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Evaluation of edible films and coatings formulated with cassava starch, glycerol, carnauba wax and stearic acid

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ABSTRACT

This study aimed at characterizing four formulations of cassava starch, glycerol, carnauba wax and stearic acid-based edible coatings/films, evaluating their water vapor resistance, the respiration rate of coated apple slices, surface solid density, solubility, mechanical properties, thermal properties and microstructure. Among the formulations evaluated, only the formulation with higher wax content did not promote an effective barrier to oxygen and water vapor and resulted in more rigid films. Formulations with higher glycerol content promoted lower respiration rate of apple slices, good water vapor resistance and flexible films, but the microstructure analysis showed a non-homogenous surface of the films with higher wax content. The glycerol added in formulations increased the solubility and reduced the melting temperature of the films. Formulation with 0.2% carnauba wax showed intermediate values of analyzed properties and promoted films with a more regular surface. Formulation containing 3% (w/w) cassava starch, 1.5% (w/w) glycerol, 0.2% (w/w) carnauba wax and 0.8% (w/w) stearic acid, presented films with a cohesive matrix, resulting in better mechanical properties, barrier to moisture and gas exchange.

1. Introduction

The market for minimally processed fruits and vegetables has increased in recent years. These products are ready to eat, convenient and maintain the freshness and nutritional quality of the whole product. On the other hand, the peeling and cutting operations can accelerate the metabolic activities of plant tissue, making the minimally processed product more perishable than intact fruits and vegetables (Olivas & Barbosa-Cánovas, 2005). So, new strategies and technologies to maintain quality and extend shelf life are required.

The use of edible coatings is a promising technology to preserve the quality of whole and minimally processed fruits (Han & Gennadios, 2005; Talens & Krochta, 2005; Vargas, Pastor, Chiralt, McClements, & González-Martínez, 2008; Zahedi, Ghanbarzadeh, & Sedaghat, 2010). The coatings act as barriers to water loss and gas exchange, controlling the transfer of moisture, oxygen, carbon dioxide, lipids and flavor components, with similar effect to that promoted by storage under controlled or modified atmosphere (Vargas et al., 2008). A range of polymers can be used in edible coatings formulation. However, their mechanical and barrier properties are intrinsically linked to physical and chemical characteristics of their constituents. The polymers most commonly used in the preparation of edible films and coatings are proteins (gelatin, casein, wheat gluten and zein), polysaccharides (starch, pectin, cellulose, alginate and carrageenan) and lipids (stearic acid, waxes and fatty acid esters), which can be used alone or in combinations (Sothornvit & Krochta, 2001; Vargas et al., 2008).

Polysaccharides-based coatings have low oxygen permeability, which can reduce the respiration rate of minimally processed products. Starch is the most important polysaccharide used in the formulation of biodegradable films and edible coatings. Cassava starch-based coatings are tasteless, odorless and transparent, not changing the taste, aroma and appearance of the product (Chiumarelli, Pereira, Ferrari, Sarantópoulos, & Hubinger, 2010; Garcia, Pereira, Sarantópoulos, & Hubinger, 2010; Pareta & Edirisinghe, 2006). Although the starch is a cheap and abundant material, able to form a continuous polymer matrix, it exhibits a strong hydrophilic character, constituting poor barriers to water vapor (Averous & Boquillon, 2004; Ghanbarzadeh, Almasi, & Entezami, 2011; Karbowiak, Debeaufort, & Voilley, 2007; Liu, 2005; Vargas et al., 2008). The addition of lipids can reduce water vapor permeability, but it can affect coatings transparency and mechanical properties, despite the lipid offers after taste, which may impair the sensory characteristic of food (Bourlieu, Guillard,

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Vallès-Pamiès, Guilbert, & Gontard, 2009; Fakhouri et al., 2007; Rhim & Shellhammer, 2005).

The most used lipids in coatings for minimally processed products are stearic acid, palmitic acid, and some vegetable oils such as soybean and sunflower ones (Bourlieu et al., 2009; Colla, Sobral, & Menegalli, 2006; Garcia, Martino, & Zaritzky, 2000; Martín-Belloso, Soliva-Fortuny, & Baldwin, 2005). Despite the good results obtained in some formulations, these materials have lower water vapor permeability than that of natural waxes, such as carnauba wax (Rhim & Shellhammer 2005; Rojas-Argudo, del Rio, & Pérez-Gago, 2009; Talens & Krochta, 2005).

Glycerol is a plasticizer used to enhance the films/coatings flexibility, but can affect the water vapor and gases permeability, since it is very hydrophilic and hygroscopic (Sothornvit & Krochta, 2001). Glycerol has low molecular weight, modifying the interactions between the macromolecules, which increase mobility of the polymer chains and reduce the glass transition temperature of the system (Krochta, 2002).

In this context, the objective of this work was to characterize four formulations containing cassava starch, glycerol, carnauba wax and stearic acid-based edible coatings/films, through the evaluation of their water vapor resistance, respiration rate of coated apple slices, solubility, mechanical properties (tensile strength, elongation at break, elastic modulus and coating strength), thermal properties (transition temperature and enthalpy) and microstructure.

2. Material and methods

2.1. Material

Cassava starch (17% amylose content, Pilão Amidos Ltda., Guaíra, Brazil), carnauba wax type 1 (Cresal Comércio e Representações Ltda., São Paulo, Brazil), stearic acid (Synth, Diadema, Brazil) and glycerol as plasticizer agent (ECIBRA, São Paulo, Brazil) were used for coating/film formulations.

Apples (*Malus domestica* Borkh cv 'Gala') were obtained from the local market (Ceasa, Campinas, Brazil). A lot of 150 apples was bought and the fruits of uniform weight (120.59 ± 5.24 g), maturity stage (based on skin color and firmness) with no physical damage were selected to the experiments.

2.2. Methods

2.2.1. Coating/film preparation

Cassava starch water suspensions were prepared at 75 °C with constant stirring. Glycerol was added after starch gelatinization. Carnauba wax and stearic acid were melted at 85 °C and homogenized into the cassava starch suspensions with a rotor–stator homogenizer (model MA 102, Marconi Ltda., Piracicaba, Brazil) for 3 min at 12,000 rpm. The temperature of homogenization was 85 °C and emulsions were then cooled until room temperature. The coatings/films formulations are presented in Table 1. The cassava starch, glycerol, carnauba wax and stearic acid concentrations were chosen through an experimental design, and these formulations were obtained in optimized area, as described in a previous work (Chiumarelli & Hubinger, 2012). The stearic acid was used to reduce the carnauba wax melting point.

Apple slices and cylinders were dipped into cassava starch–carnauba wax–stearic acid emulsions for 2 min and used in respiration rate and water vapor resistance analyses. For the other analyses, films were prepared by weighing an emulsion amount that provided 130 ± 2 μm of film thickness on a Teflon casting plate resting on a leveled surface. Films were dried until constant moisture content at 40 °C and 60% RH to avoid cracking, peeled off the casting surface and conditioned at 25 °C and 58% RH in desiccators with a saturated NaBr solution for 72 h prior to analysis.

Table 1
Cassava starch (CS), glycerol (GLY), carnauba wax (CW) and stearic acid (SA) concentrations on coatings/films formulations.

Variables	Formulation			
	1	2	3	4
CS (% w/w)	2.50	2.50	3.50	3.00
GLY (% w/w)	2.82	2.61	1.00	1.50
CW (% w/w)	0.10	0.38	0.40	0.20
SA (% w/w)	0.90	0.62	0.60	0.80

2.2.2. Respiration rate

The respiration rate of coated apple slices was measured by static method (Bierhals, Chiumarelli, & Hubinger, 2011; Garcia et al., 2010). Apples were peeled and cut into 8 slices, which were immersed in coating formulations for 2 min, placed in a sieve and left at room temperature (15 °C and 80% RH) for 1 h to dry the coating material. The samples (around 50 g) were placed in sealed 180 mL glass jars with silicon septum. The jars were closed and kept at 5 °C during 1 h. After this time, gas sampling was carried out using an O_2/CO_2 Dual Head Space Analyzer (Model PAC CHECK 325, Mocon, Minneapolis, USA), measuring the CO_2 production. Uncoated apple slices were used as control in order to calculate the coatings efficiency. The respiration rate was determined in triplicate and expressed in mL CO_2 kg^{-1} h^{-1}.

2.2.3. Water vapor resistance

The determination of coatings water vapor resistance (WVR) was carried out according to the method described by Avena-Bustillos, Krochta, Saltveit, Rojas-Villegas, and Sauceda-Pérez (1994), using a modified Fick's equation proposed by Ben-Yehoshua, Burg, and Young (1985). This method was also used by Garcia, Martino, and Zaritzky (1998), Rojas-Graü, Tapia, Rodríguez, Carmona, and Martín-Belloso (2007), Tapia et al. (2008) and Garcia et al. (2010) to calculate the WVR of different edible coatings.

Apple cylinders with 25 mm of diameter and 10 mm of thickness were used for coatings application. The exposed area, taken as the upper surface and the lateral area of the samples, was 12.76 cm^2. Coated and uncoated apple cylinders were equilibrated for 24 h at 20 ± 1 °C in desiccators maintained at 98.9% RH with a 0.6 M NaCl solution. Then, samples were placed in small test cups, weighed in an analytical balance, and placed in desiccators equilibrated at 33.3% RH with saturated $MgCl_2 \cdot 6H_2O$ at 20 °C. Weight was taken periodically during a 24 h period and the water vapor flux was calculated according to Eq. (1):

$$\mathrm{WF} = \left(\frac{\mathrm{d}P}{\mathrm{d}t}\right)\cdot\left(\frac{1}{A}\right) \tag{1}$$

where: WF is the water vapor transferred per unit of area ($g\,s^{-1}\,cm^{-2}$), dP/dt is the water vapor transferred ($g\,s^{-1}$) and A is the exposed area (cm^2).

WVR was calculated using Eq. (2), proposed by Ben-Yehoshua et al. (1985):

$$\mathrm{WVR} = \left[\left(\frac{a_w - \frac{RH}{100}}{R\cdot T}\right)\cdot P_{wv}\right]\cdot\left(\frac{1}{\mathrm{WF}}\right) \tag{2}$$

where: WVR is the resistance of the coating to water diffusion ($s\,cm^{-1}$); a_w = water activity of the sample; RH = 33.3% relative