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Performance of carnauba wax-nanoclay emulsion coatings on postharvest quality of 'Valencia' orange fruit

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ABSTRACT

For the first time, efficiency of the carnauba wax-nanoclay emulsions in preserving postharvest quality of 'Valencia' fruit was evaluated upon simulated storage and marketing. The different coatings containing nanoclay (i.e., 0.0, 0.5 and 1.0 w%) applied on orange and their performance were compared with uncoated fruit and two different commercial waxes. In general, the presence of nanoclay in the carnauba wax formulation greatly enhanced fruit sensory acceptability, nutritional quality and effectively prevented fruit weight loss during storage. Moreover, according to several statistical analyses such as cluster analysis, PCoA and Heat map-based surveys, the carnauba wax-nanoclay emulsions possessed similar behaviors with the maximum efficiency and placed accordingly in the same cluster, while the other four treatments were lonely occupied the next positions. Such nano-formulations could propose as a promising and cost-effective alternative avenue for commercial fruit waxes, towards sustainable postharvest management in retarding respiration rates and weight loss alongside preserving sensory and nutritional quality of fruits.

1. Introduction

In order to preserve the quality of stored fruit crops, the method called "coating-based treatment" has been currently regarded as a reliable and common post-harvest technique, which is mainly attributed to its key roles either in prohibition of postharvest transpiration or slowing down of respiration rate (Khalifa et al., 2016; Tesfay et al., 2017). As regards citrus industry, the utilization of various fruit coating materials is a normal activity, particularly since the method can impede fruit shrinkage and weight loss followed by providing shine, appearance improvement, and subsequently fruit marketability over postharvest storage (Contreras-Oliva et al., 2011; Shi et al., 2005; Contreras-Oliva et al., 2012). Irrespective of such remarkable advantages, several studies reported that citrus coating strategies may practically induce some inevitable physiological changes in the fruit, leading eventually to a significant amelioration in undesirable flavors referred to as "off-flavor". In fact, restricted gas exchange via the surface of peel can frequently result in overproduction of volatile compounds contributed to the anaerobic circumstances in the internal atmospheres of fruit and flavor changes, as well (Petracek et al., 1998; Seehanam et al., 2010; Hagenmaier, 2002; Hagenmaier and Shaw, 1992; Baldwin et al., 1995). Moreover, the coatings performance to extend the fruit shelf life intrinsically linked to physiology of the fruit as well as chemical composition of coatings, structure and thickness of the polymeric film formed on the fruit, and production process (Puttalingamma, 2014; Khorram et al., 2017). Along with the contemporary used commercial synthetic waxes which mainly composed of oxidized polyethylene, nowadays, there has been an increasing shift towards development of natural polysaccharide-, protein- and/or lipid-based edible fruit coatings. Carnauba wax, beeswax, candelilla wax, paraffin wax, mineral oil, and various vegetable oils are assumed as the most common lipid components of commercial fruit coating formulations (Oregel-Zamudio et al., 2017). In addition, each coating composition commonly contains several minor ingredients including emulsifiers, plasticizers, surface active agents, antioxidants, and antimicrobial agents to improve functional properties of coating (Njombolwana et al., 2013; du Plooy et al., 2009; Guerreiro et al., 2015; Valencia-Chamorro et al., 2011). Some of these supplements aid in structural features of coating compositions, for

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example in making stable emulsions, improving surface tension properties, film integrity or coating plasticity (Rojas-Argudo et al., 2009). The others, nonetheless, affect functional features of coatings including controlling barrier and permeability alongside ability of fruit protection against postharvest physiological disorders (Njombolwana et al., 2013; Navarro-Tarazaga et al., 2008; Contreras-Oliva et al., 2012).

On the other hand, the addition of modified clay with an alkylammonium salt surfactant (i.e., nanoclay) to polymer/wax matrixes has been utilized widely, as an active research area over recent years (Pu and Severtson, 2013; Ray and Okamoto, 2003). Comparing to the pristine polymer or the composites possessing traditional additives, the presence of nanoclay in polymeric/wax nanocomposites (even in low quantities) resulted in various outstanding features including a great increment in heat distortion temperature (also known as heat deflection temperature; HDT), optical clarity, dimensional stability, flame retardancy, improved mechanical characteristics, and lastly gas barrier performance (Durmus et al., 2007). Significant enhancements either in barrier or mechanical features of nanoclays composites are actually taken place through fully exfoliation of clay plates into polymers. For this reason, the clay surface must be primarily modified, predominantly to make it well-suited with polymers and waxes which are hydrophobe. In this context, a high-molecular-weight quaternary amine is adsorbed in the basal platelets surface of the clay which have negative charge through an ion-exchange reaction (Chaiko and Leyva, 2005). Such nanoclay wax nanocomposites exhibit superior barrier properties, actually due to the exfoliation of clay plates resulted from their great aspect ratio, imparting a tortuous path which retards the transport of diffusing gases where extend their potential implications to develop high-performance, and cost-effective barrier coatings (Wang et al., 2006).

Carnauba, also known as palm wax or Brazil wax, is usually extracted from the palm (*Copernicia prunifera*) leaves and utilized widely in commercial fruit coating compositions to reduce weight loss, prolong shelf life and enhance fruit gloss (Puttalingamma, 2014; Hagenmaier et al., 1991). However, as mentioned above, mechanical and barrier properties of these emulsion coatings are dependent upon physical and chemical characteristics of constituents thereof. Accordingly, this study was mainly aimed to synthesize carnauba-based wax emulsions as citrus coatings with incorporation of various amounts of nanoclay, actually to practically improve fruit coating performance over storage. The current synthesized formulations were initially validated via various characterization procedures, applied then on "*Valencia*" oranges (*Citrus sinensis* L. Osbeck), and subsequently effectiveness thereof were compared with the two additional commercial waxes and uncoated fruits as control. To the best of our knowledge, this report is the first one focusing on the evaluation of nanoclay effects on the carnauba wax emulsion formulations to barricade respiration rates and weight loss along with preserving sensory and nutritional quality of citrus throughout the storage.

2. Materials and methods

2.1. Materials

Refined carnauba wax flakes, beeswax and food grade oleic acid were purchased from Pasargad Novin Co. The nanocly (d001 = 32 A, manufactured via the Na-Bentonite modification using a dimethyl, dihydrogenated tallow, quaternary ammonium) was kindly supplied by NanoSav Co. The following two commercial waxes known as "Commercial wax 1" (purchased from Pushesh hayatesabz Co.) and "Commercial wax 2" (from Decco Co.) kindly provided by Darab farmers who normally utilize this product in wax treatment of 'Valencia' oranges in that region. Ammonia solution (30%), diphenyl-2-picryl hydrazyl (DPPH) and other chemicals/reagents were of analytical grade and purchased from Sigma–Aldrich.

Table 1
Different wax formulations for 'Valencia' citrus coating.

Treatments	Coating conditions	Solid content of coating
T1	Synthesized carnauba wax emulsion without organoclay	16.8%
T2	Synthesized organoclay (0.5 w%) carnauba wax emulsion	16.8%
T3	Synthesized organoclay (1 w%) carnauba wax emulsion	16.8%
T4	Commercial wax 1	17.1%
T5	Commercial wax 2	17.6%
T6	Uncoated (control)	–

2.2. Preparation of coatings

Emulsion coatings were prepared using a modified water-to-wax method (Hagenmaier, 1998), where the mixture of carnauba wax and beeswax (20 g), along with oleic acid as emulsifier and nanoclay were heated in an oil bath to the melting point of the waxes. Then, 3.0 g ammonia solution (30%) was gradually added to the resultant melted mixture. The stirring continued for 30 min at 90 °C, in conjunction with the addition of 20 mL of hot deionized water (100 °C). Notably, to avoid a sudden increase in temperature, make foam and loss of materials, the water addition process was controlled in a careful manner. The resultant mixture, was stirred for another 60 min, and further diluted to approximately 150 mL with hot water, as the mixture color changed from brownish viscose syrup to creamy emulsion. Subsequent to performing some pretests, the best ratios for carnauba wax-beeswax (4:1), waxes-oleic acid (5:1) were selected to prepare stable emulsions which make thin gloss coatings after drying. Table 1 summarized the wax formulations employed for 'Valencia' citrus coating; Briefly, the efficiency of three synthesized formulations with different amounts of nanoclay were compared and contrasted with two commercial waxes typically applied for coating the citrus in Iran (Table 1).

Higher amounts of nanoclay in the formulations disturbed the stability of emulsions and caused to macroscopic phase separation which may be due to the immiscibility and incompatibility of the wax and water phases in the presence of higher dosage of nano-filler.

Since solid content of wax coatings have been proven to affect efficiency of such coatings on postharvest life of fruit (Perez-Gago et al., 2005; Baker and Hagenmaier, 1997), in the present work the solid contents of synthesized wax emulsions were adjusted to be close to the commercial waxes in order to their dried film thickness and so their performance being comparable (Cisneros-Zevallos and Krochta, 2003). The solid contents of wax emulsions were determined as follows (Zhu et al., 2018) and the results were presented in Table 1:

$$\text{Solid }\% = [W_f/W_s] * 100$$

where W_f and W_s are the weights of dried wax emulsion and as-prepared/as-received wax emulsions, respectively.

2.3. Fruit preparation, coating application and storage conditions

Fruit used in this study were 'Valencia' oranges (*C. sinensis*) which were harvested in May 2016, from a local grove in Darab, Fars Province, Iran. Then the fruit were immediately transported to the research laboratory of Department of Horticulture, College of Agricultural and Natural Resources, University of Tehran, Karaj. Before any coating treatment, the fruits were selected for size, uniformity, color and absence of physical damage. Then the selected 'Valencia' oranges washed with tap water, and dried at room temperature. In the following, a total of 126 'Valencia' fruit were divided into six sets of 21 fruits each. The six coating treatments were assigned as follows (Table 1): Three groups were individually treated with the three synthesized coating composites