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Nanoreinforced alginate–acerola puree coatings on acerola fruits

Henriette M.C. Azeredo [a,*], Kelvi W.E. Miranda [b], Hálisson L. Ribeiro [b], Morsyleide F. Rosa [a], Diego M. Nascimento [b]

[a] Embrapa Tropical Agroindustry, R. Dra. Sara Mesquita 2270, CEP 60511-110 Fortaleza, CE, Brazil
[b] Federal University of Ceara, Av. Mister Hull 2977, CEP 60356-000 Fortaleza, CE, Brazil

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ABSTRACT

Combinations of fruit purees with polysaccharides have been explored to produce edible films and coatings. In this study, the combination between acerola puree and alginate was reinforced with cellulose whiskers (CW) or montmorillonite (MMT) to form nanocomposite edible films (casted on glass plates) and edible coatings (applied on acerola fruit surfaces). Three film/coating dispersions were formulated, based on unfilled alginate–acerola puree (AA), CW-reinforced alginate–acerola puree (CWAA), and MMT-reinforced alginate–acerola puree (MMTAA). Both nanofillers (CW and MMT) reduced water vapor permeability (WVP) of films. When applied to fresh acerolas, the coatings decreased fruit weight loss, decay incidence, and ripening rates. Ascorbic acid retention by the fruits were favored by the coatings, especially the nanocomposite ones. The MMTAA coating was the most effective in reducing weight loss of acerolas. Moreover, it was the coating which best maintained its red color and the visual acceptance of coated acerolas.

1. Introduction

Difficulties in disposing of the huge waste volumes generated by non-biodegradable food packaging have motivated the study of biopolymers as materials to be used as edible coatings in food packaging. Edible coatings are not supposed to completely replace conventional food packaging, but they can help the packaging in the function of food preservation.

Important functionalities of edible coatings for fresh fruits include: moderate oxygen permeability, modifying the internal atmosphere of fruits, delaying senescence (Rojas-Graü et al., 2009); low water vapor permeability, preventing desiccation and maintaining fruit firmness (Ayranci and Tunc, 2004; Del-Valle et al., 2005; Han et al., 2004); mechanical protection, reducing injury effects; and sensory appeal.

Film forming properties of alginate are related to its ability to form strong gels or insoluble polymers in the presence of multivalent metal cations like Ca^{2+} (Mancini and McHugh, 2000; Rhim, 2004). The gelling mechanism involves interactions between Ca^{2+} and carboxylic groups of alginate, forming a three-dimensional cross-linked network (Oms-Oliu et al., 2008). Alginate coatings, as other polysaccharide-based coatings, are expected to present low oxygen permeabilities due to their ordered hydrogen-bonded network structure. On the other hand, polysaccharides coatings are not good moisture barriers because of their hydrophilic nature (Nisperos-Carriedo, 1994; Yang and Paulson, 2000). Indeed, the main effect of polysaccharide-based coatings on shelf-life of fruits is that of reducing respiration rates due to selective permeabilities to O_2 and CO_2 (Nisperos-Carriedo, 1994; Maqbool et al., 2011).

Acerola is a red fruit whose demand has increased in the last decades, thanks to its high ascorbic acid (Johnson, 2003). However, because of the short postharvest shelf life of the fresh fruit, it is mainly commercialized as puree. Some studies have described the production of edible films (Azeredo et al., 2009; Rojas-Graü et al., 2006, 2007; Senesi and McHugh, 2002) and coatings (Sothornvit and Rodsamran, 2008) from fruit purees, combined or not with polysaccharides. The presence of polysaccharides such as pectin and starch in fruit purees is responsible for their film forming ability (Kaya and Maskan, 2003). The development of films and coatings from fruit purees is an interesting way of combining the mechanical and barrier properties provided by those polysaccharides with the sensory and nutritional properties of the fruit. The high polarity of fruit puree based coatings make them relatively good barriers to O_2, but poor barriers to water vapor.

Mechanical and water vapor barrier properties of biopolymer films can be improved by adding nanoreinforcements, such as cellulose whiskers (Azizi Samir et al., 2005; Saxena and Ragauskas, 2009) or layered silicates (Cyras et al., 2008; Kampeerapappun et al., 2007). In some previous studies, cellulose nanoreinforcements have demonstrated to improve water vapor barrier and

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* Corresponding author. Tel.: +55 85 3391 7236; fax: +55 85 3391 7222.
E-mail address: ette@cnpat.embrapa.br (H.M.C. Azeredo).

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tensile properties of mango (Azeredo et al., 2009) and acerola (Azeredo et al., 2012) puree based films.

The objectives of this study were: (a) to compare water vapor barrier of two nanocomposite films based on alginate–acerola puree (AA) matrix with those of an unfilled AA film; (b) to evaluate the ability of unfilled and nanocomposite coatings to enhance acceptance and stability of fresh acerolas.

2. Materials and methods

2.1. Film/coating materials and formulations

Two nanofillers were used to formulate nanocomposite coatings, namely: (a) the montmorillonite-type layered silicate Proenol CN 45 (provided by Flow Chemical Ltd., São Paulo, SP, Brazil), containing the following chemical composition (w/w, as informed by the provider): SiO_2, 66.0%; Fe_2O_3, 3.0%; CaO, 1.0%; TiO_2, 0.8%; Al_2O_3, 19.5%; MgO, 5.0%; Na_2O, 3.0%; K_2O, 0.1%; and (b) cellulose whiskers (average dimensions, 5.5 nm in diameter and 194 nm in length, as determined previously by our group, as described in Azeredo et al., 2012) extracted from coconut husk fibers by a 120-min hydrolysis preceded by one-stage bleaching (Rosa et al., 2010). In addition to the two nanocomposite coatings (cellulose whiskers reinforced alginate–acerola puree coating, or simply CWAA, and montmorillonite reinforced alginate–acerola puree coating, or MMTAA), an unfilled alginate–acerola puree coating (AA) was also formulated.

For the unfilled AA coating formulation, 1.6 g sodium alginate (Grinsted® FD175, provided by Danisco Brasil Ltd.), and 4 g of corn syrup (Karo, Unilever, São Paulo, SP, Brazil) were added to 100 g of acerola puree (AliPolpa, Aquiraz, CE, Brazil, with 6.4% total solids) and 50 mL of distilled water. Corn syrup was used as plasticizer and sweetener. The formulation was based on preliminary tests. The CWAA and MMTAA dispersions were formulated by the same procedure, including the addition of 10% (w/w, based on solid matter content of films, including alginate, acerola puree, and corn syrup solids) of cellulose whiskers (CW) or montmorillonite (MMT), respectively. The amount of added distilled water was adjusted in each case, so as to obtain film forming dispersions with the same solid contents (i.e., about 8.4%).

The plasticizer (corn syrup) was added in order to break polymer–polymer interactions (such as hydrogen bonds and van der Waals forces) and to form secondary bonds to polymer chains, causing the distance between adjacent chains to increase, thus reducing film rigidity and brittleness (Sothornvit and Krochta, 2005). Corn syrup is basically constituted by simple carbohydrates, being thus well suited to a hydrophilic matrix such as the alginate–acerola puree combination used in this study.

For all film formulations, the mixtures were homogenized in a magnetic stirrer (Fisatom 752A, Aaker Solutions Ltd., Porto Alegre, Brazil) for 60 min at 200 rpm, 50 °C, and then in a cell disruptor (DES500, Unique Group, Indaiatuba, SP, Brazil) for 18 min at 90 W. The mixture was vacuum degassed (at 25 °C), and used to form both films and coatings. Films were formed only to have their water vapor permeability (WVP) analyzed, in order to correlate this measurement with the responses obtained for the coated acerolas.

2.2. Film formation

For film formation, dispersions were cast on 30 × 30 cm glass plates and leveled with a draw-down bar to a thickness of 1.2 mm. After 1 h, the plates with the film dispersions were immersed for 15 s in a 2% (w/v) calcium chloride ($CaCl_2$) solution to crosslink sodium alginate in order to obtain films with better water resistance and barrier. Higher immersion times would possibly produce even better water resistance and decreased water vapor permeability, but previous tests revealed that the resulting films would be noticeably salty, and could impair the acceptability of coated acerolas. The films were placed on a lab bench (24 ± 1 °C, RH 76 ± 2%) for 24 h to dry. Then, samples were cut and detached from the surface.

2.3. Water vapor permeability tests

Prior to WVP determination, the detached, free-standing films were conditioned for 24 h at 25 °C in desiccators containing $Mg(NO_3)_2$ saturated solution (53% RH) (Tunç and Duman, 2007). The WVP determination, with eight replicates, was based on the method E96-80 (ASTM, 1989) at 24 °C and 85% RH, using silica gel as the desiccant material, and at least seven measurements within a 24-h period.

2.4. Coating formation

Fresh acerolas (21.2 mm in diameter, 23.2 mm in height, 4.24 g in mass)[1] were washed, sanitized by immersion in a sodium hypochlorite solution (200 mg L^{-1}), hung from their stalks, and sequentially immersed in the coating formulation (AA, CWAA or MMTAA) for 2 min, and in a $CaCl_2$ solution (2 g/100 mL) for 15 s. After treatment, fruits were placed on a bench at 25 °C, RH 76% for 24 h to allow the coating to dry. They were then weighted, packed in polyethylene terephthalate (PET) trays, and stored in a refrigerator at 6 °C. A control group of uncoated acerolas (U), also previously washed and sanitized, was stored under the same conditions. Acerolas from the four groups (U, AA-coated, CWAA-coated, and MMTAA-coated) were subjected to the determinations described in 2.5–2.9. Acceptance was determined only at day 0, and the other determinations were carried out at day 0 and after 7 days of storage. Except for the sensory analysis, all the tests were conducted in quintuplicate.

2.5. Visual acceptance

Acerolas were tested for visual acceptance, according to Meilgaard et al. (2007). Fifty non-trained panelists took part in the test, in which the visual acceptance was evaluated by using 9-Point Hedonic Score System, with ratings ranging from 1 (“disliked extremely”) to 9 (”liked extremely”). Since a coating is an integral part of the food and consumed as such, and considering that the nanoreinforcements are not yet permitted as food additives or ingredients, flavor and texture acceptance tests were not carried out. Specific toxicity tests are still required in order to establish the safety of such nanoreinforcements as edible materials.

2.6. Weight loss and decay incidence

Weight loss was calculated as percentage on a fresh weight basis. The decay incidence of acerolas was expressed as percentage of visibly decayed fruits (El-Anany et al., 2009).

2.7. Total soluble solids and total titratable acidity

Acerolas were manually ground, and the pulp was used to determine total soluble solids (TSS) and total titratable acidity (TTA). TSS content was measured by using a digital refractometer (PR-101, Atago, Japan). TTA was determined according to AOAC (2005).

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[1] Average measurements from 20 acerolas.