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Prolonged preservation of tangerine fruits using chitosan/montmorillonite composite coating

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ABSTRACT

Chitosan (CS) and chitosan/montmorillonite (CS/MMT) coatings have been applied on fresh tangerine fruits to compare their preservation effects. After coating, fruits were stored with the untreated (CK) and prochloraz treated group (PC) at 10 °C for 11 d to evaluate their quality, as well as the changes of coating structures. The free-standing films of CS and CS/MMT were also prepared and characterized. Results showed that CS coating inhibited the decay rate of fruits only at the first 5 d of storage, followed by a rapid increase. Notably, fruits coated by CS/MMT coating containing 1% (w/w) MMT (CS/MMT-1) presented lower decay rate and weight loss, higher contents of total soluble solids (TSS) and titratable acidity (TA) compared to other groups during the whole storage. At day 11, the decay rate of CS/MMT-1 was only 28.3%, which was 5.8% lower than that of CK. Moreover, micro-pores in coatings were observed during storage, which appeared much later in CS/MMT-1 coatings than in CS. For the free-standing films, addition of 1% (w/w) MMT was able to enhance the oxygen barrier properties of CS films, which further supported the good structural stability of CS/MMT films. These results demonstrated that CS/MMT coating with enhanced stability provided longer shelf life for tangerine fruits.

1. Introduction

With delicious taste and high nutritional value, citrus is one of the most popular fruits in the world (Nekvapil et al., 2018). Since 1990s, China has a rapidly increased annual production of citrus making it the largest citrus producing country around the world. However, the great production has brought great pressure to citrus storage, since more than 95% of the citrus fruits produced in China are consumed as fresh fruits (Qi, 2014).

Citrus fruits are vulnerable to micro-organism infections, physiological disorders and physical injuries, resulting in huge loss of fresh fruits every year. So far, chemical fungicides are widely used in developed countries to control the plant diseases and eliminate pests, which brings potential health and environmental issues (Palou et al., 2015). Therefore, postharvest approaches including modified atmosphere packaging (MAP) (Li et al., 2013), hot water or air treatment (Spadoni et al., 2014), application of biocontrol agents (Yao and Tian, 2005), wax coating (Duan et al., 2017), etc., have been widely studied in recent years to extend the shelf life of citrus fruits. Among them, application of edible coating is emerging as an attractive approach with good safety and satisfying performance (Arnon et al., 2015; Galus and Kadzińska, 2015; Silva-Weiss et al., 2013). Biopolymers with good biocompatiblity and biodegradablity are considered as good candidates of coating materials.

Chitosan is a natural polysaccharide with excellent film forming properties, high mechanical strength and strong antimicrobial activities (Hosseinnejad and Jafari, 2016). Chitosan coating formed on the fruit surface are able to block the stomata and lenticels of the epidermis, leading to the reduced water loss, inhibited respiration, and increased nutrient content of the fruits. Therefore, satisfying preservation performance of chitosan coating have been found on kiwi (Kaya et al., 2016), pear (Deng et al., 2017), sweet cheery (Petriccione et al., 2015), etc. However, chitosan is sensitive to water due to their hydrophilic nature, which considerably limit its effectiveness in controlling moisture transfer and maintaining the integrate structure. As a result, there have been many attempts to improve the barrier properties and stability of chitosan-based coatings. Nano-materials such as montmorillonite (MMT) (Pinto et al., 2015), nano-silica (Shi et al., 2013), nano-silver (Shah et al., 2015) and nano-TiO_2 (Lin et al., 2015) have been intensively used as nano-fillers of polymer coatings to enhance their strength, barrier properties thus further improving the preservative performances. MMT as an inorganic nano-material composed of layered silicates, is well known for its low cost, high cation exchange capacity, good dispersibility in aqueous medium, and excellent barrier properties (Meri et al., 2015). Moreover, the comparably low toxicity of MMT making it a kind of promising nanofiller to be widely used in food,

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medicine, chemical industry (Peng et al., 2017; Ma et al., 2017; Luo et al., 2009), etc. Although in vitro toxicity have been generally revealed by numerous studies, low systemic toxicity were found in human and animals according to the in vivo toxicological studies (Maisanaba et al., 2015). It was shown that pristine MMT could be absorbed by mice soon after oral administration with a dose as high as 1000 mg mL^{-1}, leaving no significant accumulations in organs (Baek et al., 2012). Researches have confirmed good dispersion of MMT in chitosan via the intercalation of cationic polymer chains into MMT interlayers, which provides the resulting nanocomposites with enhanced mechanical and barrier properties (Darder et al., 2003). Therefore, in this study, MMT was incorporated into chitosan coating with different content to investigate their effects on tangerine fruits preservation, compared with those of neat chitosan coating and commercial fresh-keeping agent treatment. The morphologies of fruits peels and coatings were also monitored during storage. Furthermore, the free-standing films of chitosan and chitosan/MMT were prepared and characterized to explore the effects of MMT on the properties of chitosan films.

2. Materials and methods

2.1. Materials

Tangerine fruits (C. *tangerine* Hort. ex Tanaka) were harvested from a local orchard in Chongqing, China in January. Chitosan with a degree of deacetylation of 90% and molecular weight of 1.8×10^5 was provided by Weifang Haizhiyuan Biological Products Co., Ltd. (Shandong, China). Sodium MMT was purchased from Southern Clay Products Inc. (USA). Acetic acid and NaClO of analytical grade were provided by Chengdu Kelong Chemical Co., Ltd. (Chengdu, China). Commercial fresh-keeping agent containing 25% (w/w) prochloraz was manufactured by Chongqing Shuangfeng Chemical Co., Ltd. (Chongqing, China). Other regents were of analytical grade and were used as received.

2.2. Coating of tangerine fruits

2.2.1. Preparation of coating solutions

Certain amount of chitosan flakes was dissolved in 1% (v/v) acetic acid and stirred for 24 h to prepare chitosan coating solution with a concentration of 1.5% (w/w). Three CS/MMT composite coating solutions were prepared by adding certain amount of MMT (0.5, 1 and 2% based on the weight of chitosan) into the prepared 1.5% (w/v) chitosan solution. After ultrasonic treatment for 30 min, the mixtures were stirred for at least 20 h at room temperature until homogeneous solution was obtained.

2.2.2. Coating of fruits

Tangerine fruits were delivered to the laboratory on the day of harvest. Uniform fruits without diseases and damages were selected out for use. After cleaned by 100 mg L^{-1} NaClO aqueous solution and dried in air, fruits were randomly divided into six groups with 120 fruits each. The first group was untreated set as control (CK), while fruits in the second group were immersed in a diluted solution of commercial fresh-keeping agent containing 1.25% (w/w) prochloraz for 2–3 min and were dried under ambient conditions, which was designated as PC. Other four groups were immersed into the prepared neat chitosan coating solution and three chitosan/MMT solutions for 2–3 min, which were subsequently dried under ambient conditions. Groups coated by neat chitosan and chitosan/MMT solution containing 0.5, 1 and 2% (w/w) MMT were designated as CS, CS/MMT-0.5, CS/MMT-1 and CS/MMT-2, respectively. Each fruit of the above six groups was packaged separately in a PE bag right after the treatment and stored at ambient conditions with a temperature around 10 °C and a relative humidity around 70%.

2.3. Evaluation of fruit quality

2.3.1. Weight loss

All the fruits were taken out to weigh and were returned back immediately over a certain time interval during storage. The weight loss during storage relative to the initial weight before storage was calculated and presented as percentage.

2.3.2. Ascorbic acid (AA) content

Contents of ascorbic acid in fruit juice were determined using 2, 6-dichlorophenolindophenol (DCPIP) titration method (Saba and Sogvar, 2016). Ten-milliliter aliquots of juice, extracted from five fruits randomly picked from one group, were diluted to 100 mL by 20 g L^{-1} oxalic acid solution. Subsequently, 10 mL of the supernatant were taken out and were titrated by 0.1 g L^{-1} DCPIP solution to a permanent pink color. AA content was calculated and expressed in mg of AA per 1 kg juice (mg kg^{-1}).

2.3.3. Total soluble solids (TSS) content

TSS in the juice was determined by an Abbe Refractometer (2WAJ, Shanghai Optical Instrument Co., Ltd, China) and expressed as percentage.

2.3.4. Titratable acidity (TA) content

Ten-milliliter aliquots of juice, extracted from five fruits randomly picked from one group by boiling water, were diluted to 100 mL using de-ionized (DI) water. Afterwards, 10 mL supernatant was titrated using 1 mol L^{-1} NaOH solution to a permanent pink color. TA contents (mol L^{-1}) was calculated using Eq. (1).

$$\text{TA content (mol L}^{-1}) = (V_{NaOH} \times N \times K)/V_{juice} \quad (1)$$

where N is the molar concentration of NaOH solution (mol L^{-1}); V_{NaOH} is the volume of NaOH solution consumed during titration (L); V_{juice} is the volume of juice sample used for titration (L); K is the milli-equivalent factor of citric acid, which is 0.064.

2.3.5. The internal CO_2 concentrations

Internal CO_2 concentrations were analyzed using an oxygen analyzer (PAC CHECK Model 650EC, Mocon Inc. of USA). The probe was carefully inserted into the blossom end of fruits avoiding contact with the segments. The mean values were calculated from the results obtained from at least five fruits randomly picked per group, and were presented as percentages.

2.3.6. The accumulated decay rate

Accumulated decay rate was calculated as the percentages of the accumulated decayed fruits to the initial total number of each group.

2.4. Morphologies of fruits peels and coatings

Peels with and without coatings were carefully cut off from the fruits and were freeze-dried overnight. After fruit peels were fixed with the outer layer on the top and were sputter-coated with platinum, the surfaces morphologies were observed using a scanning electron microscope (SEM, JEM-2100, JEOL, Japan).

2.5. Preparation of free-standing films

The neat CS solution and CS/MMT composite solutions with the same content of MMT were prepared using the same procedure given in Section 2.2. The free-standing films were then prepared by solvent evaporation according to the method described in our previous study (Zhou et al., 2016). The homogenous solutions were poured into Petri dishes, followed by drying at 40 °C to fully evaporate the solvent. The obtained films were soaked in 1 mol L^{-1} NaOH solution for 20 min and