Abstract

Ozone technology is an emerging and environmentally friendly technology, which is able to change both starch molecules size and charge. Consequently, new properties are achieved. In this study, biodegradable films were produced from starch modified by ozone technology. Potato starch was ozonated in water suspension using different conditions. The films were produced by casting technique using potato starch, glycerol as the plasticizer, and water as the solvent. The films were characterized in term of morphology, crystallinity, colour and their mechanical, barrier and functional properties. The ozonation changed the structure and properties of the polymeric matrix, resulting in films with a more homogeneous morphology and enhanced mechanical properties. The 30 min ozonated potato starch formed films with higher Young's Modulus (64 MPa) and decreased elongation at break (19 %), in comparison to the non-modified potato starch (45 MPa and 81%). Moreover, an increase in the contact angle, was observed from 31.5° to 60.7°, which was directly related to the ozonation time. This indicate a more hydrophobic surface, which is a desired characteristic. The water vapour permeability (26 g·mm/day·m^2·kPa) was not affected by the ozone processing. Finally, the film transparency was highly improved when ozone was applied, highlighting an interesting property from a commercial perspective. In conclusion, starch modification through ozonation demonstrated to be a good alternative for packaging production.

Keywords: bioplastic, biodegradable plastic, starch, starch modification, ozone, ozonation

Nomenclature

a^*	redness/greenness CIELab parameter (-)
A	area (m^2)
b^*	yellowness/blueness CIELab parameter (-)
C	chroma (-)
CI	crystallinity Index
E	Young's Modulus (MPa)
E^*	CIELab total color change (-)
L^*	brightness/darkness CIELab parameter (-)
m	mass (g)
p	pressure (kPa)
S	solubility (%)
t	time (h)
TS	Tensile Strength (MPa)
WVP	Water Vapour Permeability ($g \cdot mm/m^2 \cdot day \cdot kPa$)
x	thickness (mm)
Y	opacity (%)

Subscripts

0	initial
b	black standard
f	final
w	white standard

Greek

Δ	delta
ε	elongation at break (%)

1. Introduction

Technological advances have led to increased constraints regarding packaging, mainly due to environmental issues, consumer health concerns, and economic restrictions (Caribé et al. 2011; Shah et al. 2016). Consequently, the demand for biodegradable films and renewable sources is increasing abruptly.

Among the renewable sources with film-forming ability, starch is highlighted as a promising material for developing biopolymer packages (Shah et al. 2016). In fact, films produced with native starches from different botanical sources are widely studied, i.e., corn, cassava, potato, tapioca, among others. However, the properties of native starches are limited, once the molecular and granule structures are defined by each botanical source. To overcome some of these limitations, native starches are usually modified, diversifying their structures and functionality to suit in diverse applications (Ashogbon and Akintayo 2014; Din et al. 2017; Zhu 2015, among others).

Chemical, physical, enzymatical, biotechnological or their combinations are common methods of starch modifications (Ashogbon and Akintayo 2014; Zhu 2015). However, there is an increasing importance for methods that meet safety and health standards for both consumers and the environment (Kaur et al. 2012).

Ozone can be regarded as an interesting alternative to starch modification due to its unique reactiveness. In fact, ozone is a very powerful oxidizing agent and it is quickly decomposed into oxygen, leaving no residues and meeting the global demand for sustainability. Moreover, ozone is able to react with starch even at ambient temperature, without problems of wastewater disposal (Çatal and İbanoglu 2014).

Ozonation increases the starch carboxyl and carbonyl contents, also reducing the starch molecular size and its distribution (Castanha et al. 2017). Therefore, ozonated starch present different molecular sizes and electrical charges in relation to the native starch, which affect their behaviour for re-association. The exactly balance between the changes on molecular interactions promote different properties to the modified starch. Different starch sources were already modified by ozonation, such as corn, sago, and tapioca (Chan et al. 2009; Chan et al. 2011), cassava (Klein et al. 2014; Maniglia et al. 2019; Matta Junior et al. 2019), wheat (Çatal and İbanoglu 2014) and potato (Castanha et al. 2017; Castanha et al. 2018), leading to different properties.

Recently, we proposed the ozonation process as an alternative of starch modification focusing on film production (La Fuente et al. 2019). In that work, cassava starch was processed using ozone and films were produced using glycerol and water through casting. Ozonation increased the films tensile strength and Young's modulus, although decreased elongation. The process increased both water vapour permeation and oxygen permeation. Ozonation resulted in films with a more hydrophilic surface and less soluble. The films produced with ozonated starch presented higher (15 min of processing) or lower (30 min of processing) opacity than the native cassava films. Although ozonation has demonstrated to be a good alternative for starch modification and film formation, its exactly contribution is different for each starch source, being necessary further evaluation.

In fact, different ozonated starches/conditions present different molecular size distribution and electrical charges, which affect their behaviour for re-association. These molecular changes are competitive in relation to film production and properties. Consequently, the properties of films produced with ozone modified starches are unpredictable, and dependent on the relations among the source, reactor and processing conditions. For example, cassava and potato starches are different form both granular and molecular structure. Cassava starch had both polygonal and spherical shaped granules, while potato starch contained larger granules, which had spherical to oval shapes (Hung et al. 2017). Their molecular size and branched distribution are also different (Jane et al. 1999). However, the most important difference between cassava and potato starches in the presence of phosphate groups in potato starch. These groups can affect several characteristics of starch, such as rheological, thermal and structural properties, due to the to the high electronegativity of the phosphate group when ionised (Castanha et al. 2017). Therefore, the ozonation process resulted in different characteristics for cassava (Maniglia et al. 2019) and potato (Castanha et al. 2017) starches. Consequently, different properties are expected to their films (which, in fact, is demonstrated in this work).

Therefore, the aim of this study was to produce biodegradable films from ozone-modified potato starch, characterizing them and comparing them with those obtained from native potato starch and ozonated cassava starch.

2. Material and Methods

2.1.Materials

The starch was extracted from native potatoes (*Solanum tuberosum* L., Monalisa cultivar) purchased in a local market. The ozone modification was carried out in the same way as in the previous work, deeply explained in Castanha et al. (2017). The starch was suspended in distilled water (10 g/100 g in dry basis; 700 mL) and then ozonated for different periods under constant stirring in a glass reactor. The ozone rich stream was produced from industrial oxygen by the coronal discharge method. This stream was dispersed in the sample in small bubbles through a gas disperser. A gas flow of 0.5 $L \cdot min^{-1}$ was used, with an ozone concentration in the gas current of 47 mg $O_3 \cdot L^{-1}$. After processing, the excess of water was removed and the starch samples were dried in an air circulation oven for ~ 12 h at 35 °C until moisture content of ~12 g/100 g w.b.

Three samples were evaluated: the native starch and those ozonated for 15 and 30 min. Glycerol P.A. grade (Sigma-Aldrich, Brazil) and distilled water were also used for film production.

A full characterization of the modified potato starch structure and properties is provided by Castanha et al. (2017) and Castanha et al. (2018). The 15 min ozonated starch has a carbonyl and carboxyl content of: (0.070 and 0.033) groups/100 glucose units and amylose content of: 27.3 g/100 g. Moreover, the 30 min ozone-modified starch has a with carbonyl and carboxyl content of: (0.104 and 0.044) groups/100 glucose units and amylose content of: 25.6 g/100g.

2.2.Film preparation

The films were produced by *casting* technique. A solution containing 5 g/100 g of potato starch in distilled water was homogenized with a magnetic stirrer (GEHAKA, HU-30/2, Brazil) for 10 min. Then the solution was heated for 45 min in a becker with recirculation, until starch gelatinization, which occurred at ~70 °C. The glycerol was added as the plasticizer (25 g /100 g of starch), according to Souza et al. (2012) and the suspension was heated for more 15 min under agitation. To eliminate the bubbles, the filmogenic solution was placed in an ultrasonic bath for 30 min at 70 ºC (154 W, 25 kHz; UNIQUE, model USC-1850, Brazil). The solution was then poured into acrylic Petri dishes (0.15 g/cm^2) for ~12 h and dried at 35 °C for ~ 10 h in a convective oven (NOVA ÉTICA, model 410/4, Brazil). The films were conditioned for at least 48 h in desiccators

containing a saturated solution of NaCl (75 % RH) before characterization at room temperature (~ 25 °C).

2.3. Films characterization

2.3.1. Mechanical properties

The film thickness was determined using a digital micrometer with a precision of 0.001 mm (MITUTOYO, Japan) at five random positions. The mechanical properties were evaluated through a uniaxial tensile assay, according to ASTM D882-12 Standard Method (ASTM, 2012). Tensile strength (*TS*) [MPa] and percent elongation at break (ε) [%] were evaluated on a texture analyzer (TAXT2i Stable Micro Systems, UK) with a load cell of 30 kgf (294 N), using the A/TGT self-tightening roller grips fixture. The initial grip separation and the crosshead speed were set at 50 mm and 1 mm·s^{-1}, respectively. Young's modulus (*E*) was calculated as the slope of the initial linear portion of the stress versus strain curve. Ten strips (100 mm x 25 mm) were evaluated for each formulation and only those films that were broken far from the grips were considered.

2.3.2. Barrier Properties

Water vapour permeability (WVP) of films was measured gravimetrically according to the ASTM E96/E96M-16 Standard Method (ASTM, 2016). The films were placed in circular permeation cells containing silica gel, and then placed in a climatic chamber (TIRACLIMA, model TCC 7034, Germany) maintained at 75% RH and temperature of 25 °C. The cell weight was recorded hourly for 8 hours. The Water Vapour Permeability were calculated according to Eq. (1).

$$WVP = \frac{\Delta m \cdot x \cdot 24}{\Delta t \cdot A \cdot \Delta p} \quad (1)$$

wherein: $\Delta m/\Delta t$ is the moisture gain per unit of time (g·h^{-1}); x is the film thickness (mm); A is the film area exposed to permeation ($1.96 \cdot 10^{-3}$ m^2); Δp is the vapour pressure difference (kPa) of the atmosphere over silica gel and pure water (3.168 kPa at 25 °C).

2.3.3. Functional Properties

The film wettability was determined by the measurement of the contact angle with water, according to ASTM D7334 − 08 Standard Methods (ASTM, 2013) using an OCA15- Dataphysiscs (OCA 15, Dataphysiscs, Germany). Two angle measurements were carried out (one on each drop edge) quickly to avoid changes due to water

vaporization on each drop. The contact angle was defined as the average of six angle measurements.

The film solubility in water was evaluated with discs (diameter of 20 mm) immersed in 50 mL of water at 25 °C for 24 h, under mechanical stirring at 120 rpm, according to Gontard et al. (1992). The solubility in water was calculated as the percentage of dry matter of the solubilized film, as described in Eq. (2).

$$S = \frac{m_f - m_o}{m_o} \cdot 100 \quad (2)$$

wherein: m_o and m_f are the initial and the final discs' mass (g), respectively.

The films moisture was determined through the gravimetric method in an oven, without recirculation, at 105 °C until a constant mass (~24 h), according to Gontard et al. (1992).

2.3.4. Colour and Opacity

The film colour was determined using a colorimeter (HUNTERLAB, model ColorQuest XE, USA) with the CIELab scale (L^*, a^*, b^*). The colour measurements were expressed in terms of L^* (L^* = 100 brightness and L^* = 0 darkness); a^* (+a^* = redness and -a^* = greenness) and b^* (+b^* = yellowness and -b^* = blueness). The change of each of the parameters was calculated according to Eq. (3), (4) and (5).

$$\Delta L^* = L^* - L_0^* \quad (3)$$

$$\Delta a^* = a^* - a_0^* \quad (4)$$

$$\Delta b^* = b^* - b_0^* \quad (5)$$

wherein: L_0^* =94.04; a_0^*= -0.86 and b_0^*=1.53 determined from a white standard pattern. The total colour change (ΔE^*), the opacity (Y) and the Chroma (C) (Francis 1975; Maskan 2001) were calculated using Eq. (6), (7) and (8) respectively.

$$\Delta E^* = \left[\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2 \right]^{1/2} \quad (6)$$

$$Y = \frac{Y_b}{Y_w} \quad (7)$$

$$C = (a^2 + b^2)^{1/2} \quad (8)$$

wherein: Y_b is the opacity on the black standard and, Y_w is the opacity on the white standard. Three measurements were performed per film formulation to determine all the colour parameters.

2.3.5. Crystallinity

The relative crystallinity of the films was quantitatively estimated as the ratio between the crystalline area and the total area of the X-ray diffractogram (plotted from 2° to 40°), as described by Nara and Komiya (1983). An X-ray diffractometer (PANalytical, model X'Pert PRO, Netherlands), with detector X'Celerator operating at 45 mA, and voltage of 40 kV was used. The scanning rate was 0.02°/s with 2Θ angles varying between 2° to 40°. The software Origin 2018b was employed for calculation (OriginLab Corporation, Massachusetts, USA).

2.3.6. Morphology

The surface and cross-section morphology of the films were visualized by a scanning electron microscope (SEM). The films were frozen using liquid nitrogen to ensure a more accurate and finer cut. They were then horizontally and vertically placed on an adhesive tape placed over circular stubs. The films were then coated with a 30-nm gold layer and observed using the microscope (Leo Electron Microscopy, model, LEO 435 VP, England) with an acceleration voltage of 20 kV.

2.4.Statistical analyses

The obtained data was evaluated through analysis of variance (ANOVA), applying Tukey`s test at a 95 % level of confidence as a post-hoc test through Statgraphics Centurion XV software (StatPoint, Inc., USA).

3. Results and Discussion

The mechanical properties are shown in Table 1. No statistical difference was observed in the tensile strength (*TS*) for the 15 and 30 min ozonated films in comparison to the non-modified film, demonstrating that the ozone processing did not weaken the obtained films. However, the ozone processing for 30 min increased the films Young's Modulus (*E*) when compared to the non-modified starch, while the elongation at break (ε) significantly decreased with ozonation time (Table 1).

Zavareze et al. (2012) observed films with increased *E* due to the oxidation process of potato starch with sodium hypochlorite. The authors reported that oxidised potato starch films are less flexible and more rigid when compared with native starch films. Zamudio-Flores et al. (2006) studied films produced by oxidized banana starch with active chlorine. Contrary to the results obtained herein, their process increased the films tensile strength. However, we highlight the differences between ozonation and other oxidation processes, as well as the structural differences among starches from different sources. La Fuente et al. (2019) studied the ozonation of cassava starch to produce films whose tensile strength (*TS*) increased according to the ozone processing time. Therefore, differences in starch source and ozonation conditions are also important to define the final product properties.

Ozone processing reduces the starch molecular size and its distribution (Castanha et al. 2017). Consequently, ozonated starch molecules can present a size distribution suitable for re-association, which can also contribute to a more rigid polymeric matrix.

Furthermore, ozonation increases the starch carboxyl and carbonyl contents, and this increase is directly related with processing time (Castanha et al. 2017; Kaur et al. 2012). The carbonyl groups are available to form strong hydrogen bonds with the hydroxyl groups on starch, resulting in films more rigid with reduced elongation. However, carboxylic groups are known to be electronegatively charged and, thus, they cause an electrostatic repulsion between the molecules, making difficult their association (La Fuente et al. 2019).

Therefore, the ozonation is a complex process and the results obtained are the balance between both molecular size and charge, with different tendency of the molecules to re-association. Moreover, in the case of potato, the presence of phosphate groups, which are negatively charged, influence the balance of the total charges in the polymeric matrix – which certainly affects the different behaviours observed in this study and also when compared with the ozonated cassava starch (La Fuente et al. 2019).

The Water Vapour Permeation (*WVP*), which measures the easiness with which the water vapour permeates the material (Biduski et al. 2017), is shown in Table 1.

As exposed previously, the increase of carboxyl groups by oxidative processes promotes repulsive forces between the polymer chains, increasing the mobility of water, and, consequently, making the film more permeable to water (Biduski et al. 2017). Moreover, this space promoted water vapour diffusion through the film (higher diffusivity) and accelerated the water vapour transmission (higher permeability) (Zhang

and Han 2006). This is a drawback for many applications of films based on oxidised starches. For cassava films, the water vapor permeation and the oxygen permeation were increased by increasing the ozonation time (La Fuente et al. 2019). However, this was not evident for the films produced with ozone modified potato starch, as no statistical difference was observed among the treatments (Table 1). Therefore, the balance between the molecular changes, at the conditions here evaluated, did not modify the water permeability through the films, which can be considered a good result.

Figure 1 shows images of the first water drops deposited onto the film surface. The film's contact angle with water is an indicator of its hydrophilicity (Su et al. 2010), once lower values of contact angle are characteristic of film surface with wetting properties (Basiak et al. 2017). The ozonation process significantly increased the contact angle between the films and water, indicating the ozone processing of potato starch resulted in films with a more hydrophobic surface. This is a very interesting result, once a more hydrophobic surface is in general desirable considering different applications. For instance, the obtained films would be useful for partial impermeabilization of cardboard boxes used for fruit packages, which is currently achieved by using non-biodegradable materials. Further studies are needed focusing on this and other applications.

According to Zavareze et al. (2012), the interactions between amylose and amylopectin and strengthened of the intramolecular bonds promoted by the oxidation of starch can increasing the contact angle between the films and water, which can explain the results obtained herein. Cassava films resulted with a more hydrophilic surface (La Fuente et al. 2019), which highlights the ozonation can be a versatile technology to produce materials with diverse characteristics.

Table 1 presents the film moisture content, with values close to those reported in the literature (Fonseca et al. 2018; La Fuente et al. 2019; Talja et al. 2007). No statistical difference was observed for the non-modified and ozonated potato films.

In spite of the higher surface hydrophobicity of ozonated films, a slight increase in the film solubility was observed for the film produced with the 30 min of ozonated starch (Table 1). In fact, Castanha et al. (2018) observed that the water solubility index of ozonated potato starch increased with increasing ozonation time. Chong et al. (2013) reported a similar behaviour for films of corn starch oxidized with hypochlorite. The film solubility values were also in accordance with those reported by Hu et al. (2009) with oxidized potato starch films.

According to Zhang et al. (2009), the progressive oxidation of corn starch with hydrogen peroxide produced a replacement of hydrophilic hydroxyl groups by more hydrophobic aldehyde groups. When the aldehyde groups were further oxidized to carboxylic groups (with increasing processing time), the hydrophilicity again increased, resulting in an increase of moisture absorption. Moreover, the distribution of hydroxyl, aldehyde and carboxylic groups into the polymeric matrix could also influence the water solubility, since more hydrophobic groups could be placed in the surface.

Therefore, this could explain why the 30 min ozonated film is more hydrophobic in the surface at the first contact with water, although being more soluble after 24 h.

Once again, a different behaviour was observed for cassava films, as lower solubility after 24 h was observed for the 15 and 30 min ozonated starches (La Fuente et al. 2019).

Table 1 shows the colour parameters and opacity of the obtained films, which are in accordance to those related in the literature, such as Zavareze et al. (2012) and Hu et al. (2009).

Ozonation slightly changed the film colour parameters L^*, a^*, b^* and ΔE^* (Table 1). Similar values for L^* and ΔE^* were observed in the potato starch films studied by Zavaraze et al. (2012). The decrease in Chroma (C) (achromatic) represents the loss of colour intensity (Golasz et al. 2013), as observed with the ozone processing (Table 1).

As shown in Table 1, the ozonated starch films are more brightness and less opaque than the non-modified starch films. The film opacity is a critical property, where transparent films are characterized by low values of opacity (Zavareze et al. 2012). It is also clearly demonstrated in Figure 2. It is worth mention that this is a highly desirable result for different packaging and coating applications, with an important marketing impact.

This result is different from the ones observed for cassava starch (La Fuente et al. 2019), where ozonated films presented higher (15 min of processing) and lower (30 min of processing) opacity than the native starch.

According to Basiak et al. (2017), matrices which contain more amylose are thicker and thus opaquer, a fact that can also corroborate the results obtained herein since a decrease in amylose content is observed due to ozone processing (Castanha et al. 2017). Furthermore, potato starch is characterized by the presence of phosphate groups. This electronegative groups results in repulsion between molecules, prevents molecules from hydrogen bonding to each other, helping to keep the molecules fully hydrated and thus

329 promoting light transmittance (Craig et al. 1989). The carboxylic groups resulted of starch
330 oxidation have the same repulsion characteristic, also increasing the starch paste clarity
331 (Craig et al. 1989). In fact, ozonated potato starches presented more clear paste in
332 comparison to native starch (Castanha et al. 2017).
333 Therefore, ozonation can be an interesting alternative to enhance potato starch film
334 transparency.
335 Ozonation also affected the film morphology (Figure 3). In general, the ozonated
336 films present a compact structure and smooth surfaces with no pores, in comparison to
337 the non-modified starch films. A more homogeneous morphology can be related with the
338 depolymerization of starch molecules, allowing a higher penetration of the plasticizer in
339 the starch chains, and improving the interaction between the starch and plasticizer
340 (Biduski et al. 2017). Similar behaviour was observed in films produced with potato
341 (Fonseca et al. 2018) and sorghum (Biduski et al. 2017) starches oxidised with active
342 chlorine, and ozonated cassava films (La Fuente et al. 2019). Futhermore, Basiak et al.
343 (2017) indicate that the reduction in amylose content also enhances the homogeneity of
344 films, which also confirmed the results obtained herein. Therefore, ozonation which
345 resulted in the depolymerization of starch molecules and the reduced amylose content
346 provides a good alternative to produce materials with smoothie surface.
347 Figure 4 shows the X-ray diffraction patterns of the obtained films, as well as their
348 respective Relative Crystallinity (RC). Figure 4 demonstrates that the X-ray
349 diffractograms show semi-crystalline characteristic (presence of amorphous and
350 crystalline zones), with peaks located at: 17.2, 19.6, and 22.5° (2θ). According to
351 standards from a database of Powder Diffraction Files (PDF-4) (Faber & Fawcett, 2002),
352 these peaks may correspond to the amylose crystalline structure.
353 Castanha et al. (2017) reported that native and ozonated potato starch showed B-
354 type patterns. The X-ray diffractograms presented for the films (Figure 4) also showed
355 peaks located in some of the same regions (17.2, 19.6, and 22.5°) reported for the potato
356 starch, indicating that the films maintained part of the diffraction pattern of the starch
357 samples. It suggests that the molecular re-association after gelatinization and addition of
358 glycerol follows the same pattern of the original material.
359 The ozonated potato starches films showed two more peaks than the non-modified
360 starch films, in 5.8° (samples ozonated by 15 minutes) and 26.2° (samples ozonated by
361 15 and 30 minutes), that can be corresponds to the presence of starch nanocrystals
362 (Alonso-Gomez et al. 2016).

The non-modified starch films showed a lower RC (9.89 %) in relation to 15 min ozonated (15.39 %), and 30 min ozonated (14.19 %) starch films. The same behaviour observed for the ozonated cassava films (La Fuente et al. 2019).

Once again, the reason for the structure more ordered, as mentioned, can be related with the changes on the molecular length and with the carbonyl and carboxyl content in the ozonated starches. In films made of native starch, the linear structure of amylose allows the molecules to orient parallel to each other, which facilitate the formation of hydrogen bonds between the hydroxyl groups of adjacent polymers and gives rise to films with higher crystallinity (Tako et al. 2014). Once ozonation promote cleavage on both amylose and amylopectin moleculess (Castanha et al. 2017), it is expected that the remained molecules are more linear, resulting in films with more organized structure.

Summarizing, ozonation has demonstrated to be an interesting tool for starch modification and this work demonstrated that biodegradable films with unique properties can be obtained from that.

4. Conclusions

This work successfully produced films using potato starch modified by ozonation. The ozonation changed the structure and properties of the polymeric matrix resulting in films with enhanced mechanical properties. Indeed, for the 30 min ozonated potato film the Young's Modulus increased in 42 % and the elongation at break reduced in 76 %, in comparison to the non-modified film. The contact angle increased from 31.5° to 60.7°; thus a more hydrophobic surface was achieved. Films resulted with a more homogeneous morphology with a reduction in the opacity of 75 %. Finally, the water vapour permeability was not affected by the ozone processing, while the solubility after 24 h in water was increased to 36 % for the 30 min ozonated film. In conclusion, the ozonated potato starch produced are a good alternative for packaging production.

References

Alonso-Gomez L, Niño-López AM, Romero-Garzón AM, Pineda-Gomez P, Real-Lopez A, Rodriguez-Garcia ME (2016) Physicochemical transformation of cassava starch during fermentation for production of sour starch in Colombia. Starch-Stärke 68(11-12):1139-1147.

Ashogbon AO, Akintayo ET (2014) Recent trend in the physical and chemical modification of starches from different botanical sources: A review. Starch/Stärke 41–57.

ASTM Standard D 882-12. Standard test method for tensile properties of thin plastic sheeting. West Conshohocken, PA: ASTM International, 2012.

ASTM Standard D 7334-08. Standard practice for surface wettability of coatings, substrates and pigments by advancing contact angle measurement. West Conshohocken, PA: ASTM International, 2013.

ASTM Standard E96/E96M-16. Standard test method for water vapor transmission of material. West Conshohocken, PA: ASTM International, 2016.

Basiak E, Lenart A, Debeaufort F (2017) Effect of starch type on the physico-chemical properties of edible films. Int J Biol Macromol 98: 348–356.

Biduski B, Silva FT, Silva WM, El Halal SLM, Pinto VZ, Dias ARG, Zavareze ER (2017) Impact of acid and oxidative modifications, single or dual, of sorghum starch on biodegradable films. Food Chem 214: 53–60.

Caribé L. Reis B, Barcellos AD, Aparecida B, Machado S (2011) Filme biodegradável incorporado com glicerol e aditivos naturais. Cadernos de Prospecção 4: 23–32.

Castanha N, Matta Junior MD, Augusto PED (2017) Potato starch modification using the ozone technology. Food Hydrocolloids 66: 343–356.

Castanha N, Santos BN, Cunha RL, Augusto PED (2018) Properties and possible applications of ozone-modified potato starch. Food Res Int. Article impress.

Çatal H, Ibinaglu Ş (2014) Effect of aqueous ozonation on the pasting, flow and gelatinization properties of wheat starch. LWT - Food Sci and Technol 59: 577-582.

Chan HT, Bhat R, Karim AA (2009) Physicochemical and functional properties of ozone-oxidized starch. J Agr Food Chem 57(13): 5965–5970.

Chan HT, Leh CP, Bhat R, Senan C, Williams PA, Karim AA (2011) Molecular structure, rheological and thermal characteristics of ozone-oxidized starch. Food Chem 126(3): 1019–1024.

Chong WT, Uthumporn U, Karim AA, Cheng LH (2013) The influence of ultrasound on the degree of oxidation of hypochlorite-oxidized corn starch. LWT - Food Sci Technol 50: 439-443.

Craig SSA, Maningat CC, Seib PA, Hoseney RC (1989) Starch paste clarity. Cereal Chem 66: 173-182.

Din Z, Xiong H, Fei P (2017) Physical and chemical modification of starches: A review. Critical Rev Food Sci Nut 57(12): 2691–2705.

Faber J, Fawcett T (2002) The powder diffraction file: present and future, Acta Crystallogr. Section B: Structural Science 58: 325–332.

Francis FJ (1975) A Research Note: The origin of tan $^{-1}$ a/b. J Food Sci, 40(2): 412-412.

Fonseca LM, Henkes AK, Bruni GP, Viana LAN, Moura CM, Flores WH, Galio AF (2018). Fabrication and Characterization of Native and Oxidized Potato Starch Biodegradable Films. Food Biophys 13:163–174.

Golasz LB, Silva J, Silva SB (2013). Film with anthocyanins as an indicator of chilled pork deterioration. Ciênc. Tecnol. Aliment. 33(1).

Gontard N, Guilbert S, Cuq JL (1992) Edible wheat gluten films: influence of the main process variables on film properties using response surface methodology. J Food Sci 57 (1): 190-195.

Hu G, Chen J, Gao J (2009) Preparation and characteristics of oxidized potato starch films. Carbohyd Polym 76: 291–298.

Hung PV, Huong NTM, Phi NTL, Tien NNT (2017). Physicochemical characteristics and in vitro digestibility of potato and cassava starches under organic acid and heat-moisture treatments, Int J Biol Macromol, 95: 299–305.

Jane J, Chen YY, Lee LF, McPherson AE, Wong KS, Radosavljevic M, Kasemsuwan T (1999). Effects of Amylopectin Branch Chain Length and Amylose Content on the Gelatinization and Pasting Properties of Starch. Cereal Chem 76(5): 629–637.

Kaur B Ariffin F, Bhat R. Karim AA (2012) Progress in starch modification in the last decade. Food Hydrocol 26: 398-404.

Klein B, Vanier NL, Moomand K, Pinto VZ, Colussi R, Zavareze ER, Dias ARG (2014) Ozone oxidation of cassava starch in aqueous solution at different pH. Food Chem 155: 167–173.

La Fuente CIA, Souza AT, Tadini CC, Augusto PED (2019). Ozonation of cassava starch to produce biodegradable films. Int J Biol Macromol, 141: 713–720.

Maniglia BC, Lima DC, Matta Junior MD, Le-Bail P, Le-Bail A, Augusto PED (2019). Hydrogels based on ozonated cassava starch: effect of ozone processing and gelatinization conditions on enhancing 3D-printing applications, Int. J. Biol. Macromol,138: 1087–1097.

Maskan M (2001) Kinetics of colour change of kiwifruits during hot air and microwave drying. J Food Eng 48: 169-175.

Matta Junior DM, Castanha N, Prudentedos CBA, Augusto PED, Sarmento SBS (2019) Ozone technology as an alternative to fermentative processes to improve the oven-expansion properties of cassava starch. Food Res Int. Article in press.

Nara S, Komiya T (1983) Studies on the relationship between water-saturestate and crystallinity by the diffraction method for moistened potato starch. Starch /Starke 35(12): 407-410.

Shah U, Naqash F, Gani A, Masoodi FA (2016) Art and Science behind Modified Starch Edible Films and Coatings: A Review. Compressive Reviews in Food Science and Food Safety 15: 568–580.

Souza AC, Benze R, Ferrão ES, Ditchfield C, Coelho ACV, Tadini CC (2012) Cassava starch biodegradable films: Influence of glycerol and clay nanoparticles content on tensile and barrier properties and glass transition temperature. LWT - Food Sci Technol 46(1): 110–117.

Su JF, Huang Z, Yuan, XY, Wang XY (2010) Structure and properties of carboxymethyl cellulose/soy protein isolate blend edible films crosslinked by Maillard reactions. Carbohyd Polym 79: 145–153.

Talja RA, Helén H, Roos YH, Jouppila K (2007) Effect of various polyols and polyol contents on physical and mechanical properties of potato starch-based films. Carbohyd Polym 67: 288–295.

480 Tako M, Tamaki Y, Teruya T, Takeda Y (2014) The principles of starch gelatinization
481 and retrogradation. Food Nut Scie 5: 280-291.

482 Zamudio-Flores PB, Vargas-Torres A, Pérez-González J, Bosquez-Molina E, Bello-Pérez
483 LA (2006) Films prepared with oxidized banana starch: mechanical and barrier
484 properties. Starch/Stärke 58: 274–282.

485 Zhang Y, Han JH (2006) Plasticization of pea starch films with monosaccharides and
486 polyols. J Food Sci 71(6): 253-261.

487 Zhang SD, Zhang YR, Wang XL, Wang YZ (2009) High carbonyl content oxidized starch
488 prepared by hydrogen peroxide and its thermoplastic application. Starch/Stärke 61: 646–
489 655.

490 Zavareze ER, Pinto VZ, Klein B, Halal SLM, Elias MC, Prentice-Hernández C, Dias
491 ARG (2012) Development of oxidised and heat–moisture treated potato starch film. Food
492 Chem 132: 344–350.

493 Zhu F (2015) Composition, structure, physicochemical properties, and modifications of
494 cassava starch. Carbohyd Polym 122: 456–480.

495

Figure Caption

Fig 1. Contact angle of the evaluated films with a drop of water. Non modified potato starch **(A)**; 15 min ozonated **(B);** and 30 min ozonated potato starches **(C)**. Same letters in the same row are not significantly different ($p>0.05$)

Fig. 2. Pictures representing the potato starch film opacity. The logo of University of São Paulo (USP) was photographed in four conditions: without any film over it, and with potato starch films placed over it. The films were made using native potato starch and those ozonated for 15 min and 30 min.

Fig. 3. Scanning electron micrographs of the surfaces and cross-sections of the films prepared with non-modified and ozonated potato starch. In the cross-sections images, the red bars represent 20 µm. In the surface images, the white bars represent 100 µm.

Fig. 4. X-ray diffraction patterns of the films prepared with non-modified and ozonated potato starch (15 and 30 minutes) and their respectively Relative Crystallinity (RC).