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Barrier properties, mechanical properties and antimicrobial activity of hydroxypropyl methylcellulose-based nanocomposite films incorporated with Thai essential oils

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ABSTRACT

Hydroxypropyl methylcellulose (HPMC) is a promising hydrocolloid for use as a biopolymer film. Organically modified clay Cloisite 30B and beeswax were combined in the HPMC film to improve barrier and mechanical properties of HPMC films. However, HPMC-based nanocomposite film does not show any antimicrobial activity, which would enhance the film properties as an active package. Thus, the objective of this study was to determine the effect of Thai essential oils (EOs) on HPMC-based nanocomposite films. Three Thai EOs were selected—ginger (G), fingerroot (F) and plai (P). The addition of P or F increased the HPMC-based nanocomposite film oxygen permeability, but the addition of G did not. Incorporation of P in HPMC-based nanocomposite film increased the water vapor permeability of the films. As expected, EOs affected the total film color. Decreases in the elastic modulus and tensile strength accompanied with an increase in elongation were observed in film incorporated with G and F. HPMC-based nanocomposite films incorporated with F showed antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli* using agar disc-diffusion assay. Therefore, HPMC-based nanocomposite films incorporated with EO might be suitable to apply as an active packaging material or as an active coating on agricultural produce such as fresh fruits to maintain their quality and extend their shelf life.

1. Introduction

Nowadays, the development of edible films and coatings aims to partially replace synthetic materials such as plastics due to the biodegradable properties of the former. Biopolymer edible films and coatings can enhance the quality and extend the shelf life of commodities. Edible film based on hydroxypropyl methylcellulose (HPMC) has shown good film properties such as transparency, flexibility and being odorless and tasteless. Moreover, it is an excellent barrier to oxygen and aromatic compounds (Sothornvit, 2009). However, HPMC films have a drawback of being a poor moisture barrier due to their hydrophilic biopolymers. Thus, the combination of lipids in the HPMC film is needed to increase the effectiveness as a water barrier. Lipids such as beeswax (BW) have been shown to reduce the water vapor permeability (WVP) of HPMC-lipid composite coated paper (Sothornvit, 2009). Furthermore, the addition of BW to the HPMC film matrix reduced film mechanical resistance and the oxygen barrier, but improved the film moisture barrier (Navarro-Tarazaga, Massa, & Perez-Gago, 2011).

Thai herbal oils from ginger, plai and fingerroot have shown medicinal properties as they are antibacterial, antifungal and antioxidant (Stoilova, Krastanov, Stoyanova, Denev, & Gargova, 2007; Supreetha et al., 2011; Wannissorn, Maneesin, Tubtimted, & Wangchanachai, 2009). Generally, Thai herbs are natural antimicrobial agents used to replace organic acids and esters such as sorbet, benzoate, propionates and organic or inorganic acid salts (Sothornvit, 2007). HPMC-based nanocomposite films containing fingerroot, ginger and plai oils could inhibit *Colletotrichum gloeosporioides* of anthracnose disease (Klangmuang & Sothornvit, 2012). Sanchez-Gonzalez, Vargas, Gonzalez-Martinez, Chiralt, & Chafer (2009) reported that tea tree essential oil (EO) added to HPMC edible film reduced the WVP, tensile strength and elastic

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modulus of the HPMC composite films. Therefore, the addition of natural EO from Thai herbal oils (ginger, plai and fingerroot) in edible films might be beneficial or be a suitable, active packaging material in terms of antimicrobial activity.

Clay is regarded as a natural reinforced substance. Clay such as montmorillonite (MMT) consists of silicates, which are multi-layered in shape having a width and length of 100–150 nm. Its thickness (only 1 nm) is the crucial factor in improving the mechanical properties of the composite films (Sorrentino, Gorrasi, Tortora, & Vittoria, 2006). Clay is the most widely used nanofiller in polymer nanocomposites to improve the mechanical and barrier properties compared to the counterpart biopolymer films (Lim, Jang, & Song, 2010; Sothornvit, Hong, An, & Rhim, 2010; Sothornvit, Rhim, & Hong, 2009). The tensile strength and elastic modulus increased in HPMC films incorporated with clay (Mondal et al., 2013). Clay Cloisite 30B has a strong antimicrobial activity against Gram-positive (*Staphylococcus aureus* and *Listeria monocytogenes*) bacteria in chitosan films due to quaternary ammonium salt of the organically modified MMT (Rhim, Hong, Park, & Ng, 2006). However, adding nanoclay to improve the film properties of HPMC-lipid composite films has not been explored. Moreover, the EO was incorporated into the HPMC-based nanocomposite film to enhance antimicrobial activity as an active packaging film material. Therefore, the objective of this work was to determine the effect of EO from Thai herbs on the properties of HPMC-based nanocomposite films such as water vapor permeability, oxygen permeability and mechanical, optical and antimicrobial properties.

2. Materials and methods

2.1. Materials

Hydroxypropyl methylcellulose (HPMC) type K4M supplied by Dow Chemical (USA) was purchased from Vicchi Enterprise Co., Ltd. (Bangkok, Thailand). An organically modified montmorillonite (Cloisite 30B) was obtained from Southern Clay Co., Ltd. (Gonzales, TX, USA). Beeswax (BW), stearic acid (S) and glycerol (Gly) were obtained from Fluka Co., Ltd. (Buchs, Germany), Ajax Fine Chemicals Co., Ltd. (Sydney, NSW, Australia) and Ajax Fine Chemicals Co., Ltd. (Auckland, New Zealand), respectively. Three essential oils (EOs) from plai (P), ginger (G) and fingerroot (F) prepared by the steam distillation method were obtained from Thai-China Flavors and Fragrances Industry Co., Ltd. (Ayutthaya, Thailand).

2.2. Film preparation

An HPMC solution was prepared by dissolving 2.0% w/w in distilled water using a hot/cold technique. The HPMC was first dispersed by mixing thoroughly with 1/3 of the total volume of water and heated to above 90 °C until all particles were thoroughly hydrated. The balance of water was added as cold water to lower the dispersion temperature. Gly as a plasticizer was added to the HPMC solution and kept at a constant ratio of HPMC to Gly of 3:1 (w/w). An emulsifier of BW and S at a ratio of BW to S of 5:1 (w/w) was used to prepare a composite solution. To melt the BW, the solution was heated above the lipid melting point (62 °C). For the preparation of HPMC/clay nanocomposite solution mixtures, 5% of HPMC (w/w) of clay was used, which is the clay content commonly used for preparation of nanocomposites with biopolymers (Rhim et al., 2006). At first, precisely weighed clay was dispersed with distilled water and stirred using a magnetic stirrer overnight to reach complete hydration/swelling. Then the clay solution was added to the HPMC-lipid solution to obtain the HPMC-based nanocomposite solution. EO from P, G or F was added into the HPMC-based nanocomposite solution to reach the final concentrations of EO in the solution of 15 g/L. These film-forming solutions were named as HPMC+P, HPMC+G and HPMC+F. The mixture solutions were homogenized with a homogenizer (Polytron model PT 3100, Littau, Switzerland) at 20,000 rpm for 5 min.

The film-forming solution was degassed and poured into a 21 cm × 30 cm casting plate at 10 g of total solids per plate to minimize thickness variations between formulations. The plates containing the film-forming solution were placed on a level surface and dried at 40 °C until films could be peeled from the casting surface.

2.3. Moisture content and water activity

The moisture content of the HPMC-based nanocomposite film and the HPMC-based nanocomposite film incorporated with EOs was determined using a Sartorius MA40 moisture meter (Sartorius, Inc., Goettingen, Germany). The water activity (a_w) was determined using an AquaLab Model CX3TE water activity meter (Decagon Devices, Inc., Pullman, WA, USA).

2.4. Moisture sorption isotherms

The equilibrium moisture contents of the HPMC-based nanocomposite films were determined at 25 °C using the static gravimetric method. This method is based on the use of nine saturated salt solutions (LiCl, CH_3COOK, $MgCl_2 \cdot 6H_2O$, K_2CO_3, $Mg(NO_3)_2 \cdot 6H_2O$, $NaNO_2$, NaCl, KCl and K_2SO_4), representing 0.12, 0.22, 0.33, 0.43, 0.53, 0.65, 0.75, 0.85 and 0.97 a_w, respectively. Weights of moisture-equilibrated samples were determined after all films had been dried at 105 °C for 24 h. The experiment was run in triplicate and the experimental moisture sorption isotherm values were averaged and fitted using the Langmuir isotherm model as shown in Eq. (1). The standard error of estimate (SEE) and the coefficient of determination (R^2) between the experimental (exp.) and the predicted (pre.) data were determined (Eq. (2)). All calculations were performed using Microsoft Office Excel 2007 solver and analysis Toolpac (Microsoft Corp., Redmond, WA, USA).

$$M = \frac{M_0 C k a_w}{(1 + C a_w)} \quad (1)$$

$$SEE = \sqrt{\sum_{i=1}^{n} \frac{(M_{i,\exp} - M_{i,pre})^2}{n}} \quad (2)$$

where, M = moisture content (g of water/g of dried film), a_w = water activity, M_o = monolayer moisture content (g of water/g of dried film) and C = a constant.

2.5. Color

Color was determined using a spectrophotometer (Spectro-guide sphere gloss, model CD-6834, BYK, Geretsried, Germany) on the HPMC-based nanocomposite film and the HPMC-based nanocomposite film incorporated with EO using the CIELAB color parameters, L^*, a^* and b^* at 60° angle. A white colored paper ($L^* = 90.71$, $a^* = 0.84$, $b^* = -4.37$ and gloss = 3.7 GU) was used as a background for the color measurements. The total color difference (ΔE^*) was calculated as shown in Eq. (3) with the HPMC-based nanocomposite film without EO as reference.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (3)$$