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Influence of cassava starch and carnauba wax on physical properties of cashew tree gum-based films

Delane C. Rodrigues [a], Carlos Alberto Caceres [b], Hálisson L. Ribeiro [c], Rosa F.A. de Abreu [d], Arcelina P. Cunha [e], Henriette M.C. Azeredo [f,*]

[a] Chemical Engineering Department, Federal University of Ceará, Campus Pici, Bloco 709, 60455-760 Fortaleza, CE, Brazil
[b] Universidade da Integração Internacional da Lusofonia Afro-Brasileira, Instituto de Engenharias e Desenvolvimento Sustentável, CE 060, km 51, 62785-000 Acarape, CE, Brazil
[c] Federal University of Ceará, Av. Mister Hull, 2977, 60356-000 Fortaleza, CE, Brazil
[d] University of Fortaleza, Av. Washington Soares, 1321, 60811-905 Fortaleza, CE, Brazil
[e] Federal University of Ceará, Organic and Inorganic Chemistry Department, Campus Pici, 60440-900 Fortaleza, CE, Brazil
[f] Embrapa – Secretariat for International Affairs, Edifício Embrapa Sede, Prédio CECAT, 3° andar, Parque Estação Biológica, Av. W3 Norte, CEP 70770-901 Brasília, DF, Brazil

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ABSTRACT

Composite cast films were prepared from different proportions of cashew tree gum (70–85%), cassava starch (15–30%), and carnauba wax (0–15%), according to a simplex-centroid mixture design, and some physical properties were modeled as functions of the mixture components. Water vapor permeability and water solubility were decreased by carnauba wax, indicating that the presence of carnauba wax may be interesting for applications which require good water barrier and resistance. On the other hand, carnauba wax presented plasticizing effect on the composite films, lowering glass transition temperature, and decreasing film strength and stiffness while enhancing elongation. The film opacity was increased as a function of carnauba wax concentrations, which may impair the applicability of emulsion films when a high transparency is required. The relative proportions of cassava starch and cashew tree gum did not present significant effects on the physical properties of the resulting films within the ranges studied, probably because both components are polysaccharides with some similar properties when forming films.

1. Introduction

Cashew tree gum (CTG) is a complex water soluble heteropolysaccharide exudated from cashew tree (*Anacardium occidentale* L.) bark, whose composition is comprised by galactose (72%), glucose (14%), arabinose (4.6%), rhamnose (3.2%), and glucuronic acid (4.5%) (De Paula, Heatley, & Budd, 1998). The cashew tree cultivation is focused on the production of cashew nuts, whose kernels are commercialized and appreciated all around the world. CTG is an abundant by-product of the cashew industry demanding for industrial applications, which have not yet been adequately explored. The film forming ability of CTG was employed by Carneiro-da-Cunha et al. (2009) to coat apples. However, similarly to gum arabic (Al-Assaf, Phillips, Aoki, & Sasaki, 2007), the branched structure and polyanionic character of CTG result in low viscosity solutions (1.0 mPa s for a CTG solution at 1%, w/v) when compared to other polysaccharides with similar molecular weights (De Paula & Rodrigues, 1995). This low viscosity makes film casting on a flat surface difficult at concentrations lower than 40% (w/v), since the solution will run down the edges of the surface. Then, combinations with other biopolymers are helpful to form more viscous film forming solutions.

Cassava starch is obtained from the roots of cassava, which is a tropical crop probably originated from the Amazon region (Demiate & Kotovicz, 2011). Cassava starch typically contains 17–20% amylose, which has a higher molecular weight when compared to amylose from other starches (Breuninger, Piyachomkwan, & Sririth, 2009). Cassava starch has been extensively studied as a biopolymer to develop edible food coatings (Bierhals, Chiumarelli, & Hubinger, 2011; Chiumarelli, Pereira, Ferrari, Sarantópoulos, & Hubinger, 2010), as well as biodegradable packaging films (Bergo, Moraes, & Sobral, 2012; Bergo, Sobral, & Prison, 2010) and more rigid containers such as trays (Kaisangsri, Kerdchoechuen, &

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* Corresponding author.
E-mail addresses: henriette.azeredo@embrapa.br, ette@mpc.com.br (H.M. C. Azeredo).

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Laohakunjit, 2012; Matsuda, Verceheze, Carvalho, Yamashita, & Mali, 2013; Silva, Nievola, Tischer, Mali, & Faria-Tischer, 2013).

Edible films based on polysaccharides show good mechanical and oxygen barrier properties, but their water vapor barrier and moisture resistance are poor, because of their inherent hydrophilic nature (Giancone et al., 2011; Janjarasskul & Krochta, 2010). Water solubility affects the applicability of edible films. For example, films for water soluble pouches must be readily soluble, while films to be applied on high-moisture food surfaces must be insoluble in water. Lipids improve the resistance of films to moisture due to their hydrophobic nature (Limpisophon, Tanaka, & Osako, 2010; Pérez-Mateos, Montero, & Gómez-Guillén, 2009; Pommet, Redl, Morel, & Guilbert, 2003), but have poor tensile properties, lack cohesive structural integrity to form stand-alone films, and are usually opaque. Therefore, advantages are expected from combining polysaccharides and lipids in emulsion films.

Waxes are the most efficient lipids to reduce water vapor permeability (WVP) of films, because of their high hydrophobicity related to high contents in long-chain fatty alcohols and alkanes (Morillon, Debeaufort, Blond, Capelle, & Voilley, 2002). Carnauba wax is a plant exudate from a Brazilian palm tree (*Copernicia cerifera*), composed almost entirely of wax acid esters of C24 and C28 carboxylic acids and saturated long-chain mono-functional alcohols (Shellhammer & Krochta, 1997).

The objective of this study was to combine cashew tree gum with cassava starch and carnauba wax, and to study the influence of the components on physical properties of the resulting emulsion films. Cassava starch was added to facilitate film formation due to its higher viscosity (when compared to CTG), and carnauba wax was incorporated to improve water vapor barrier and moisture resistance of the films.

2. Materials and methods

The films were formulated from cashew tree gum (CTG), cassava starch (from Fecularia Juriti, Querência do Norte, PR, Brazil), and carnauba wax (Foncepi Exportadora Ltda., Fortaleza, CE, Brazil). CTG was obtained from exudates from cashew trees (Embrapa Tropical Agroindustry, Experimental Station at Pacajus, CE, Brazil) and purified by a method adapted from Torquato et al. (2004). Basically, the exudate was ground, dissolved in distilled water at room temperature (24 °C ± 1 °C), vacuum filtered, and precipitated with commercial ethanol (96°GL) at an ethanol:gum weight ratio of 3:1. The precipitate was drained and placed on Petri dishes to be dried in a fume hood. The dried gum was ground in an analytical mill (A11 Basic, Ika, Staufen, Germany) and passed through a 212 μm sieve, producing a fine powder.

A simplex-centroid mixture design with 10 treatments (Table 1) was used to study the influence of the ternary mixture proportions on the film properties. In order to produce the film forming formulations, cassava starch was gelatinized in water (8 g starch/100 mL water) at 90–95 °C for 10 min. Separately, carnauba wax was added with two surfactants: Tween 80 (polyoxyethylene sorbitan monooleate) and Span 80 (sorbitan monooleate), both from Sigma–Aldrich (St. Louis, MO, USA), at constant concentrations of 5% and 15%, respectively, on a carnauba wax weight basis. The wax–surfactant mixture was melted on a hot plate at 85 °C for 5 min, and mixed to the gelatinized starch in a 400 W ultrasonic processor (UP400S, Hielscher, Teltow, Germany), working at 24 kHz in ten 1 min cycles interleaved with 15 s pauses. CTG was then mixed to the emulsion for 15 min at 4000 rpm with Ultra-Turrax T-50 (Ika, Staufen, Germany). Glycerol (Impex, Diadema, Brazil) was added as plasticizer at a constant concentration of 30% on starch + CTG dry basis.

Table 1
Proportions of the components in the ternary mixture.

Treatment	Real concentrations			Pseudocomponents		
	CS (%)	CTG (%)	CW (%)	CS (%)	CTG (%)	CW (%)
1	30	70	0	1.00	0.00	0.00
2	15	85	0	0.00	1.00	0.00
3	15	70	15	0.00	0.00	1.00
4	22.5	77.5	0	0.50	0.50	0.00
5	22.5	70	7.5	0.50	0.00	0.50
6	15	77.5	7.5	0.00	0.50	0.50
7	20	75	5	0.33	0.33	0.33
8	25	72.5	2.5	0.67	0.17	0.17
9	17.5	80	2.5	0.17	0.67	0.17
10	17.5	72.5	10	0.17	0.17	0.67

CS: cassava starch, CTG: cashew tree gum; CW: carnauba wax.

The emulsion was vacuum degassed by using a vacuum pump V-700 (Büchi Labortechnik AG, Flawil, Switzerland) at 30 mbar for 3 h in an ultrasonic cell disruptor (DES500, Unique Group, Indaiatuba, SP, Brazil). The film was obtained by using a laboratory coating/drying unit LTE-S (Werner Mathis AG, Oberhasli, Switzerland). The emulsion was cast onto a Mylar® substrate with a thickness selected to obtain a film with a final thickness of about 0.15 mm, and the coating/drying unit was operated at 60 °C for 15 min at an air flow rate of 3 $m^3 h^{-1}$.

After cooling, dried samples were cut and detached from the surface. Before film characterization, the detached, free-standing samples were conditioned for 24 h at 25 °C in desiccators containing a saturated solution of calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), in order to maintain a constant relative humidity of 48%.

The water vapor permeability (WVP) determination, with eight replicates, was based on the method E96-80 (ASTM, 1989) at 25 °C and 85% RH, using silica gel as the desiccant material. At least seven measurements were made within a 24-h period.

The water solubility determination on the films (2 cm disc samples, in quadruplicate) was based on the method proposed by Gontard, Duchez, Cuq, and Guilbert (1994). Samples were immersed in 45 mL distilled water for 24 h, under stirring at 175 rpm in an orbital shaker (Tecnal, model TE-420, Piracicaba, SP, Brazil) at room temperature (25 °C ± 2 °C). The dried weight of the samples (before and after water immersion) was determined by drying them in an air oven (Quimis, model Q314M, Diadema, SP, Brazil) at 105 °C for 24 h. The difference in dry weight was used to calculate the water soluble matter as a percentage of the initial dry weight.

Film opacity determination (in triplicate) was based on the method described by Irissin-Mangata, Bauduin, Boutevin, and Gontard (2001). Films were cut into rectangular (1 × 5 cm) shaped strips and placed onto the internal side of a Varian Cary 50 UV–VIS spectrophotometer test cell (Agilent Technologies, Santa Clara, CA, USA), perpendicularly to the light beam. The absorbance spectrum (400–800 nm) of film samples were recorded and then film opacity was defined as the area under the recorded curve (calculated by the linear trapezoidal rule) and expressed as absorbance units × nanometers (A nm).

Tensile properties of 100 mm × 6.3 mm film strips (with ten replicates) were measured according to D882-00 (ASTM, 2000), in an Emic DL-3000 Universal Testing Machine with a load cell of 100 N, initial grip separation of 0.05 m, and crosshead speed of 10 $mm\ min^{-1}$ ($1.67 \times 10^{-4}\ m\ s^{-1}$).

The scanning electron microscopy (SEM) images of film surfaces were taken using a Hitachi TM 3000 scanning electron microscope (Tokyo, Japan), with the samples mounted on an aluminum stub with a double side adhesive. The samples were examined using an accelerating voltage of 5 kV, and a magnification of 200 times.