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Physical Properties and Water Vapour Permeability of Blends Produced with Gelatin and Modified *Maranta Arundinacea* Starch

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Biopolymer-based films are an alternative to replace plastic packaging. These films may be produced from various raw materials, such as polysaccharides and proteins. Among them, the most used are starch and gelatin, which have good filmogenic properties, although they present some limitations. These isolated macromolecules produce films with good mechanical properties (gelatin) and adequate barrier properties (starch). Thus, the use of these polymers in association to produce blends becomes a good option to overcome the weaknesses of each macromolecule when used individually. Also in this context, starch physicochemical characteristics can be modified by ozonation to improve the interaction between the macromolecules. The aim of this work was to study the mechanical properties and the water vapour permeability (WVP) of gelatin:arrowroot starch blends. Native starch and treated with ozone at three times (5, 10 and 20 minutes) were studied. The blends were produced by casting and dried in an oven at 30 °C. The mechanical properties were measured by tensile tests and WVP was determined by gravimetry. Visually, the blends were homogeneous without phase separation. In general, the blends produced with native starch presented better WVP results and no difference for the mechanical properties. In other words, longer treatment time with ozone resulted in higher water vapour permeability and did not change the mechanical properties when compared to blends formulated with native starch. Therefore we can conclude that the ozonation time, for the studied conditions, was not enough to improve the mechanical properties and besides that increased blend WVP.

1. Introduction

Plastics have been widely used because they are light, inert, transparent, have comparatively high mechanical properties and low cost (Hu et al., 2009). Annually, about a billion tons are produced in the world and a lot of waste is generated. To decrease pollution, an alternative to replace plastics partially or totally are green plastics or biodegradable plastics. These materials are biopolymers such as gelatin (Sobral et al., 2001; Vanin et al., 2014), castor bean protein (Bittante et al., 2014), chitosan (Ma et al., 2016) and starch (Souza et al., 2012). Many studies employed starches obtained from conventional or unconventional sources to produce films. For example, cassava starch (Bergo et al., 2012; Bonilla-Lagos et al., 2015), corn starch (Ortega-Toro et al., 2016), potato starch (Fonseca et al., 2015), rice starch (Zhang et al., 2016), pinhão starch (*Araucaria angustifolia*) (Daudt et al., 2016), pea starch (Saberi et al., 2016), yam starch (*Xanthosoma robustum*) (Londoño-Restrepo et al., 2014), and sugar palm starch (*Arenga pinnata*) (Sanyang et al., 2016) were studied for film production. Though many sources are employed, in general starch based films present poor mechanical properties. Arrowroot starch (*Maranta arundinacea*) is an unconventional starch source not yet studied in film technology. Many other studies used gelatin, a protein derived from collagen by partial hydrolysis to produce films (Sobral et al., 2001; Vanin et al., 2014). Gelatin has excellent filmogenic properties

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and can be easily found in several countries, with low cost, though its structure and amino acids composition change according to collagen origin and extraction method. Gelatin films are, generally, transparent, homogeneous, flexible and with high manageability, but present high water vapour permeability and are susceptible to changes in ambient relative humidity (Sobral et al., 2001). A good perspective is to produce blends with biopolymers to create a material that overcomes the limitations of each polymer individually. Gelatin-starch blends are biomaterials with appropriate mechanical and barrier properties (Acosta et al., 2015; Zhang et al., 2013). The starch:protein ratio employed influences blend properties. The authors agreed that 50/50 (w/w) presented best results (Acosta et al., 2015; Zhang et al., 2013). The functional, organoleptic and mechanical properties of starch films can be modified by addition of various chemical agents or physical modifications in certain amounts (Hu et al., 2009; Vanier et al., 2017). These changes can improve the properties of starch when used to produce films. Nowadays oxidation is one of the most studied starch modification options (Vanier et al., 2017). Oxidized-starch is widely used in industries to provide surface sizing and coating properties. Besides that, applications for oxidized starch in the food industry are increasing because of its low viscosity, high stability, high transparency, excellent film-forming and binding properties (Hu et al., 2009). However, its application as a food packaging material, especially as an edible film, is still incipient. Oxidized starches have been used for preparing biodegradable packaging. Fonseca et al. (2015) prepared biodegradable films from native and oxidized potato starch and Zamudio-Flores et al. (2006) made banana starch based films (native and oxidized) both authors obtained good results for the studied properties. Oxidation can improve the binding properties of the starch and increase the emulsion stability (Vanier et al., 2017). The properties were affected by the level of oxidation as indicated by the numbers of carboxyl and carbonyl groups on oxidized-starch (Hu et al., 2009). Starch can be oxidized in different ways, for example with sodium hypochlorite, hydrogen peroxide and ozone (Vanier et al., 2017). Oxidation with ozone is a clean technology; the final products of an ozone oxidation reaction are carbon dioxide, water and inorganic ions and less toxic by-products. However, the interaction of oxidised starch with gelatin in a blend has not been studied. Therefore, the aim of this work was to apply ozone oxidation to starch from arrowroot (an unconventional source) at different times and then evaluate the physical properties of blends made with this starch and gelatin at a 50/50 (w/w) ratio.

2. Experimental

2.1 Materials

The macromolecules used were pigskin gelatin (Gelnex, SC, Brazil) and native arrowroot starch (commercial source, Brazil) to perform the blends. The plasticizer employed was glycerol (Synth) and potassium bromide (Dinâmica) was the salt used in desiccators.

2.2 Arrowroot starch chemical composition

The proximate composition of arrowroot starch was determined (moisture content, lipids, proteins, ashes and crude fiber). The protocol used was the standard methodologies reported in the AOAC manual (AOAC, 1995).

2.3 Arrowroot starch oxidation

Ozone was produced in an ozone generator unit (OzônioBras, GBO, São Paulo/Brazil) by the coronal-discharge method from industrial oxygen (95 % purity). The starch suspension (30 wt%) was placed inside a cylindrical reactor (1L capacity, 30 cm height, 4 cm diameter) and the ozone-rich gas current (17.4 mg O_3 L^{-1}) was dispersed in the suspension for (5, 10 and 20) min. The gas flow was maintained constant at 1.0 L min^{-1}. After processing, the suspension was allowed to settle and the supernatant liquid was discarded. Starch was dried in an oven (35 °C/16 h), then ground in a mortar, sieved (48 mesh) and stored in a glass container.

2.4 Blends production

The blends were produced by casting. The conditions studied were blends produced with native and ozonated arrowroot starch (5, 10 and 20 minutes) with gelatin. The film forming solutions (FFS) were produced with 4 g of the macromolecules/100 g FFS. In this case, 2 g of arrowroot starch (native or ozonated depending on the case) and 2 g of gelatin. Glycerol was used as plasticizer (30 g/ 100 g of the macromolecules). Arrowroot starch with glycerol was dissolved in distilled water at 90 °C for 30 min (solution A). At the same time, gelatin was hydrated for 30 min at room temperature, and then dissolved at 70 °C for 15 min using a thermostatic water bath (Marconi TE 184, Brazil) (Solution B) (Sobral et al., 2001). Solution A was cooled to 60 °C and then solution B was added under magnetic stirring. The FFS was dispersed onto Plexiglas plates (d = 150 mm) and dried in an oven with forced air circulation (Marconi, MA037,Brazil) at 30 °C and controlled relative humidity (55 – 65%), for (18 – 20) h. Then the films were prepared for testing and stored for 7 days in desiccators containing saturated potassium bromide solution (58% relative humidity) at 25 °C before characterization.

2.5 Visual Aspect and thickness

The visual aspect of blends was evaluated subjectively. Parameters like homogeneity (color, presence of insoluble particles, bubbles, etc.) and manageability (ease of sample preparation), plasticizer exudation on the film's surface and ease of detachment from support were observed. Film thickness was determined as the average of ten random measurements performed with a digital micrometer (resolution 0.001 mm, MITUTOYO) (Makishi et al., 2013).

2.6 Water vapour permeability (WVP)

For the determination of water vapour permeability, circular film samples were fixed onto cells with a perforated ring (exposed area 31.17 cm²) containing silica gel. The test was performed by gravimetry (ASTM E96-96M, 2010a), with a relative humidity gradient equal to 100%. The system (cell + silica gel +films) was stored in a desiccator containing distilled water, and weighed daily for 5 days on a semi-analytical balance (Mars AS2000). Water vapour permeability was calculated from Eq. (1) and the result expressed in g.mm/m^2.h.kPa.

$$WVP(g.mm/h.m^2.kPa) = \frac{G \,.\, x}{t \,.A_e.(P_1 - P_2)} \quad (1)$$

Where: x: average film thickness (mm); Ae: exposed area (m²); P1: water vapour pressure of pure water; P2: silica gel vapour pressure; G/t (g/h): angular coefficient of the linear regression of the system mass gain line versus time.

2.7 Mechanical Properties (Tensile tests)

Film mechanical properties were evaluated by tensile tests using an iCON Texture analyzer (TA Instruments). Data was analysed by the Software Exponent Lite Express (version 4.013,0 XT Express). Film samples of (15 x 90) mm² were prepared and affixed to the tensile probe with an initial separation of 50 mm and tested at a speed of 1.0 mm/s. Based on the tensile versus elongation curves, the tensile strength (TS, in MPa), the elongation at break (EB, in %) and the elastic modulus (EM, in MPa/%) were determined in the linear portion of the curve (ASTM D882-10, 2010b).

2.8 Statistical analyses

The data obtained were analyzed to determine whether the variances were statistically homogeneous. The results were expressed as means ± standard deviation (SD). Statistical comparisons were made by analysis of variance (Tukey's multiple range tests) using the "Statistical Analysis Systems" software (version 9.2, SAS, Statistical Analysis Systems, North Carolina, USA). The significance level was set at 0.05.

3. Results and discussions

3.1 Arrowroot starch chemical composition

The arrowroot starch showed low content of lipids, proteins, ashes and crude fiber. This results were according with Villas-Boas and Franco (2016) working with the same starch source (Table 1). Also for the moisture content, the value was similar to that found by Charles et al. (2016) working with arrowroot starch.

Table 1: Chemical composition of arrowroot starch

Composition	Content (g/100g)
Moisture (TM)	11.58±0.10
Lipids (DB)	0.11±0.03
Proteins (DB)	2.01±0.02
Ashes (DB)	0.27±0.04
Crude Fibe (DB)	0.60±0.02

(TM): Total matter; (DB): dry basis

3.2 Visual Aspect and thickness

The blends produced presented a homogeneous aspect, with no plasticizer exudation, no bubbles or insoluble particles; and were easily removed from the Plexiglas plates. There was significant difference ($p<0.05$) for the

film thickness results. The film produced only with native arrowroot starch presented a higher thickness value (0.118 ± 0.005 mm). For the others films the average thickness was approximately 0.104 ± 0.002 mm (Table 2). Therefore, starch ozonation did not affect this property. The arrowroot native starch film retracted during the drying process, this can explain the differences observed.

3.3 Water vapour permeability (WVP)

As shown in Table 2, water vapour permeability (WVP) of starch oxidized for different times showed significant differences. The lowest WVP was observed for the films made with gelatin, therefore the ozonation process performed increased film permeability. Halal et al. (2015) observed that film properties depended on starch oxidation degree. Zamudio-Flores et al. (2006) also observed the WVP increased for the films based on oxidized banana starch, which had been synthesized with active chlorine. The authors noted that higher active chlorine concentrations were associated with increased WVP. These authors related the increase of WVP to the change of the crystal pattern and to the structural arrangement of the polymer molecules, which promoted greater structural spacing and, consequently, easier water vapour transfer. This model probably explains the results obtained for the blends produced with ozonated starch and gelatin in this work. The values were lower than those obtained by Zamudio-floeres et al (2006) (0,720 a 5,04 g.mm/h.m².kPa). Ozonation probably ruptured some structures decreasing the water barrier. A different result was achieved by Fonseca et al. (2015) who studied potato starch modified with sodium hypochlorite, WVP decreased with increasing modification degree.

Table 2: Thickness value and water vapour permeability of the blends

Formulation	Thickness (mm)	WVP (g.mm/h.m².kPa)
Arrowroot starch native	0.118±0.005^{a}	0.452±0.034^{b}
Gelatin	0.102±0.003^{ab}	0.416±0.007^{b}
SG50_50 – native	0.103±0.005^{ab}	0.442±0.052b
SG50_50 - 5 min	0.106±0.005^{ab}	0.625±0.080^{a}
SG50_50 10 min	0.106±0.002^{ab}	0.549±0.076^{ab}
SG50_50 20 min	0.102±0.012^{b}	0.557±0.053^{ab}

Where: SG50_50 – native: 50% native starch and 50% gelatin; SG50_50 - 5 min; SG50_50 10 min; SG50_50 20 min: 50% starch with (5, 10 and 20) minutes of ozonation, respectively, and 50% gelatin.

3.4 Mechanical properties (tensile tests)

According to the tensile test results the lowest tensile strength (TS) was for the intermediate ozonation time (10 minutes). There is no significant difference between the other blends studied. In case of elongation at break (EB), the film made with the arrowroot starch ozonated for 20 minutes was more deformable than the blend with native starch, ozonation tended to increase film flexibility (Table 3). Regarding the resistance (Elastic modulus, EM) the most resistant formulations were the blends performed with native starch and with starch ozonated for 5 minutes.

Table 3: Results for the mechanical properties of the blends

Formulation	TS (MPa)	EB (%)	EM (MPa/%)
Arrowroot starch native	3.9±0.2^{c}	45.3±1.8^{ab}	0.8±0.3^{d}
Gelatin	19.1±3.4^{a}	43.5±6.8^{b}	4.0±0.5^{a}
SG50_50 – native	11.5±1.3^{b}	44.4±9.5^{ab}	2.5±0.1^{b}
SG50_50 - 5 min	12.9±0.0^{b}	56.3±0.0^{ab}	2.3±0.0^{bc}
SG50_50 10 min	8.7±0.8^{b}	53.9±0.1^{ab}	1.6±0.1^{c}
SG50_50 20 min	11.6±0.0^{b}	59.1±0.2^{a}	2.0±0.2^{bc}

Where: SG50_50 – native: 50% native starch and 50% gelatin; SG50_50 - 5 min; SG50_50 10 min; SG50_50 20 min: 50% starch with (5, 10 and 20) minutes of ozonation, respectively, and 50% gelatin.

Usually, starch modification researches suggest that film physical properties improve (Fonseca et al., 2015; Halal et al., 2015; Vanier et al., 2017, Zamudio-Flores et al., 2006) but the results obtained in this work did not present significant differences when compared to the blend with native starch. Starch nature affects the interaction with ozone and the new structural configuration can stabilize the matrix or produce an unstable polymer (Vanier et al., 2017). Besides that, in Table 3 the results suggest that starch ozonation at the tested

times did not provide enough content of carbonil and carboxyl groups to promote bonding between the H and OH groups present in the amylose and amylopectin molecules. This may provide greater structural integrity in the polymer matrix, improving the mechanical resistance in the films based on starch ozonated, like reported by Zhang et al. (2009) and Fonseca et al (2015) but not observed here.

4. Conclusions

Modification of arrowroot starch with ozone as tested in this work presents little effect on the mechanical properties while decreasing the barrier properties of the blends (increased WVP). Further studies, like structural characterization of ozonated arrowroot starch are necessary, to better explain the results obtained in this work and indicate if different process conditions can improve film properties.

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