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Development of polysaccharides-based edible coatings for citrus fruits: A layer-by-layer approach

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ABSTRACT

Biodegradable coatings for citrus fruits that would replace the currently used polyethylene-based waxes, are of great interest. Methylcellulose (MC), hydroxypropyl methylcellulose (HPMC), carboxymethyl cellulose (CMC) and chitosan (CH) coatings were examined on the most sensitive citrus fruit model: mandarins. Among the examined polysaccharides, CMC provided mandarins with the best firmness, lowest weight loss and satisfying gloss, while not affecting natural flavour and the respiration process. To enhance coating performance, glycerol, oleic acid and stearic acid were added; however, mandarin quality generally deteriorated with these additives. Then, a layer-by-layer (LBL) approach was applied. LbL coatings, based on a combination of two polysaccharides, CMC as an internal layer and chitosan as an external layer, gave the best performance. Different concentrations of chitosan were examined. The LbL coatings notably improved all quantified parameters of fruit quality, proving that polysaccharide-based edible coating may offer an alternative to synthetic waxes.

1. Introduction

Citrus fruits enjoy great popularity all over the world, due to their taste, beneficial nutrients, and widespread availability (Liu, Heying, & Tanumihardjo, 2012). After harvest, citrus fruits are prone to physiological and microbiological decay. A successful approach to prolonging their storage lifetimes has involved the application of a transparent, uniform coating layer on the surface of the fruit peel (Hagenmaier & Baker, 1995). The coating decreases water loss and shrinkage and improves the external appearance of the fruit by providing gloss (Petracek, Hagenmaier, & Dou, 1999). Today most of the commercially harvested citrus fruits undergo such a coating (waxing) process in packing houses. The applied commercial coatings are usually based on oxidised polyethylene, organic solvents and different surfactants and stabilizers (Porat, Weiss, Cohen, Daus, & Biton, 2005). Presently, greater public awareness and international regulations have emphasised the application of materials that show health benefits and are environmentally friendly, especially in applications involving food products. This has resulted in calls for research to develop alternative materials for the coating of citrus fruits (Dhall, 2013).

Edible coatings have proved themselves promising for extending the shelf-life of various agricultural products (Baldwin, Hagenmaier, & Bai, 2011; Park, 1999). They were shown to protect products from mechanical and microbial damage, to provide an aesthetic appearance, and to prevent the escape of favourable volatiles. Edible coatings are based on biodegradable and edible materials from natural sources and they therefore satisfy environmental concerns and respond to customer demands (Pavlath & Orts, 2009). Most of the studies which have investigated the application of edible coatings on citrus fruits have utilised lipid-containing composites. Lipid-based coatings benefit from an excellent water barrier features and therefore inhibit the coated products' water loss (Dhall, 2013). However, lipid-based coatings are also less permeable to gases and therefore may encourage accumulation of CO_2 and ethanol, causing the development of off-flavours (Baldwin, Nisperos carriedo, Shaw, & Burns, 1995; Hagenmaier, 2002; Hagenmaier & Shaw, 1992). Being relatively fragile, lipid-based coatings are often supported by auxiliary components, such as polysaccharides, that provide mechanical strength (Contreras-Oliva, Rojas-Argudo, & Perez-Gago, 2012; Valencia-Chamorro, Perez-Gago, Del Rio, & Palou, 2009). Composite coatings of natural waxes with hydroxypropyl methylcellulose (HPMC) were widely studied with regard to improving the storability and quality of

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citrus fruits (Navarro-Tarazaga, Del Rio, Krochta, & Perez-Gago, 2008; Perez-Gago, Rojas, & Del Rio, 2002; Valencia-Chamorro, Palou, Del Rio, & Perez-Gago, 2011; Valencia-Chamorro, Perez-Gago, Del Rio, & Palou, 2010). However, it was reported that lipids containing edible coatings may damage the appearance and gloss of the coated products (Perez-Gago et al., 2002; Valencia-Chamorro et al., 2010). Polysaccharide coatings of citrus fruit that have no lipid components are scarcely studied. To the best of our knowledge there are only three related reports. One report studied the effect of sucrose-based coatings on antioxidant enzymes in mandarins, (Tao, Ao, Liu, & Huang, 2012) and two reports studied the antimicrobial effect of chitosan on citrus fruits (Chien & Chou, 2006; Chien, Sheu, & Lin, 2007). The effect of polysaccharide only-based coatings on physiological features of citrus fruits is practically unexplored.

Polysaccharide-based coatings have many advantages: they are low-cost, biodegradable, and water-soluble; hence they do not require organic solvents prior to, or during application (Debeaufort, Quezada-Gallo, & Voilley, 1998). In addition, polysaccharides have well defined chemical structures that allow for the tuning of their coating properties. For instance, cellulose is the most abundant natural polysaccharide that can be easily modified to produce a wide variety of cellulose derivatives with variable properties (Pavlath & Orts, 2009). An additional polysaccharide of interest is chitosan, a de-acetylated form of chitin, which possesses intrinsic antimicrobial activity and is widely used in food research and applications (Elsabee & Abdou, 2013). Being a cationic polyelectrolyte, chitosan can be utilised in layer-by-layer (LbL) rationally designed edible coatings.

The layer-by-layer (LbL) electrostatic deposition technique originated in materials science and has a wide range of applications (Decher, 1997). The approach is based on the alternate deposition of oppositely charged polyelectrolytes, and aims at an efficient control of material properties and functionality. Recently in our laboratory, layer-by-layer edible coatings, based on alginate and chitosan, were applied and found to significantly enhance physiological and microbial quality of fresh-cut melons with no addition of active agents (Poverenov et al., 2014). Multilayered edible coatings, made of chitosan and pectin, were reported to extend the shelf life of fresh-cut papaya (Brasil, Gomes, Puerta-Gomez, Castell-Perez, & Moreira, 2012).

In this work, we performed a series of systematic experiments with the aim of finding polysaccharide-based edible coatings that convey: enhanced quality, improved storage times, and an attractive appearance onto citrus fruits and that, importantly, may provide a natural alternative to synthetic waxes. Polysaccharides (carboxymethyl cellulose (CMC), methyl cellulose (MC), hydroxypropyl methylcellulose (HPMC) and chitosan) were tested to find a primary component that would be used as the coating matrix. All of these polysaccharides are based on a β-(1 → 4)-D-glucopyranose backbone, but possess different substituents. CMC is polyanionic when dissolved in aqueous solution, due to its carboxylic substituent. Chitosan, on the other hand, is (overall) polycationic when dissolved in a slightly acidic aqueous solution, due to its protonated amine groups. Polyelectrolytes CMC and chitosan are more polar than are the neutral MC and HPMC which, in turn, are even slightly hydrophobic due to their alkyl chain substituents (Park, 1999). After selecting the optimal polysaccharide coating matrix, the effect of auxiliary additives on coating performance was examined. Finally, the layer-by-layer electrostatic deposition (LbL) method was applied to form bi-layered polysaccharide coatings. Among all citrus fruits, mandarins are the most prone to quality deterioration and off-flavours development (Shi, Porat, Goren, & Goldschmidt, 2005). Therefore, they were chosen as a sensitive model for citrus fruits.

2. Materials and methods

2.1. Plant material

‘Rishon’ and ‘Michal’ mandarins (*Citrus reticulata* Blanco) were harvested from a commercial citrus plantation in Nir Zvi, Israel. On the day of harvest, the fruits were transferred to the Department of Postharvest Science in the Volcani Institute, where they were cleaned by rinsing with tap water under a set of brush rollers, and dried by passing through a hot-air tunnel at 37 °C for ~1 min.

2.2. Experimental design

Four series of experiments were performed. In each experiment the mandarins coated by an edible coating were compared with the mandarins coated by a polyethylene based commercial wax (PE-CW) and with the uncoated fruits. The first experiment included four edible coating formulations: chitosan (1.5% w/v), MC (1% w/v), HPMC (1% w/v), CMC (1.5% w/v). The second experiment included four edible coating formulations of CMC (1.5% w/v) with 0%, 2%, 4% and 6% v/v of glycerol. The third experiment included five edible coating formulations of CMC (1.5% w/v), CMC (1.5% w/v) with 0.3% and 0.6% w/v of stearic acid, and CMC (1.5% w/v) with 0.3% and 0.6% v/v of oleic acid. The fourth experiment included five edible coating formulations of CMC (1.5% w/v), chitosan (1.5% w/v) and bi-layered formulations of CMC (1.5% w/v) as an inner layer with 0.5%, 1.0% and 1.5% w/v of chitosan as an external layer. In experiments 1–4, each treatment group included 25–30 mandarins kept in cardboard boxes. The mandarins were stored for 10 days at 20 °C and relative humidity (RH) of ~80–85% (shelf-life conditions).

2.3. Preparation of edible coating formulations

2.3.1. CMC coating

Carboxymethyl cellulose (CMC) sodium salt was purchased from BDH Limited Poole (England). CMC powder was dissolved in sterilized water upon stirring at 80 °C for 2 h to obtain a 1.5% (w/v) solution.

2.3.2. HPMC coating

Hydroxypropyl methylcellulose (HPMC) of 400 cPs viscosity was purchased from Alfa Aesar (Ward Hill, MA 01835 USA). HPMC powder was dissolved in sterilized water upon stirring at 80 °C for 4 h to obtain a 1.0% (w/v) solution.

2.3.3. MC coating

Methylcellulose (MC) of 400 cPs viscosity was purchased from Alfa Aesar (Ward Hill, MA 01835 USA). MC powder was dissolved in sterilized water upon stirring at 50–60 °C for 2 h to obtain a 1.0% (w/v) solution.

2.3.4. Chitosan (CH) coating

Medium molecular weight chitosan (200–800 cP) was purchased from Sigma–Aldrich (St Louis, MO, USA). Chitosan powder was dissolved in sterilized water that included 0.7% (v/v) of acetic acid upon stirring at room temperature to obtain 0.5%, 1.0% and 1.5% (w/v) solutions.

2.3.5. CMC-glycerol coatings

Glycerol (Bio Lab LTD, Jerusalem, Israel) at different concentrations of 2%, 4% and 6% (v/v) was added to 1.5% CMC solution that was prepared as described above and the homogeneous solutions were obtained upon vigorous stirring at room temperature.