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Oxidation of potato starch with different sodium hypochlorite concentrations and its effect on biodegradable films



Laura Martins Fonseca ^a, Júlia Rosa Gonçalves ^a, Shanise Lisie Mello El Halal ^b,
Vânia Zanella Pinto ^b, Alvaro Renato Guerra Dias ^b, Andressa Carolina Jacques ^a,
Elessandra da Rosa Zavareze ^{b,*}

^a Curso de Engenharia de Alimentos, Universidade Federal do Pampa, 96413-170, Bagé, Brazil

^b Departamento de Ciência e Tecnologia Agroindustrial, Universidade Federal de Pelotas, 96010-900, Pelotas, Brazil

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ABSTRACT

The objective of this study was to evaluate the effects of oxidation with sodium hypochlorite at different concentrations of active chlorine (0.5, 1.0 and 1.5 g/100 g) on the physicochemical, morphological, pasting, thermal and gel texture properties of potato starch. The native and oxidized starches were used in different concentrations (3.0, 4.0 and 5.0 g starch/100 mL) for the preparation of biodegradable films using glycerol as plasticizer. The films were evaluated for their mechanical properties, color, water solubility and permeability of water vapor. The degree of oxidation potato starches was more intense as there was an increased concentration of active chlorine in the reaction. Films made with oxidized starch with the highest level of active chlorine had lower tensile strength when compared to native starch films. Also, these films had a lower water solubility and water vapor permeability as compared to the native starch films.

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1. Introduction

Starch is a renewable raw material, abundant and available in all the world, and shows properties that are modifiable from the physical (Zavareze & Dias, 2011), chemical (Kuakpetoon & Wang, 2001; Menzel et al., 2013) and enzymatic (LeCorre, Vahanian, Dufresne, & Bras, 2012; Rajan & Abraham, 2006) or combined (Spier, Zavareze, Silva, Elias, & Dias, 2013) ways, which can result in resistant films and coatings (Cyras, Zenklusen, & Vazquez, 2006; Mali, Grossmann, Garcia, Martino, & Zaritzky, 2004; Zavareze et al., 2012). Some studies about starch films' functional properties characterization have been developed, with the result that the biggest technological problems and application are high water vapor permeability and low mechanical resistance. One way to improve these properties of starch films is to modify the chemical structure of the starch molecules (Hu, Chen, & Gao, 2009).

Although the main application for oxidized starch is in the paper and textile industries, its use in other areas is increasing due to its low viscosity at a high solid concentration, high paste transparency (Wang & Wang, 2003), high stability and good film forming

capacity (Sangseethong, Lertphanich, & Sriroth, 2009). The starch oxidation allows the formation of carbonyl and carboxyl groups in glucan chain by a hydroxyl groups substitution (Wang & Wang, 2003). Some different oxidizing agents can be used to oxidize starches, such as sodium hypochlorite and hydrogen peroxide (Dias et al., 2011; Hu et al., 2009; Klein et al., 2014; Kuakpetoon & Wang, 2001; Wang & Wang, 2003). Following oxidation, the relatively bulky carboxyl (COOH) and carbonyl (CO) groups are introduced with a partial depolymerization of the starch chains (Chan, Bhat, & Karim, 2009) resulting in a low retrogradation of oxidized starch paste, whereas carbonyls play a minor role in the prevention of the retrogradation of starches (Sandhu, Kaur, Singh, & Lim, 2008). This conformation can increase the free space between glucan molecules and it is an important property for the plasticizer interaction during the starch filming formation.

Numerous research about starch oxidation was done with different raw materials, such as corn, potato, cassava, and beans (Spier et al., 2013; Vanier et al., 2012; Wang & Wang, 2003; Zavareze et al., 2012). However, a few studies were done using oxidized starches to produce biodegradable films. The most recent research is about potato and banana oxidized starches (Hu et al., 2009; Zamudio-Flores, Vargas-Torres, Pérez-González, Bosquez-Molina, & Bello-Pérez, 2006).

* Corresponding author. Tel./fax: +55 53 32757258.

E-mail address: elessandra@yahoo.com.br (E.R. Zavareze).

Properties of biodegradable starch films are dependent on starch raw material, starch concentration on polymeric suspension, the type and modification conditions, the type and concentration of the plasticizer used, as well as drying conditions. [Zavareze et al. \(2012\)](#) made potato starch films using oxidized and HMT (heat–moisture treatment) starches; however, they used only one modification degree to produce the films. Therefore, the aim of this study was to assess the effect of the different sodium hypochlorite concentration upon the starch physicochemical, morphological, thermal, paste and gel texture properties, the film forming capacity, water solubility, mechanical properties, and the water vapor permeation of the films.

2. Material and methods

2.1. Material

Potatoes from the Baronesa (*Solanum tuberosum* L.) cultivar were used. Potato starch was isolated according to the method described by [Liu, Weber, Currie, and Yada \(2003\)](#). Potato samples were dehulled and soaked in 0.1 g/100 g sodium bisulphite at a 1:7 (g:mL) ratio for 2 h after the dispersion was ground in a blender (Britania, Brazil) for 5 min, passed through a 63 µm screen and decanted. The starch was washed a minimum of three times with distilled water and dried at 40 °C until the moisture content of the samples reached approximately 9 g/100 g.

2.2. Starch oxidation

Starch oxidation was performed according to the method described by [Dias et al. \(2011\)](#), with some modifications. A starch sample (200 g dry basis (d.b.)) was suspended in 500 mL of distilled water in a glass reactor of 1 L, heated at 40 °C and subjected to a sodium hypochlorite treatment. The pH of the starch slurry was adjusted to 7.0 with 0.5 mol equi/L NaOH and 0.5 mol equi/L HCl. After the addition of sodium hypochlorite, the pH value of the slurry was maintained at 7.0 with 0.5 mol equi/L NaOH for an additional 60 min. The slurry was then filtered by suction with a Buchner filter funnel, washed with a twofold volume of distilled water and dried in a convection oven at 40 °C for 16 h until there was approximately 9 g/100 g moisture content. The same procedure was applied for different active chlorine concentrations (0.5, 1.0 and 1.5 g/100 g).

2.3. Amylose content

The amylose content was determined by the colorimetric method with iodine according to the method of [McGrance, Cornell, and Rix \(1998\)](#), with the modifications suggested by [Hoover and Ratnayake \(2001\)](#). Starch (20 mg, dry basis) was dissolved in 8 mL of dimethylsulfoxide (90 g/100 mL) in 10 mL screw–cap reaction vials. The contents of the vials were vigorously mixed for 20 min and then heated in a water bath (with intermittent shaking) at 85 °C for 15 min. The vials were then cooled to ambient temperature, and the contents diluted with water to 25 mL in a volumetric flask. The diluted solution (1 mL) was mixed with water (40 mL) and 5 mL I₂/KI solution (0.0025 M I₂ and 0.0065 M KI) and then adjusted to a final volume of 50 mL. The contents were allowed to stand for 15 min at ambient temperature, before absorbance measurements at 600 nm.

2.4. Carbonyl and carboxyl contents

The carbonyl content was determined according to the titrimetric method adapted by [Vanier et al. \(2012\)](#). A starch sample (2 g)

was added to 100 mL of distilled water in a 500-mL flask. The suspension was gelatinized in a boiling water bath for 20 min, cooled to 40 °C, and adjusted to a pH value of 3.2 with 0.1 mol equi/L HCl. A hydroxylamine reagent (15 mL) was then added to the mixture. The flask was stoppered and placed in a 40 °C water bath for 4 h with slow stirring. The excess hydroxylamine was determined by rapidly titrating the reaction mixture to a pH value of 3.2 with standardized 0.1 mol equi/L HCl. A blank determination with only the hydroxylamine reagent was performed in the same manner. The hydroxylamine reagent was prepared by first dissolving 25 g of hydroxylamine hydrochloride in 100 mL of 0.5 mol equi/L NaOH, before the final volume was adjusted to 500 mL with distilled water. The carbonyl content was expressed as the quantity of carbonyl groups per 100 glucose units (CO/100 GU), as calculated by Equation (1).

$$\text{CO}/100\text{GU} = \frac{(V_b - V_s) \times M \times 0.028 \times 100}{W} \quad (1)$$

where V_b is the volume of HCl used for the blank (mL), V_s is the volume of HCl required for the sample (mL), M is the molarity of HCl and W is the sample weight (dry basis).

The carboxyl content of the oxidized starch was determined according to the modified procedure of [Chattopadhyay, Singhal, and Kulkarni \(1997\)](#). Approximately 2 g of a starch sample was mixed with 25 mL of 0.1 mol equi/L HCl, and the slurry was stirred occasionally for 30 min with a magnetic stirrer. The slurry was then vacuum filtered through a 150 mL medium porosity fritted glass funnel and washed with 400 mL of distilled water. The starch cake was then carefully transferred into a 500 mL beaker, and the volume was adjusted to 300 mL with distilled water. The starch slurry was heated in a boiling water bath with continuous stirring for 15 min to ensure complete gelatinization. The hot starch dispersion was then adjusted to 450 mL with distilled water and titrated to a pH value of 8.3 with standardized 0.01 mol equi/L NaOH. A blank test was performed with unmodified starch. The carboxyl content was expressed as the quantity of carboxyl groups per 100 glucose units (COOH/100 GU), as calculated by Equation (2).

$$\text{COOH}/100\text{GU} = \frac{(V_b - V_s) \times M \times 0.045 \times 100}{W} \quad (2)$$

where V_s is the volume of NaOH required for the sample (mL), V_b is the volume of NaOH used to test the blank (mL), M is the molarity of NaOH and W is the sample weight (dry basis).

2.5. Scanning electron microscopy (SEM)

The morphology of the starch granules was examined using a Shimadzu SSX-550 scanning electron microscope. The starch samples were initially suspended in acetone at 1 g/100 mL. A small quantity of each sample was spread directly on the surface of the stub and dried in an oven at 32 °C for 24 h. Subsequently, all of the samples were coated with gold and examined using a scanning electron microscopy under an acceleration voltage of 15 kV at a magnification of 200×.

2.6. Pasting properties

The pasting properties of the starch samples were determined using a Rapid Visco Analyser (RVA–4, Newport Scientific, Australia) with a Standard Analysis 1 profile. The viscosity was expressed in rapid visco units (RVU). The starch (2.0 g of 14 g/100 g wet basis) was weighed directly in the RVA (Rapid Visco Analyser) canister, and 25 mL of distilled water was then added to the canister. The

sample was held at 50 °C for 1 min, heated to 95 °C in 3.5 min, and then kept at 95 °C for 2.5 min. The sample was cooled to 50 °C in 4 min and then kept at 50 °C for 1 min. The rotating speed was maintained at 960 rpm for 10 s, and it was maintained at 160 rpm during the remaining process.

2.7. Thermal analysis

The gelatinization characteristics of starches were determined using a differential scanning calorimeter (DSC model 2010, TA Instruments, New Castle, USA). Starch samples (approximately 2.5 mg, dry basis) were weighed directly in an aluminum pan, and distilled water was added to obtain a starch–water ratio of 1:3 (g:g). The sample pans were then heated from 30 to 100 °C at a rate of 10 °C/min.

2.8. Swelling power and solubility of starches

The swelling power and solubility of the starches were determined as method adapted by Vanier et al. (2012). Samples (1 g) were mixed with 50 mL of distilled water in centrifuge tubes. The suspensions were heated at 90 °C for 30 min. The gelatinized samples were then cooled to room temperature and centrifuged at 1000 g for 20 min. The supernatant was dried at 110 °C until a constant weight was achieved, so that the soluble fraction could be quantified. Solubility was expressed as the g/100 g of the dried solid weight based on the dry sample weight. Swelling power was represented as the ratio of wet sediment weight to initial dry sample weight (deducting the amount of soluble starch).

2.9. Gel texture profile analysis

The gel texture profile was analyzed with a Texture Analyser (TA.XTplus, Stable Micro Systems) according to the method reported by Horndok and Noomhorm (2007) with some modifications. After taking the RVA measurement, the gelatinized mixture in the canister remained at 20 °C for 24 h allowing the formation of a solid gel (2.0 g with 14 g/100 g moisture basis). The canister was sealed with parafilm to prevent moisture loss during storage. The gels were punctured at 1.0 mm/s for a distance of 10.0 mm using a stainless steel cylindrical probe (P/20; diameter of 20 mm). The hardness, springiness, cohesiveness and gumminess parameters of the gel were analyzed.

2.10. Preparation of starch films

Films were prepared by casting 3.0, 4.0 and 5.0 g potato starch/100 mL water, using glycerol as the plasticizer (0.30 g/g of starch). The film-forming suspension was heated with continuous mixing at 90 °C for 5 min according to Talja, Helén, Roos, and Jouppila (2007). Film-forming solutions were poured onto plexiglass plates and dried at 40 °C for 16 h in an oven with circulating air. The dried film samples were conditioned at 25 °C.

2.11. Film thickness, color and water solubility

The thickness of the starch films was determined using a micrometer to the nearest 0.001 mm at eight random positions around the film, and the average values were used in the calculations. The color of the starch films was determined with a Minolta colorimeter operating with D65 (day light) and using the CIELab color parameters. The CIELab color parameter was determined by the attribute L^* (white: 100; black: 0). The solubility of the starch films was calculated as the g/100 g of solubilised film dry matter after immersion for 24 h in water at 25 °C (Contard, Duchez, Cuq, &

Guilbert, 1994). Film discs (diameter of 2 cm) were cut, weighed, immersed in 50 mL of distilled water, and stirred at 125 rpm. The amount of dry matter in the initial and final samples was determined by drying the samples at 105 °C for 24 h.

2.12. Mechanical properties

The tensile strength was evaluated by a tensile test using a Texture Analyser (TA.XTplus, Stable Micro Systems) based on the ASTM D-882-91 method (ASTM, 1996). The films were cut in strips (25 mm × 85 mm) and conditioned for 2 days. Before testing, the thickness of the strips was measured at eight points. The force and distance were recorded during extension of the strips at 0.8 mm/s up to the breaking point. The tensile strength was calculated by dividing the maximum force by the film cross-section. The tensile strength (Equation (3)) value was calculated with the following equation:

$$TS = \frac{F_m}{A} \quad (3)$$

where TS is the tensile strength (MPa); F_m is the maximum force (N); A is the area of film cross-section (thickness × width; m²).

2.13. Water vapor permeability

Water vapor permeability (WVP) tests were conducted using the E96-95 ASTM standard method (ASTM, 1995). Each film sample was sealed over the circular opening of a permeation cell containing anhydrous calcium chloride (0% RH). These cells were then placed on desiccators with a saturated sodium chloride solution (75% RH) at 25 °C. After the samples reached steady-state conditions, the cell weight was measured at 24 and 48 h. The WVP was calculated by the Equation (4).

$$WVA = \frac{\Delta W}{t} \frac{X}{A \Delta P} \quad (4)$$

where WVP is the water vapor permeability (g·mm/m²·day·kPa); ΔW is the weight gain by desiccant (g); X is the film thickness (mm); t is the incubation time period (days); A is the area of the exposed film surface (m²); and ΔP is the difference of partial pressure (kPa).

2.14. Statistical analysis

Analytical determinations for the samples were performed in triplicate and standard deviations were reported, except for thermal analysis. A comparison of the means was ascertained by Tukey's test to a 5% level of significance using analysis of variance (ANOVA).

3. Results and discussion

3.1. Carbonyl and carboxyl contents

The carbonyl and carboxyl contents of native starch and starches oxidized with different concentrations of active chlorine are shown in Table 1. Oxidation with sodium hypochlorite increased the carbonyl content of potato starch, but there is no significant difference between the carbonyl content of the modified starches with 1.0 and 1.5 g/100 g of active chlorine. The oxidized starch with the highest active chlorine concentration (1.5 g/100 g) showed a higher carboxyl content as compared to other oxidized potato starches (Table 1). The presence of carbonyl and carboxyl groups in oxidized

Table 1
Carbonyl and carboxyl contents and amylose content of the oxidized potato starches.

Active chlorine (g/100 g) ^a	Carbonyl content (CO/100 GU)	Carboxyl content (COOH/100 GU)	Sum (CO + COOH)	Amylose content (g/100 g)
Native	0.028c	–	–	26.90c
0.5	0.068b	0.039b	0.107b	25.76c
1.0	0.111a	0.052ab	0.164a	31.49b
1.5	0.139a	0.067a	0.191a	34.97 ^a

^a Different letters in the same column differ statistically ($p < 0.05$). GU: glucose units.

starches is due to oxidation of the hydroxyl groups of starch molecules in carbonyl groups and then the carboxyl groups.

Several authors studied the oxidation of corn, banana, potato, rice and common bean starches with different concentrations of sodium hypochlorite and reported that there was a gradual increase in the carbonyl and carboxyl contents with the increasing concentration of active chlorine (0, 1 and 2 g/100 g) (Kuakpetoon & Wang, 2001; Spier et al., 2013; Vanier et al., 2012). However, in this work, the oxidized starches with 1.0 and 1.5 g/100 g did not show significant differences (Table 1), since the levels of carbonyl and carboxyl in oxidized starches depend on various factors such as the starch source, oxidant type and concentration, time, pH and temperature of reaction.

3.2. Starch granules morphology

The micrographs of native and oxidized (1.5 g/100 g active chlorine) starch granules are shown in Fig. 1. The SEM data showed that native and oxidized potato starch granules have both oval and spherical shapes presenting large and small granules, which is characteristic of potato starch. The oxidation did not affect the morphology of the potato starch granules (Fig. 1). However, other authors have shown that oxidation can affect the granule with the presence of pores in the surface (Kuakpetoon & Wang, 2008). Spier et al. (2013) modified corn starch and reported that the oxidation in combination with an alkaline treatment affected the granule surface with the presence of holes. According to Martínez-Bustos, Amaya-Llano, Carbajal-Arteaga, Chang, and Zazueta-Morales (2007), the oxidized starch granules from cassava, potato and jicama showed little erosion in the form of grooves; and they reported that on the contrary, oxidation left the granules with a very smooth surface.

3.3. Pasting properties

The pasting properties were observed by the changes in viscosity during the heating of starch slurry. The pasting properties

Table 2
Pasting properties of potato starches oxidized with different concentrations of active chlorine.

Active chlorine (g/100 g) ^a	Pasting temperature (°C)	Peak viscosity (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)
Native	61.1a	504.2c	359.7b	173.8c	29.3a
0.5	61.1a	642.9a	397.5a	275.5a	30.0a
1.0	60.5a	560.6b	392.6a	195.8b	27.9a
1.5	61.7a	324.6d	190.3c	151.8d	17.5b

^a Different letters in the same column differ statistically ($p < 0.05$).

of native starch and starches oxidized with 0.5, 1.0 and 1.5 g/100 g active chlorine are shown in Table 2 and the viscoamylographic curves are shown in Fig. 2. The oxidation of potato starches with sodium hypochlorite resulted in changes in paste characteristics, and these changes were more intense for the oxidized starch with the highest concentration of oxidant.

The oxidation of potato starch at low levels (0.5 and 1.0 g/100 g active chlorine) increased the peak viscosity while the starch oxidized with the highest active chlorine concentration (1.5 g/100 g) presented a reduction in peak viscosity as compared to the native starch (Fig. 2). The increase in viscosity of starches with a low degree of oxidation may be due to partial depolymerization of the starch, facilitating swelling (Vatanasuchart, Naivikul, Charoenrein, & Sriroth, 2005). Xie, Liu, and Cui (2005) also reported that with low levels of oxidation with sodium hypochlorite occur an increase in paste viscosity. The effect of the oxidation on peak viscosity is dependent of the reaction conditions and intensity. According to Dias et al. (2011), the oxidation promotes depolymerization of the starch amylose and amylopectin molecules, which decreases the viscosity and retrogradation. The carboxyl and carbonyl radicals are larger than hydroxyls, increasing the space between the amylose chains, and this avoids the approximation of the molecules, preventing retrogradation.

The oxidation with different concentrations of active chlorine did not change the pasting temperature of potato starches; this behavior is consistent with that found by Vanier et al. (2012). They studied the oxidation of common bean starch, and also found no change in the pasting temperature between native starch and oxidized starches. However, Spier et al. (2013) reported a reduction in the pasting temperature of corn starch resulting from oxidation with 1 and 2 g/100 g of active chlorine as compared to the native starch where there was a reduction in pasting temperature as increased with the active chlorine concentration.

Based on the results of the breakdown it is possible to assess the starch stability at high temperatures, which is the resistance of starch to the heating and mechanical stirring. The samples of oxidized starches with 0.5 and 1.0 g/100 g of active chlorine showed

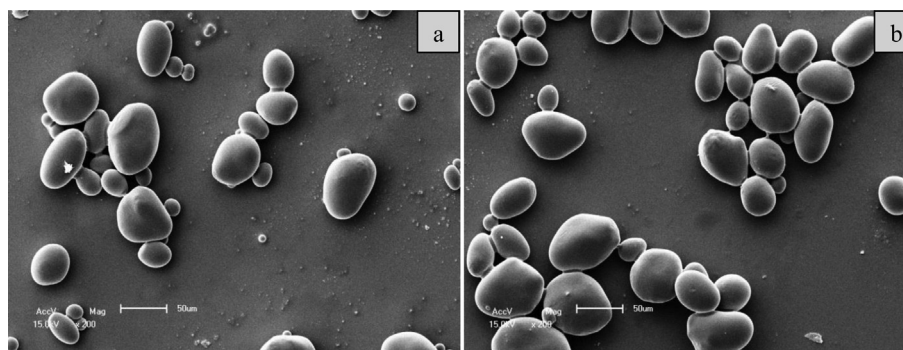


Fig. 1. Scanning electron micrographs of potato starches: native starch (a) and starch oxidized with 1.5 g/100 g of active chlorine (b).

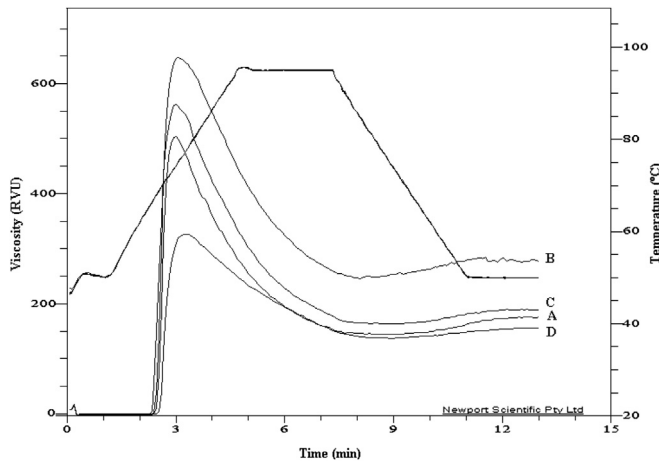


Fig. 2. RVA curves of potato starches: native starch (A); starch oxidized with 0.5 g/100 g of active chlorine (B); starch oxidized with 1.0 g/100 g of active chlorine (C); starch oxidized with 1.5 g/100 g of active chlorine (D).

a higher breakdown as compared to native starch. However, oxidation at the highest active chlorine concentration reduced the breakdown of potato starch, showing a greater stability to heat and mechanical agitation and a lower retrogradation compared to other oxidized starches.

After lowering the temperature of the RVA analysis equipment of 95 °C–50 °C, retrogradation occurs, which is a re-association between the molecules of amylose and amylopectin. The retrogradation of native starch, oxidized with 0.5 and 1.0 g/100 g of active chlorine starches, does not differ statistically, only when the oxidation at the highest concentration of active chlorine (1.5 g/100 g) was applied, the capacity of oxidized starch retrogradation reduced, when comparing to native starch (Table 2). The decrease in the ability of retrogradation of the oxidized starch with 1.5 g/100 g of oxidant may be due to a high formation of carboxylic and carbonyl groups during the oxidation process, since after the gelatinization it is difficult to re-associate the amylose molecules in the presence of these groups.

3.4. Thermal properties

The gelatinization process is characterized by an endotherm obtained by a differential scanning calorimetry (DSC). The parameters of temperature at the onset of gelatinization (T_0), the temperature at peak (T_p), the temperature at the end of gelatinization (T_c) and the gelatinization enthalpy (ΔH) are shown in Table 3.

The oxidized potato starches with different concentrations of active chlorine had gelatinization temperatures similar to native starch; however, the oxidized starch with 1.5 g/100 g active chlorine showed higher gelatinization enthalpy compared to native starch and to starches oxidized with the lowest levels of active

Table 3
Thermal properties of potato starches oxidized with different concentrations of active chlorine.

Active chlorine (g/100 g) ^a	T_0 (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	ΔT (°C)
Native	61.6	65.3	70.4	-14.5	8.8
0.5	61.2	64.9	70.3	-14.7	9.1
1.0	60.7	64.2	69.5	-14.7	8.9
1.5	62.0	65.6	71.2	-16.1	9.2

^a T_0 : temperature at the onset of gelatinization, T_p : temperature at peak, T_c : temperature at the end of gelatinization, ΔH : enthalpy of gelatinization and ΔT : range of gelatinization ($T_c - T_0$).

chlorine (0.5 and 1.0 g/100 g) (Table 3). Unlike in studies with corn (Sandhu et al., 2008) and cassava (Sangseethong, Termvejsayanon, & Sriroth, 2010) oxidized starches, the authors found a reduction in the gelatinization temperatures (T_0 , T_p and T_c) and lower values of enthalpy of oxidized starches when compared to native starch. These thermodynamic characteristics of gelatinization can be largely associated with the weakening of the intermolecular bonds responsible for the crystal structure of amylopectin, due to the incorporation of carboxyl groups in the starch granules (Sandhu et al., 2008). In addition, the starch granules undergo a chemical modification that may show, on the surface, disturbances such as fractures and pores, which also facilitate the penetration of water in the granules (Garg & Jana, 2011). Variations in the thermal properties of starches from different sources may be due to the granule composition which could be the ratio of amylose/amylopectin, the residual lipids and protein, the molecular structure of amylopectin, morphology and the distribution of starch granules.

3.5. Swelling power, solubility and gel texture of starches

The swelling power indicates the ability of the starch to hydrate under specific conditions, after weighing the tubes containing swollen starch granules; and the solubility indicates the percentage of molecules leached from the granules after their swelling. The results of the swelling power and the solubility of the starches are presented in Table 4. The oxidation with 1.5 g/100 g active chlorine reduced the swelling power of the potato starch as compared to the native and oxidized (0.5 and 1.0 g/100 g active chlorine) starches. This reduction in swelling power after oxidation can be attributed to structural disintegration within the starch granule during the modification process.

Lawal, Adebowale, Ogunsanwo, Barba, and Ilo (2005) who studied the effects of acid and the oxidative modification of corn starch observed a reduction in the swelling power promoted by these chemical modifications compared to native starch. These authors also attribute the reduction in the swelling power after oxidation to a structural disintegration within the starch granule during the modification process. However, the oxidation did not alter the solubility compared to native starch, with no significant difference between samples.

The oxidation process results in a depolymerization of both the chains of amylose and amylopectin. Amylose is more susceptible to depolymerization because it is more accessible and has linear structure (Wang & Wang, 2003). Wang and Wang (2003) reported a lower swelling power (analyzed at 95 °C) of oxidized corn starch as compared to native corn starch. They suggested that this phenomenon occurs due to hydrolysis of the amylopectin chain at high temperatures and the presence of a porous structure in the granule, which is able to absorb water during heating, but cannot retain absorbed water under centrifugation.

The parameters of hardness, springiness, cohesiveness and gumminess of the starch gels are shown in Table 4. The oxidation increased the hardness and adhesiveness of the potato starch gels, with the exception of the oxidized starch with 1.0 g/100 g active chlorine. The oxidized starch with the highest concentration of active chlorine (1.5 g/100 g) had the highest gel hardness (Table 4). This is unlike Vanier et al. (2012), who reported that the oxidation of common bean starch was affected differently depending on the level of oxidation. The oxidized starches with a low concentration of active chlorine (0.5 g/100 g) did not differ from native starch; and modified starches with 1.0 and 1.5 g/100 g active chlorine had lower gel hardness than the native starch.

The springiness corresponds to the capacity of the sample to return to its original state after compression. For springiness, only the oxidized starch with 1.5 g/100 g active chlorine was different

Table 4
Swelling power, solubility and gel texture of potato starches oxidized with different concentrations of active chlorine.

Active chlorine (g/100 g) ^a	Swelling power (g/g)	Solubility (g/100 g)	Hardness (g)	Springiness (mm)	Cohesiveness	Gumminess (g)
Native	15.8a	5.6a	203.1b	0.85b	0.61a	123.5b
0.5	15.0a	5.2a	331.9a	0.86b	0.55a	181.2a
1.0	15.0a	5.1a	247.2b	0.88b	0.85a	162.3a
1.5	11.7b	6.4a	360.4a	0.92a	0.53a	189.9a

^a Different letters in the same column differ statistically ($p < 0.05$).

from the other samples, with a higher value compared to native starch. The oxidation did not affect the cohesiveness of the starch gels. However, the oxidation of the potato starch with sodium hypochlorite increased the gumminess of the gels (Table 4).

3.6. Physical, mechanical and barrier properties of films

The films after drying were shown to be continuous, without fractures or breaks and visually transparent. The results of the thickness, solubility, L^* parameter, tensile strength and water vapor permeability of the films of native and oxidized potato starches are shown in Table 5. The film thickness the potato starch ranged from 0.150 to 0.290 mm; this parameter influences the film properties and should be controlled to allow a uniform material. Film thickness may vary with the composition, the amount of the filmogenic solution and the film processing.

The potato starch films maintained their integrity after immersion in water for 24 h under constant stirring. The dissolution of a hydrophilic polymer involves penetration or diffusion of water inside and the swelling due to rupture of polymer chains and relaxation (Turhan & Afbaz, 2004). Therefore, the low dissolution rate of the films shows a high cohesion of the matrix. For all the films of potato starch, the water solubility was increased when the starch concentration increased from 3 g/100 mL to 5 g/100 mL (Table 5). The films prepared with 3 g/100 mL oxidized starch to 0.5 and 1.5 g/100 g active chlorine had a lower water solubility compared to native starch. The film prepared with 5 g/100 mL oxidized starch with the highest concentration of active chlorine showed a lower solubility compared to the film produced with 5 g/100 mL native starch (Table 5), demonstrating that this concentration of starch oxidation reduced the solubility of the film. The reduction in water solubility of the films of oxidized potato starches can be attributed to the increase of the interactions between the amylose molecules, as well as the strong intramolecular bonds promoted by the oxidation of the starch, which reduces the capacity of the film to absorb water (Zavareze et al., 2012).

The L^* parameter of the colorimetric assay characterizes the whiteness of the material. The values of lightness (L^*) vary between zero (black) to 100 (white). The lightness (L^*) of the films ranged

from 87.6 to 89.7. The films with higher starch concentration showed a lower lightness compared to the films with less starch; and the oxidation of the starch did not affect the lightness of the films. This parameter is important in diverse applications of the films in which the visual characteristic of the product is required.

Films must have sufficient strength to ensure their integrity when used as packaging. The tensile strength of the films ranged from 1.5 to 6.7 MPa and, regardless of the starch type used in the film solution of the films, there was an increase in the tensile strength of films (Table 5), probably due to the increased thickness of the films, which is a variable that influences the mechanical properties. The films prepared with potato starch oxidized with the highest concentration of active chlorine (1.5 g/100 g) had lower a tensile strength when compared to films prepared with native starch and oxidized with 0.5 and 1.0 g/100 g active chlorine (Table 5). This behavior can be attributed to weakened hydrogen bonding between starch chains.

Zavareze et al. (2012) found a higher RT in films of oxidized potato starch with 0.5 g/100 g active chlorine when compared to native starch. The different results of tensile strength films between Zavareze et al. (2012) and the present study could be attributed to the content of carboxylic groups formed since our study found 0.039 COOH/100 GU in content, and in the study of Zavareze et al. (2012) the carboxyl content was 0.214 COOH/100 GU. According to Zhang, Zhang, Wang, and Wang (2009) the presence of carbonyl and carboxyl groups in oxidized starch can produce hydrogen bonds with the OH groups of the amylose and amylopectin molecules, and these links may provide greater structural integrity in the polymer matrix, thus increasing the tensile strength.

The water vapor permeability of the films ranged from 4.4 to 9.9 g·mm/m²·day·kPa and the starch film with a higher level of oxidation showed a higher water barrier (Table 5). As previously noted, this oxidation level formed more carbonyl groups in the molecule of potato starch (Table 1), which, when compared with hydroxyl groups, which have been substituted, have a lower affinity for water molecules; the film consequently has less ability to transfer water. There are also other important factors that may affect the PVA films, such as the degree of crystallinity of the polymer, the presence of a plasticizer during its preparation, the

Table 5
Thickness, solubility, color, tensile strength and water vapor permeability (WVP) of films of oxidized potato starches with different concentrations of active chlorine.

Active chlorine (g/100 g) ^a	Starch (g/100 mL)	Thickness (mm)	Solubility (g/100 g)	L^*	Tensile strength (MPa)	WVP (g·mm/m ² ·day·kPa)
Native	3	0.15c	14.0d	89.6a	3.8d	9.3*
	4	0.18c	23.9b	89.2a	4.3d	9.4*
	5	0.23b	24.8ab	87.7b	6.7a	9.9*
0.5	3	0.16c	12.7e	89.3a	3.5d	8.5*
	4	0.23b	18.2c	88.3ab	3.9d	9.3*
	5	0.28a	21.7bc	87.6b	5.3c	9.5*
1.0	3	0.17c	15.3d	89.4a	4.1d	7.4ab
	4	0.23b	21.9bc	89.1a	5.8bc	7.7ab
	5	0.29a	26.0a	87.7b	6.4ab	7.6ab
1.5	3	0.16c	12.9e	89.7a	1.8e	5.8bc
	4	0.20bc	12.7e	89.4a	1.9e	4.4c
	5	0.25ab	18.3c	88.6b	2.3e	4.5c

^a Different letters in the same column differ statistically ($p < 0.05$).

size of the molecule, as well as the thickness and the presence of pores or fractures on the film surfaces (Argüello-García et al., 2014). Another factor that may influence the barrier property of the films is the relative humidity, which brings as a consequence the increase in volume of the material and therefore an increase in PVA of films.

4. Conclusions

The oxidation with different concentrations of active chlorine affects differently the characteristics of potato starches. The increase in active chlorine concentration increased the intensity of oxidation of the potato starches. The films produced with oxidized starches have different properties depending on the degree of oxidation. The films made with oxidized starch with the highest level of active chlorine (1.5 g/100 g) had a lower tensile strength, regardless of the amount of starch used, when compared to native starch films. However, these films exhibited lower water solubility and water vapor permeability, which enables the use of the oxidized starch films in products with higher water activity as compared to the native starch films.

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