Food Hydrocolloids 84 (2018) 58–67

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Effect of halloysite nanoclay on the physical, mechanical, and antioxidant properties of chitosan films incorporated with clove essential oil

Min Hyeock Lee[1], Seong Yeon Kim[1], Hyun Jin Park[*]

School of Life Sciences and Biotechnology, Korea University, 5-Ka, Anam-Dong, Sungbuk-Ku, Seoul 136-701, Republic of Korea

ARTICLE INFO

Keywords:
Chitosan film
Clove essential oil
Halloysite nanotube
Food packaging
Physical property
Antioxidant property

ABSTRACT

In this study, chitosan (Ch)-based films containing clove essential oil (CEO) as an active agent were developed by incorporating halloysite nanotubes (HNTs) to stabilize the oil droplets. The physical, mechanical, and antioxidant properties of the films were investigated toward their application as food packaging materials. The water vapor barrier property of the films improved upon the addition of the CEO as well as HNTs, owing to the hydrophobicity of the CEO and formation of tortuous pathways by the HNTs. Scanning electron micrographs of films without HNTs showed a large number of micropores on the film surface while few pores were observed on the film surface with the HNTs. Further, the incorporation of CEO decreased the elongation of the film, whereas the HNT particles dispersed in the film matrix mitigated this effect. The antioxidant activity of the films with different concentrations of HNT was determined by total phenolic content, 2,2-diphenyl-1-picrylhydrazyl, and reducing power assays. The highest antioxidant activity was achieved for the Ch/CEO film with 15 wt% HNT. In migration studies, the release of CEO from the film was found to be faster in 50% ethanol (simulant for oil-in-water emulsions and alcoholic foods) than in 10% and 95% ethanol, which are stimulants of aqueous and fatty foods, respectively.

1. Introduction

As concerns for environmental issues and consumer demand have increased, biopolymers are being studied as food packaging materials since many years (Garavand, Rouhi, Razavi, Cacciotti, & Mohammadi, 2017; Peelman et al., 2013; Siripatrawan & Vitchayakitti, 2016; Wang, Qian, & Ding, 2018). Chitosan, which is composed of β-1,4-linked glucosamine and N-acetylglucosamine, is the second most abundant polysaccharide following cellulose. It is considered one of the ideal biopolymers for use in food packaging, owing to its non-toxicity, biodegradability, biocompatibility, and good film-forming ability. Interestingly, the intrinsic antimicrobial property of chitosan, owing to its positively charged amino group, has been proven in many previous studies (Kong, Chen, Xing, & Park, 2010). However, the intrinsic antimicrobial property of chitosan film has exhibited only in aqueous media. Moreover, chitosan-based films have poor moisture barrier properties because of their hydrophilic nature, although they are widely known to have excellent oxygen barrier properties (Ojagh, Rezaei, Razavi, & Hosseini, 2010). One strategy to overcome these limitations is to incorporate essential oils and inorganic materials including nanoclay and zinc oxide as additives into chitosan-based films (Bajpai, Chand, & Chaurasia, 2010; Casariego et al., 2009).

Recently, the food industry has focused increased attention toward the application of natural additives in food packaging systems owing to consumer concerns over the chemical residues in/on food. Essential oils, which have antimicrobial and antioxidant activities, are outstanding alternatives to chemical preservatives. Among the various essential oils, clove essential oil (CEO) has proven to be the most effective against microorganisms with strong antioxidant activity (Holley & Patel, 2005; Shiratsuchi, Chang, Wei, El-Ghorab, & Shibamoto, 2012). Therefore, a large number of studies have focused on the incorporation of essential oils including CEO into biopolymers such as chitosan, cellulose, alginate, and whey protein for food packaging (Bahram et al., 2014; Benavides, Villalobos-Carvajal, & Reyes, 2012; Dashipour et al., 2015; Ojagh et al., 2010). However, these biopolymer films require surfactants to disperse the essential oils evenly in the polymer matrix, because essential oils are volatile hydrophobic liquids. Thus, it is important to disperse and stabilize the essential oil in a hydrophilic biopolymer matrix as well as to control the release rate of the essential oil from the polymer matrix for the desired duration of action.

Halloysite nanotube (HNT), $Al_2Si_2O_5(OH)_4.nH_2O$, belongs to a subgroup of kaolin clay, which is generally recognized as a safe (GRAS)

* Corresponding author.
E-mail address: hjpark@korea.ac.kr (H.J. Park).
[1] Min Hyeock Lee and Seong Yeon Kim contribute equally to this work.

https://doi.org/10.1016/j.foodhyd.2018.05.048
Received 3 April 2018; Received in revised form 23 May 2018; Accepted 26 May 2018
Available online 28 May 2018
0268-005X/ © 2018 Published by Elsevier Ltd.

food packaging material by the U.S. Food and Drug Administration owing to its non-toxicity, biocompatibility, and environmental friendliness (Lee & Park, 2015). Unlike other clay minerals belonging to the kaolin group, HNT has a unique hollow tubular structure, making it possible to encapsulate active agents into its lumen (Abdullayev, Price, Shchukin, & Lvov, 2009; Lee, Seo, & Park, 2017). In addition, HNT has been studied as a nanomaterial for developing nanocomposites (Gorrasi, Pantani, Murariu, & Dubois, 2014). One of the advantages of using HNT in nanocomposite films is that HNT could be easily exfoliated because of its structure with a high aspect ratio, whereas kaolinite requires prolonged processing to be exfoliated, owing to its stacked platy shape (Abdullayev, Joshi, Wei, Zhao, & Lvov, 2012). As nanoclay minerals are added and exfoliated in the polymer matrix, they form tortuous pathways for vapor and gas molecules to pass through, resulting in enhanced barrier properties of the polymer. Further, some researchers have demonstrated that the mechanical property of a polymer could be improved by adding nanoclay including HNT into its matrix (Benucci et al., 2018; Liu, Zhang, Wu, Xiong, & Zhou, 2012; Prashantha, Lecouvet, Sclavons, Lacrampe, & Krawczak, 2013). Moreover, some clay minerals have been studied as water purification materials, owing to their adsorption property. In particular, HNT has been shown to have a higher adsorption property than montmorillonite (MMT), which results in a slower release rate of active agents from HNT than from MMT (Zhong et al., 2017). Furthermore, HNT has been studied as a solid particle to stabilize oil-in-water systems by the formation of a Pickering emulsion and has been used for oil spill remediation owing to its large aspect ratio and high surface area-to -volume ratio (De Silva, Pasbakhsh, Goh, Chai, & Ismail, 2013; Kpogbemabou et al., 2014; Nyankson, Olasehinde, John, & Gupta, 2015). The oil droplet was stabilized by clay minerals like HNT without any surfactant.

Although the functional effect of essential oil and the barrier effect of nanoclay on biopolymer-based films have been investigated in many previous studies, there are few studies regarding the effect of nanoclay minerals on the film properties incorporated with essential oil. Therefore, the aim of this study is to develop chitosan films incorporated with CEO and HNTs and to characterize the chitosan-based nanocomposite films. In this study, use of a surfactant was not necessary to facilitate the dispersion of CEO into the chitosan film. Instead, the HNTs were dispersed as solid particles in the chitosan films to stabilize the oil droplet. The effect of HNT concentration on the physical properties including water vapor permeability (WVP), moisture contents, water absorption, solubility and contact angle, morphological property, optical property, and mechanical property of the film was determined. The antioxidant activity of the film was determined via total phenolic content, 2,2-diphenyl-1-picrylhydrazyl, and reducing power assays. In addition, the release of CEO from the film into three standard food simulants was investigated.

2. Materials and methods

2.1. Materials

Chitosan from shrimp shell (medium molecular weight, 190–310 kDa) with a degree of deacetylation of approximately 75% and HNTs with a specific gravity of 2.53 g/cm^2 were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). CEO used in this study was acquired from Hanbit Flavor & Fragrance Co., Ltd. (Eumseong-gun, Republic of Korea). Glycerol used as a plasticizer was obtained from Junsei Chemical Co. (Tokyo, Japan). Folin and Ciocalteu's phenol reagent and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were obtained from Sigma-Aldrich Co. Potassium ferricyanide, trichloroacetic acid, and ferric chloride were purchased from Duksan Pure Chemical Co. (Ansan, Republic of Korea). All other chemicals used in this study were of analytical grade and used as received without further purification.

2.2. Sample preparation

2.2.1. Preparation of Ch/CEO/HNT solutions

Chitosan powder (10 g) was dissolved in 1000 mL of aqueous acetic acid solution (1% v/v) to obtain 1% w/v chitosan solution under overnight magnetic stirring at room temperature. Then, the solution was filtered to remove impurities. To enable film formation, glycerol was added at a concentration of 0.40 mL/g chitosan as a plasticizer. To prepare nanocomposite dispersions, selected amounts of HNT (0, 5, 10, 15, 20, 25, and 30 wt% with respect to solid chitosan) were dispersed in the chitosan solution by vigorously stirring overnight. Afterward, 0.5 mL of CEO was dropped slowly into 50 mL of Ch/HNT dispersion with mild stirring. The Ch/HNT dispersions with/without CEO were homogenized using an ultrasonic homogenizer (VCX 750 apparatus, Sonics & Materials, Newtown, CT) for 10 min with 30% vibration amplitude in an ice bath (3 ± 1 °C). The resulting film-forming solutions were degassed under vacuum for 20 min to completely remove the bubbles.

2.2.2. Preparation of the nanocomposite films

The Ch/HNT dispersions with and without CEO (50 mL) were cast in the center of glass Petri dishes with 90 mm inner diameter and dried for 96 h under ambient conditions (T = 25 °C and RH = 50 ± 2%). The obtained films were then peeled and stored at 25 °C and 50% relative humidity until evaluation.

2.3. Physical properties of the films

2.3.1. Thickness

The thickness of every film formulation was determined using a hand-held micrometer (Dial thickness gauge No. 7301, Mitutoyo Co. Ltd., Tokyo, Japan) with 0.01-mm accuracy. Measurements were carried out at five different locations on each film. The mean thickness was used to calculate the water vapor permeability and mechanical properties of the samples.

2.3.2. Water vapor permeability

The water vapor permeability (WVP) of the film samples was determined by a gravimetric cup method based on the ASTM E96-95 standard (E. ASTM, 1995) with some modifications. In brief, test cups, with 46 mm internal diameter (exposed area: 16.62 cm^2) and a depth of 21 mm, were filled with silica gel (0% RH) and completely covered by the film samples without pinholes. An O-ring was used to ensure no leakage. The cups were weighted and placed in a thermos-hygrostat (TH-G, Jeio Tech, Daejeon, Republic of Korea) at 25 °C, 50% RH. Subsequently, the cups were weighted every 1 h to determine the water vapor transmission rate (WVTR) and transmission coefficient. The WVTR is defined as the slope (g/s) divided by the effective area (m^2) and WVP (g/m·s·Pa) is calculated as follows:

$$WVP = \frac{WVTR \times d}{\Delta p}$$

where, d (m) is the average film thickness and Δp (Pa) is the water vapor pressure difference between the two sides of the film, respectively. Five replications were conducted for each film formulation.

2.3.3. Moisture content

Moisture content of the films was determined by drying the film sample at 110 °C until the weight is constant and then calculating the difference.

2.3.4. Water absorption and solubility

The water absorption and water solubility of the films was determined gravimetrically (Casariego et al., 2009; Peng & Li, 2014). In brief, every film sample (20 mm × 20 mm) was dried in an oven at 105 °C until a constant weight was obtained. Each dried film sample

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