Development of oxidised and heat–moisture treated potato starch film

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A B S T R A C T

This study investigated the effects of sodium hypochlorite oxidation and a heat–moisture treatment of potato starch on the physicochemical, pasting and textural properties of potato starches in addition to the water vapour permeability (WVP) and mechanical properties of potato starch films produced from these starches. The carbonyl contents, carboxyl contents, swelling power, solubility, pasting properties and gel texture of the native, oxidised and heat–moisture treated (HMT) starches were evaluated. The films made of native, oxidised and HMT starches were characterised by thickness, water solubility, colour, opacity, mechanical properties and WVP. The oxidised and HMT starches had lower viscosity and swelling power compared to the native starch. The films produced from oxidised potato starch had decreased solubility, elongation and WVP values in addition to increased tensile strength compared to the native starch films. The HMT starch increased the tensile strength and WVP of the starch films compared to the native starch.

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1. Introduction

There has been a renewed interest in edible and biodegradable films. These films have the potential to replace conventional packaging in some applications. Films made from edible natural polymers are an important packaging type. These types of films are primarily used to extend the shelf-life and quality of foods by preventing changes in aroma, taste, texture or handling characteristics. Starch is an important biopolymer for industries due to its large availability and low cost. Thickening agents, stabilisers, emulsifiers, fuel ethanol and bioplastics can be produced from native and modified starch (Tovanen, Mäki-Arvela, Sorokin, Salmia, & Murzina, 2009). Although the functional, organoleptic and mechanical properties of starch films can be modified by the addition of various chemicals in certain amounts (Mali, Grossmann, García, Martino, & Zaritzky, 2004), it is undesirable to add chemicals to starch films because they are edible. People prefer to modify the properties of the film by improving the properties of starch itself, so many modified starches have been developed. The films made from modified starches exhibit different properties. Starches modified by oxidation or hydrothermal treatment have a film-forming capacity.

Oxidised-starch is widely used in industries to provide surface sizing and coating properties. Although the main outlets for oxidised-starch are in the paper and textile industries, the application of oxidised starch in the food industry is increasing due to its low viscosity, high stability, high transparency, excellent film-forming capacity and binding properties (Hu, Chen, & Gao, 2009). The oxidation of starch allows carboxyl and carboxyl groups to be substituted on the polymer backbone by replacing the hydroxyl groups. Many types of oxidising reagents can be used to oxidise starch, such as hypochlorite (Dias et al., 2011; Kuakpetoon & Wang, 2001; Wang & Wang, 2003) and hydrogen peroxide (Zhang, Zhang, Wang, & Wang, 2009). Oxidised starch is produced by reacting starch with a specific amount of oxidising reagent under controlled temperature and pH conditions (Wang & Wang, 2003). During starch oxidation, hypochlorite can be consumed by three possible mechanisms as follows: lipid oxidation, depolymerisation of amyllose and amylopectin, and formation of carboxyl and carbonyl groups. The hydroxyl groups of starch molecules are first oxidised to carbonyl groups and then to carboxyl groups. The number of carbonyl and carboxyl groups on the oxidised starch indicates the level of oxidation (Kuakpetoon & Wang, 2001).

Heat–moisture treatment (HMT) is a physical modification that involves low moisture levels, which are usually in the restricted range of 10–30%, and heating at high temperatures (90–120 °C) for a period of time ranging from 15 min to 16 h. HMT controls molecular mobility at high temperatures by limiting the amount of water. HMT-induced changes in the structure and properties of starch have been found to vary with the starch source and amylose content. For instance, tuber starches are more sensitive to HMT than legume or cereal starches (Gunaratne & Hoover, 2002). HMT has been used to prepare biodegradable films. Singh, Bawa,
Riar, and Saxena (2009) characterised biodegradable films from native and HMT chestnut starches, and they reported that the film elaborated with HMT starch has higher peak force, puncture energy and tensile strength and lower solubility compared to the film made from native starch. These authors reported that the film-forming ability of native and heat–moisture-treated starches shows a promising future for exploration as packaging material.

Pure native starch films are brittle compared with synthetic polymers, such as polyethylene, and these films usually need to be plasticised. Starch films tend to absorb large quantities of water at elevated relative humidity (RH) conditions due to their inherent hydrophilic nature. The most effective plasticisers should generally most closely resemble the structure of the polymer that they plasticise. Thus, the most commonly used plasticisers in starch-based films are polysols, such as sorbitol and glycerol (Hu et al., 2009). Water is also an effective plasticiser for polysaccharide materials, and it has a significant role in determining the properties of starch film.

The development and production of biodegradable starch-based materials have been spurred by oil shortages and a growing interest in easing the environmental burden of petrochemically derived polymers. One of the unique characteristics of starch-based polymers is their processing properties, which are much more complex than conventional polymers (Liu, Xie, Yu, Chen, & Li, 2009). According to Hu et al. (2009), native potato starch film has high tensile strength because of its high molecular weight, which causes the paste of the native potato starch to have a high viscosity. Therefore, it is impossible to produce potato starch paste with high starch content because it would result in a lower efficiency in film-making. Moreover, the transparency of native potato starch paste is poorer than that of oxidised potato starch. Therefore, these authors chose oxidised potato starch to prepare edible film because it has a lower viscosity and higher transparency than native potato starch film. However, no previous studies have been reported on the production of edible and biodegradable films made from potato starch oxidised with sodium hypochlorite or treated with heat and moisture. The oxidation and hydrothermal treatment promotes a lower viscosity of starch, which is important for the development of potato starch film. The objective of this study was to evaluate the effect of oxidation with sodium hypochlorite and HMT on the physicochemical, pasting and textural properties of potato starches in addition to the WVP and mechanical properties of oxidised and HMT potato starch films.

2. Materials and methods

2.1. Materials

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% sodium bisulphite at a 1:7 (w/v) ratio for 2 h after the dispersion was ground in a blender (Brita-nia, 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 12%. The amylose content of the native potato starch was determined using the method proposed by Juliano (1971), and the amylose content of the native potato starch was determined to be 22.03%.

2.2. Oxidation

The oxidation of potato starch was performed as previously described by Dias et al. (2011). The starch (300 g and 12% moisture) was suspended in 500 ml of distilled water, heated to 40 °C and subjected to sodium hypochlorite treatment with 0.5% active chlorine. The pH value was adjusted to 7.0 with 0.5 M hydrochloric acid and 0.5 M sodium hydroxide. After 60 min of reaction, the starch was withdrawn from the reactor, filtered through medium porosity filter paper in a Buchner funnel, washed with 1200 ml of distilled water, resuspended in distilled water and refiltered three times. The oxidised starch was dried in a forced air oven at 40 °C until the starch retained approximately 12% moisture.

2.3. Heat–moisture treatment (HMT)

The HMT of the potato starch was performed on the samples with moisture levels adjusted to 20% and equilibrated at 4 °C overnight. The samples were then placed in sealed glass tubes and autoclaved at 110 °C for 1 h (Hormdok & Noomhorm, 2007). The treated samples were subsequently dried at 40 °C until the moisture content of the samples reached approximately 12%, and the samples were then ground.

2.4. Carbonyl and carboxyl contents

The carbonyl content was determined as previously described by Smith (1967). A dry sample (4 g) of starch was dispersed in distilled water (100 ml) and heated in a boiling water bath for 30 min. The solution was continuously stirred until the starch was completely gelatinised. The gelatinised samples were kept at 40 °C. The pH value was adjusted to 3.2 with 0.1 M HCl, and 15 ml of a hydroxylamine chloride solution was then added. The hydroxylamine reagent was prepared by dissolving 25 g of reagent grade hydroxylamine chloride in water and adding 100 ml of 0.5 M NaOH; distilled water was then added to reach a final volume of 500 ml. The samples were covered with plastic film and placed in an oven at 38 °C for 4 h, and they were then rapidly titrated to a pH value of 3.2 with 0.1 M HCl. The carbonyl content was expressed as the quantity of carbonyl groups per 100 glucose units (COOH/100 GU) as calculated by Eq. (1).

$$\text{COOH/100 GU} = \frac{(V_b - V_s) \times M \times 0.028 \times 100}{W}$$ (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 (d.b).

The carboxyl content was determined according to the method previously described by Parouvoari, Hamunen, Forssell, Autio, and Poutanen (1995). A dry sample (5 g) of starch was dispersed in distilled water (25 ml). The dispersions were stirred for 30 min and then centrifuged. The residue was washed with distilled water, and 300 ml of distilled water was then added to the residue. The dispersion was heated in a boiling water bath with continuous stirring for 30 min until the starch was completely gelatinised. While still hot, the samples were titrated to a pH value of 8.2 with 0.01 M NaOH. The carboxyl content was expressed as the quantity of carboxyl groups per 100 glucose units (COOH/100 GU) as calculated by Eq. (2).

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

2.5. Swelling power and solubility of starches

The swelling power and solubility of the starches were determined as described by Leach, McCowen, and Schoch (1959).
Samples (1.0 g) were mixed with 50 ml of distilled water in centrifuge tubes. The suspensions were heated at 90 °C for 30 min. The gelatinised samples were then cooled to room temperature and centrifuged at 1000g for 20 min. The supernatants were dried at 110 °C until a constant weight was achieved so that the soluble fraction could be quantified. The solubility was expressed as the percentage of the dried solid weight based on the dry sample weight. The swelling power was represented as the ratio of wet sediment weight to initial dry sample weight (deducting the amount of soluble starch).

2.6. Pasting properties

The pasting properties of the starch samples were determined using a Rapid Visco Analyser (RVA-4; Newport Scientific, Australia) with the Thermocline programme (Windows version 1.10) according to Newport Scientific. (1995). The viscosity was expressed in Rapid Visco Units (RVU). Starch (2.5 g with 14 g/100 g moisture basis) was weighed directly in the RVA-4 canister, and 25 ml of distilled water was then added. The sample was held at 50 °C for 1 min, heated to 95 °C in 3.5 min, and then held at 95 °C for 2.5 min. The sample was then cooled to 50 °C in 4 min and was held at 50 °C for 2 min. The rotating speed was held at 960 rpm for 10 s, and the speed was then maintained at 160 rpm during the process. Parameters including peak viscosity, holding viscosity and final viscosity were recorded.

2.7. Gel texture profile analysis

The gel texture profile was analysed with a Texture Analyser (TA.XTplus, Stable Micro Systems) according to the method reported by Hormdok and Noomhorm (2007) with some modifications. After taking the RVA measurement, the gelatinised mixture in the canister remained at 4 °C for 24 h allowing the formation of a solid gel (2.5 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 peak force was reported as the gel hardness (height of the first peak). The springiness (ratio between the recovered height after the first compression and the original gel height) of the gel was also determined. Cohesiveness was calculated as the percentage of the dried solid weight based on the dry sample weight. The swelling power was represented as the ratio of wet sediment weight to initial dry sample weight (deducting the amount of soluble starch).

2.8. Preparation of starch films

Films were prepared by casting 3.0%, 4.0% and 5.0% potato starch suspensions using glycerol as the plasticiser (0.30 g/g of starch). The film-forming suspension was heated with continuous immersion for 24 h in water at 25 °C (Gontard, 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. The solubility was calculated using the Eq. (3).

\[
SW(\%) = \frac{(W_a - W)}{W} \times 100
\]

where SW is solubility in water; and \(W_a\) and \(W\) are the dry sample weights before and after the test, respectively.

2.10. Film colour and opacity

The colour of the potato starch films was determined with a Minolta colourimeter operating with D65 (day light) and using the CIELab colour parameters. The CIELab colour parameters identify colour with three attributes as follows: \(L^+\) (white: 100; black: 0), \(a^+\) (positive: red; negative: green) and \(b^+\) (positive: yellow; negative: blue). The instrument was calibrated using a white standard colour calibration plate. The colour difference (\(\Delta E^+\)) as compared to a white standard tile was calculated using Eq. (4).

\[
\Delta E^+ = \sqrt{(L^* - L_{e*})^2 + (a^* - a_{e*})^2 + (b^* - b_{e*})^2}
\]

Films were prepared by casting 3.0%, 4.0% and 5.0% potato starch suspensions using glycerol as the plasticiser (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 Joupilla (2007). Film-forming solutions were poured onto plexiglass plates (diameter of 15 cm) and dried at 40 °C for 16 h in an oven with circulating air. The dried film samples were conditioned at 25 °C.

2.9. Film thickness and water solubility

Film thickness was determined using a micrometre to the nearest 0.001 mm at eight random positions around the film, and the average values were used in the calculations. The solubility was calculated as the percentage of solubilised film dry matter after immersion for 24 h in water at 25 °C (Gontard, 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. The solubility was calculated using the Eq. (3).

\[
SW(\%) = \frac{(W_a - W)}{W} \times 100
\]

where SW is solubility in water; and \(W_a\) and \(W\) are the dry sample weights before and after the test, respectively.

2.12. Water vapour permeability

Water vapour 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 Eq. (8).

\[
WVA = \frac{\Delta W}{t} \frac{X}{\Delta AP}
\]

where \( WVP \) is the water vapour permeability (g mm/m² dia kPa); \( \Delta W \) 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 \( \Delta P \) is the difference of partial pressure (kPa).

2.13. Statistical analysis

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

3. Results and discussion

3.1. Carbonyl contents, carboxyl contents, solubility and swelling power

The carbonyl contents, carboxyl contents, solubility and swelling power of the oxidised and HMT potato starches are presented in Table 1. The carbonyl and carboxyl contents in the native starch were 0.044 and 0.180, respectively, and the carbonyl and carboxyl contents in the HMT starch were 0.049 and 0.185, respectively. However, the carbonyl and carboxyl contents in the oxidised starch were higher (0.065 and 0.21, respectively) than the contents in the native and HMT starches. These results demonstrated that the starch samples modified with sodium hypochlorite had a higher content of carbonyl and carboxyl groups than the native or HMT starches. The high carbonyl and carboxyl content observed in the oxidised starch may be directly related to molecular fragmentation during the oxidative treatment. The oxidative process causes depolymerisation of starch molecules by scission of glycosidic linkages (Richardson & Gorton, 2003) and allows the formation of carboxyl and carbonyl groups. However, the HMT does not promote the scission of glycosidic linkages therefore is not present in the formation of carbonyl and carboxyl groups. Therefore, the oxidised starch has a higher carbonyl and carboxyl content than native and oxidised starches. The formation of carbonyl and carboxyl groups in oxidised starches has also been found in cassava (Dias et al., 2011) and corn starches (Wang & Wang, 2003).

The oxidation and HMT of the potato starch decreased the swelling power with 35.39% and 27.40%, respectively, compared to the native starch (Table 1). This reduction in swelling power has also been attributed to the following observations: increased crystallinity, reduced hydration, increased interactions between amylose and amylopectin molecules, strengthened intramolecular bonds (Zavareze & Dias, 2011), and changes in the arrangements of the crystalline regions of starch. Guanaratne and Hoover (2002) evaluated the effect of HMT potato starch, and they reported a similar behaviour with a reduction of swelling power relative to the native starch. This behaviour was attributed to the molecular reorganisation of the starch caused by hydrothermal treatment, which restricts hydration. Therefore, the starch was less able to swell. The oxidised starch had lower swelling power compared to the native and HMT starches as these highly associated starch granules have an extensive and strongly bonded micellar structure, thereby, displaying a relatively great resistance towards swelling. However, the oxidation and HMT of potato starch increased the solubility (Table 1).

3.2. Pasting properties

The pasting properties represent the intensity of the alterations to which the starch is subjected. Compared to the native starch, the oxidised starch did not have a significantly different pasting temperature. However, the pasting temperature of the HMT starch (91.50 °C) was higher than the pasting temperature of the native starch. The oxidation and HMT decreased the viscosity peak, holding viscosity, final viscosity and setback viscosity as compared to the native starch (Table 2). Breakdown of the oxidised starch was more intense (121.30 RVU) compared to the native and HMT starches, and the HMT starch had the lowest value of breakdown (5.89 RVU) (Table 2). Li and Vasanthan (2003) also observed the same behaviour in the pasting properties when field pea starches are oxidised with sodium hypochlorite. Sangsueethong, Termweysayanon, and Siroth (2010) evaluated the effect of reaction time in hypochlorite-oxidised and peroxide-oxidised cassava starches, and they reported that the viscosity of oxidised starches decreases with increasing reaction time. The decrease in viscosity of hypochlorite-oxidised and peroxide-oxidised starches can be attributed to the oxidative cleavage of starch chains, which results in starch of a lower molecular size (Kuakpetoon & Wang, 2001). Wang and Wang (2003) reported that the pasting temperature of oxidised common corn starches is decreased and that the pasting temperature of oxidised waxy corn starches remains unchanged compared to the native starches.

The HMT caused a significant decrease in pasting temperature, peak viscosity, holding viscosity, breakdown, final viscosity and setback (Table 2). The low values of viscosity observed for the HMT starch may indicate a partial gelatinisation of starch due to the treatment conditions. The changes in the pasting properties of the heat–moisture treated starches are due to the associations among the chains in the amorphous region of the granule and the changes in crystallinity during hydrothermal treatment. The resistance of the hydrothermally treated starches to swelling is due to the rearrangement of internal forces, thereby, reducing swelling and stabilising the already swollen granules against mechanical fragmentation. The reduction of the breakdown caused by HMT suggested that the starches were more stable during continued heating and shearing, which was in agreement with a previous report by Hormdok and Noomhorm (2007) who found a reduction in the viscosity parameters of HMT rice starch. Chung, Liu, and Hoover (2009) found that HMT reduces the leached amylose in the starch granules. This may explain the fact that hydrothermally treated starch causes a reduction in the setback because HMT promotes interactions between amylose–amylose and/or amylose–amylopectin chains which reduce leached amylose content and lower the setback.

3.3. Gel texture profile analysis

Hardness is a measure of texture that corresponds to the force applied to cause deformation of a sample and is measured by a textureometer. Gel hardness, springiness, cohesiveness and gumminess
Different letters in the same column differ statistically (*p < 0.05). The results are the mean values of three determinations ± standard deviations.

Table 2
Pasting properties of oxidised and HMT potato starches.

<table>
<thead>
<tr>
<th>Starch</th>
<th>Pasting temperature (°C)</th>
<th>Peak viscosity (RVU)</th>
<th>Holding viscosity (RVU)</th>
<th>Breakdown (RVU)</th>
<th>Final viscosity (RVU)</th>
<th>Setback (RVU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>63.23&lt;sup&gt;b&lt;/sup&gt;</td>
<td>323.28&lt;sup&gt;a&lt;/sup&gt;</td>
<td>240.62&lt;sup&gt;a&lt;/sup&gt;</td>
<td>92.04&lt;sup&gt;b&lt;/sup&gt;</td>
<td>268.33&lt;sup&gt;a&lt;/sup&gt;</td>
<td>34.33&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Oxidised</td>
<td>63.97&lt;sup&gt;b&lt;/sup&gt;</td>
<td>204.08&lt;sup&gt;b&lt;/sup&gt;</td>
<td>82.71&lt;sup&gt;b&lt;/sup&gt;</td>
<td>121.30&lt;sup&gt;a&lt;/sup&gt;</td>
<td>109.58&lt;sup&gt;b&lt;/sup&gt;</td>
<td>27.33&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>HMT&lt;sup&gt;a&lt;/sup&gt;</td>
<td>91.50&lt;sup&gt;b&lt;/sup&gt;</td>
<td>16.95&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10.79&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5.89&lt;sup&gt;a&lt;/sup&gt;</td>
<td>36.70&lt;sup&gt;c&lt;/sup&gt;</td>
<td>25.92&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> HMT: heat–moisture treatment.

Table 3
Gel hardness, springiness, cohesiveness and gumminess of oxidised and HMT potato starches.

<table>
<thead>
<tr>
<th>Gel texture</th>
<th>Native</th>
<th>Oxidised</th>
<th>HMT&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (N)</td>
<td>4.60&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.70&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.31&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Springiness (mm)</td>
<td>0.90&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.99&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.67&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cohesiveness</td>
<td>0.57&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.46&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.36&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gumminess (g)</td>
<td>2.43&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.96&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.15&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Different letters in the same row differ statistically (*p < 0.05). The results are the mean values of three determinations ± standard deviations.

<sup>1</sup> HMT: heat–moisture treatment.

Values of the oxidised and HMT potato starches are listed in Table 3. Compared to the native starch, the oxidative treatment with sodium hypochlorite increased the gel hardness of the potato starch, and the HMT decreased the gel hardness of the potato starch compared to the native starch (Table 3). Moreover, the springiness presented the same behaviour as the gel hardness. However, the cohesiveness and gumminess values were reduced for both modifications as compared to the native starch (Table 3). Similar results have been reported by Dias et al. (2011) who found that the gel hardness of cassava starch oxidised with sodium hypochlorite is increased compared to the native starch. These authors reported that the increase observed in gel hardness in the starch oxidised with sodium hypochlorite may be from increased hydrogen bonding due to the formation of carbonyl and carboxyl groups and the reduction in the size of amylose molecules because amylose molecules with intermediate weights have a greater ability to retrograde and form gels. The gel firmness is mainly caused by retrogradation of starch gels, which is associated with the syneresis of water and the crystallisation of amylpectin leading to harder gels.

Collado and Corke (1999) treated sweet potato starch with HMT and found that the starch paste becomes short and stable for shearing, and they reported a significant increase in gel hardness and adhesiveness in HMT sweet potato starch compared to the native starch. Hormdok and Noomhorm (2007) also reported an increased gel hardness caused by HMT, and they attributed the increased gel hardness to the interactions between starch chains in the amylose portion. They also suggested that these interactions allow the formation of more junction zones in the continuous phase of the gel, which results in increased gel hardness. In addition, these authors reported that there may have been a partial gelatinisation in the starch subjected to HMT using a high temperature.

3.4. Thickness, solubility in water, colour and opacity of starch films

The results of the thickness, solubility, colour and opacity of oxidised and HMT potato starch films are shown in Table 4. The film thickness increased as the starch concentration increased. The film made with 3% oxidised potato starch had the lowest solubility (0.073 mm), and the film made with 5% native potato starch had the highest film thickness (0.168 mm) (Table 4). These thickness results were similar to the findings reported by Wawro and Kazimierczak (2008) who studied the forming conditions of potato starch films and reported that the thickness varies from 0.063 to 0.140 mm.

The solubility of the films in water is an important property and may protect food with high water activity when food is in contact with water during cooking. Potential applications may require water insolubility to enhance product integrity and water resistance. In other cases, however, the film water solubility before product consumption may be useful in the encapsulation of food or additives. After being immersed in water for 24 h under stirring, all of the potato starch films were intact. The solubility of the potato starch films increased as the starch concentration was increased from 3% to 5%. The oxidised starch films had lower solubility than the native and HMT starch films (Table 4). The reduced water solubility of the oxidised potato starch films may have been attributed to the increased interactions between amylose and amylpectin molecules and strengthened intramolecular bonds promoted by the oxidation of starch, which reduce the capacity of the film to absorb water. The water solubility result agreed with the swelling power results of the oxidised starch in which the swelling power of the oxidised starch was reduced as compared to the native starch. The water solubility values of the films in the present study were lower than those reported by Hu et al. (2009) who evaluated the solubility of oxidised potato starch films and reported values ranging from 22.77% to 29.86%.

Table 4
Thickness, water solubility, colour and opacity of oxidised and HMT potato starch films.

<table>
<thead>
<tr>
<th>Starch film</th>
<th>Starch (%)</th>
<th>Thickness (mm)</th>
<th>Solubility (%)</th>
<th>L’</th>
<th>a’</th>
<th>b’</th>
<th>Colour difference (ΔE°)</th>
<th>Opacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>3.0</td>
<td>0.100&lt;sup&gt;d&lt;/sup&gt;</td>
<td>17.33&lt;sup&gt;b&lt;/sup&gt;</td>
<td>96.29&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>−5.31&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>7.23&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>10.60&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>0.104&lt;sup&gt;c&lt;/sup&gt;</td>
<td>19.87&lt;sup&gt;a&lt;/sup&gt;</td>
<td>96.07&lt;sup&gt;b&lt;/sup&gt;</td>
<td>−5.22&lt;sup&gt;ad&lt;/sup&gt;</td>
<td>7.37&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.72&lt;sup&gt;c&lt;/sup&gt;</td>
<td>11.72&lt;sup&gt;bc&lt;/sup&gt;</td>
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<td>5.0</td>
<td>0.168&lt;sup&gt;a&lt;/sup&gt;</td>
<td>19.73&lt;sup&gt;a&lt;/sup&gt;</td>
<td>95.70&lt;sup&gt;b&lt;/sup&gt;</td>
<td>−5.14&lt;sup&gt;c&lt;/sup&gt;</td>
<td>7.38&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.09&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11.73&lt;sup&gt;bc&lt;/sup&gt;</td>
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<tr>
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<td>14.26&lt;sup&gt;c&lt;/sup&gt;</td>
<td>96.86&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>−5.28&lt;sup&gt;c&lt;/sup&gt;</td>
<td>7.41&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.25&lt;sup&gt;c&lt;/sup&gt;</td>
<td>11.33&lt;sup&gt;bc&lt;/sup&gt;</td>
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<td>0.124&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>96.65&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>−5.41&lt;sup&gt;c&lt;/sup&gt;</td>
<td>7.70&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>11.93&lt;sup&gt;bc&lt;/sup&gt;</td>
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<td>96.79&lt;sup&gt;bc&lt;/sup&gt;</td>
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<td>0.118&lt;sup&gt;b&lt;/sup&gt;</td>
<td>18.89&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>96.14&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>−5.13&lt;sup&gt;d&lt;/sup&gt;</td>
<td>7.42&lt;sup&gt;bc&lt;/sup&gt;</td>
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<td>−5.15&lt;sup&gt;d&lt;/sup&gt;</td>
<td>7.37&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.78&lt;sup&gt;c&lt;/sup&gt;</td>
<td>11.96&lt;sup&gt;bc&lt;/sup&gt;</td>
</tr>
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</table>

<sup>a</sup> Different letters in the same column differ statistically (*p < 0.05).

<sup>1</sup> HMT: heat–moisture treatment.
The $L^*$, $a^*$ and $b^*$ colour parameters of the potato starch films had no significant differences among the samples. However, the colour difference ($\Delta E^*$) increased as the starch concentration increased, and the colour difference was lower in the HMT potato starch film compared to native and oxidised starches (Table 4). Bae, Cha, Whiteside, and Park (2008) also found similar colour difference values for potato starch films with a $\Delta E^*$ value of 1.76. The $L^*$ parameter of the calorimetric assay characterises the whiteness of the material. The colour parameter values of the present study were higher than the values reported by Araujo-Farro, Podadera, Sobral, and Menegalli (2010) who reported the following values for quinoa starch films: $L^* = 92.86$, $a^* = -0.87$ and $b^* = 1.96$. The film opacity is a critical property if the film is used as a food surface coating. Transparent films are characterised by low values of opacity. In this study, the obtained opacity values showed that films made with HMT starch were less transparent than the native 3% starch films. According to Mali et al. (2004), the opacity of yam starch films depends on a film thickness with higher thickness values resulting in more opaque samples. Fakhouri, Fontes, Gonçalves, Milanez, Steel and Collares-Queiroz (2007) reported the opacity of films made from gelatine and native starches from wheat, sorghum, potato and rice to be 11.5%, 40.0%, 29.9% and 19.9%, respectively. Therefore, the opacity values of the potato starch film in this study (Table 4) were lower than those previously reported by others.

3.5. Mechanical properties

Tensile strength, elongation and Young’s modulus are used to describe how the mechanical properties of film materials are related to their chemical structure. The mechanical properties of films are traditionally linked to their tensile strength as determined by unidirectional tensile strength tests. Experimental stress–strain curves are used to calculate the film tensile strength and elongation at break. These properties are dependent on the polymeric chain packing, chain interactions and film thickness, and these properties are strongly affected by the relative humidity of the environment (Lourdin, Coignard, Bizot, & Colonna, 1997). The results for tensile strength, elongation at break and Young’s modulus for all of the film samples are shown in Table 5.

Tensile strength is defined as the maximum force (stress) used during a stress–strain experiment or the force obtained at the sample break point. In this study, the tensile strength of the films increased as the potato starch concentration increased. The oxidised and HMT potato starch films had higher tensile strength when compared to native starch (Table 5). According to Zamudio-Flores, Vargas-Torres, Pérez-González, Bosquez-Molina, and Bello-Pérez (2006), the tensile strength of films increase with the degree of starch oxidation because this parameter is higher when the active chlorine concentration increases. The presence of carbonyl and carboxyl groups in the oxidised starch may produce hydrogen bridges with the OH$^-$ groups of the amylose and amylopectin molecules, and these linkages provide more structural integrity in the polymeric matrix, thereby, increasing tensile strength. These authors also suggested that the increase in tensile strength with the increase in oxidation level in the starch used for film preparation may be due to the increased interactions among polymer chains, which affect the crystallinity and flexibility of the film.

Elongation at break is the increase of the sample length from its original length in the stress–strain experiment at the break point. The percentage elongation at break of polymeric materials depends on the flexibility of the molecular chain. During the processing of potato starch film, the granular and crystal structures of starch are mostly destroyed by high temperatures and shear forces, and the resulting structures are considered to exist mainly in an amorphous phase (Hu et al., 2009). The elongation at break of the native starch film was reduced from 85.20% to 58.33% with the increase of the starch concentration from 3% to 5%. The increase of starch concentration from 3% to 5% also decreased the elongation of the oxidised starch film. The oxidised potato starch films had lower elongation values compared to the native and HMT starches. The films with 4% and 5% HMT potato starch had higher elongation values compared to the films with 4% and 5% native starch (Table 5).

According to Zhang et al. (2009), the tensile strength of thermoplastic oxidised corn starch with high carbonyl content decreases with the increase of glycerol content, whereas the elongation at break increases with the increase of glycerol content. Singh et al. (2009) studied the properties of starch films prepared from native and HMT chestnut starches, and they reported tensile strength values of 6.89 and 53.45 N, respectively.

For comparison with other biopolymer films, Kim, Ko, and Park (2002) reported that the tensile strength of carboxymethylated starch films range from 9.7 to 15.3 MPa and that the elongation values of carboxymethylated starch films range from 2.6% to 7.7%. Araujo-Farro et al. (2010) produced films from quinoa starch (4.0 g/100 ml) under different conditions, and they reported the following mechanical properties under optimised conditions: tensile strength of 7.56 MPa and 58.14% elongation at break. They reported the optimised conditions for the quinoa starch–based films to be as follows: 21.2 g of glycerol/100 g of quinoa starch, pH value of 10.7, and drying conditions at 36 °C for 14 h.

The Young’s modulus is an indicator of stiffness of the film, where higher values indicate higher stiffness. According to Table 5, the film with the higher starch concentration was more stiffness. The oxidised and HMT potato starch films had higher Young’s modulus when compared to native starch (Table 5).

3.6. Water vapour permeability (WVP)

Because an important function of food packaging is to avoid or at least to decrease moisture transfer between the food and surrounding atmosphere, film water vapour permeability should be as low as possible. The water vapour permeability of the oxidised and HMT potato starch films are shown in Fig. 1.

The WVP of the films increased as the potato starch concentration increased (Fig. 1). According to Mali et al. (2004), the WVP values of yam starch films linearly increase with increases in thickness. Hydrophilic films exhibiting increased WVP with increased film thickness have also been reported by Cuq, Gontard, Cuq, and Guilbert (1996). According to Talja et al. (2007), the WVP of film is dependent on the water solubility coefficient of the film, the water diffusion rate of the film and the partial pressure of the water vapour.

Oxidation reduced the WVP of the potato starch film at 21% as compared to the native starch film when was used 3% of starch. However, the HMT potato starch film had higher WVP values than

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Table 5 Tensile strength, percentage elongation and Young’s modulus of oxidised and HMT potato starch films.

<table>
<thead>
<tr>
<th>Starch film</th>
<th>Starch (%)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>4.0</td>
<td>3.61&lt;sup&gt;a&lt;/sup&gt;</td>
<td>56.87&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.1&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>HMT</td>
<td>4.0</td>
<td>6.38&lt;sup&gt;a&lt;/sup&gt;</td>
<td>79.92&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.01&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Different letters in the same column differ statistically ($p < 0.05$).
<sup>b</sup> HMT: heat–moisture treatment.
the oxidised and native starch films (Fig. 1). According to Zhang et al. (2009) when the degree of oxidation of oxidised starch increased from 0.176 to 0.385 the moisture adsorption decreased from 21.5% to 19.8%. These authors explained that the changes in water content resulting from progressive oxidation of the starch can be explained by a replacement of hydrophilic hydroxyl groups by more hydrophobic aldehyde groups. When the aldehyde groups were further oxidised to carboxylic groups, the hydrophilicity again significantly increased. The WVP values for the potato starch films in this study were higher than the value reported by Araujo-Farro et al. (2010) who reported a WVP value of 0.204 g mm/m² h kPa for quinoa starch film, which is equivalent to approximately 4.90 g mm/m² dia kPa. Moreover, the WVP values for the potato starches in this study (Fig. 1) were higher than those reported by Fakhouri et al. (2007) who reported a WVP value of 4.22 g mm/m² dia kPa for films made from gelatine and native potato starch.

4. Conclusions

The native, oxidised and HMT potato starches produced biodegradable films with different characteristics. Relative to native potato starch films, the oxidation of potato starch films provided higher tensile strength and lower elongation at break, solubility and water vapour permeability values. The heat moisture treatment of potato starch increased the tensile strength and water vapour permeability of the starch films when compared to the native starch films. These results suggested that potato starches modified by oxidation or HMT can provide films with different properties, and these films can be used in several applications depending on the desired characteristic of the film. However, studies varying the intensities of these modifications are necessary because the interaction between the degree of starch modification and starch concentration used in the film solution will provide numerous opportunities to produce additional films with different properties.

References