell of 500 N, a gauge length of 50 mm and a cross-head rate of 300 mm m^{-1} in at 25 °C were used. At least five test samples were measured.

2.3.7. Antimicrobial activities

Antimicrobial activities were evaluated by the agar disc diffusion method against *Escherichia coli* and *Staphylococcus aureus*. Briefly,