Journal of Polymers and the Environment (2022) 30:3974–3984
https://doi.org/10.1007/s10924-022-02488-0

ORIGINAL PAPER

Bio-Based Plastic Based on Ozonated Cassava Starch Produced by Extrusion

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Accepted: 18 May 2022 / Published online: 9 June 2022

Abstract

Green methods of modification, such as ozone, can bring new functionalities to starch. In this study, starch-based plastics were produced by extrusion, using cassava starch ozonated with a gas flow of 1 L min^{-1} at a concentration of 41 mg O_3 L^{-1} resulting in doses of 78.9 and 145.3 mg O_3/g starch. Pre-mixes (starch, glycerol, and water) were processed in a co-rotating twin-screw extruder. The main results showed that ozonated sheet produced with the treatment of 78.9 mg O_3/g starch resulted in an increase in Young Modulus by 43% and a decrease in hydrophilicity by 37% in comparison to the native one. Conversely, treatment with 145.3 mg O_3/g starch did not increase the bio-based plastic mechanical properties or surface characteristics, showing a specific behavior tendency between ozonation and extrusion processes. The ozonation of starch showed to be an alternative for producing by extrusion bio-based plastics with enhanced properties, by selecting adequate processing conditions.

A patent related to this work was filed(BR1020190112166).

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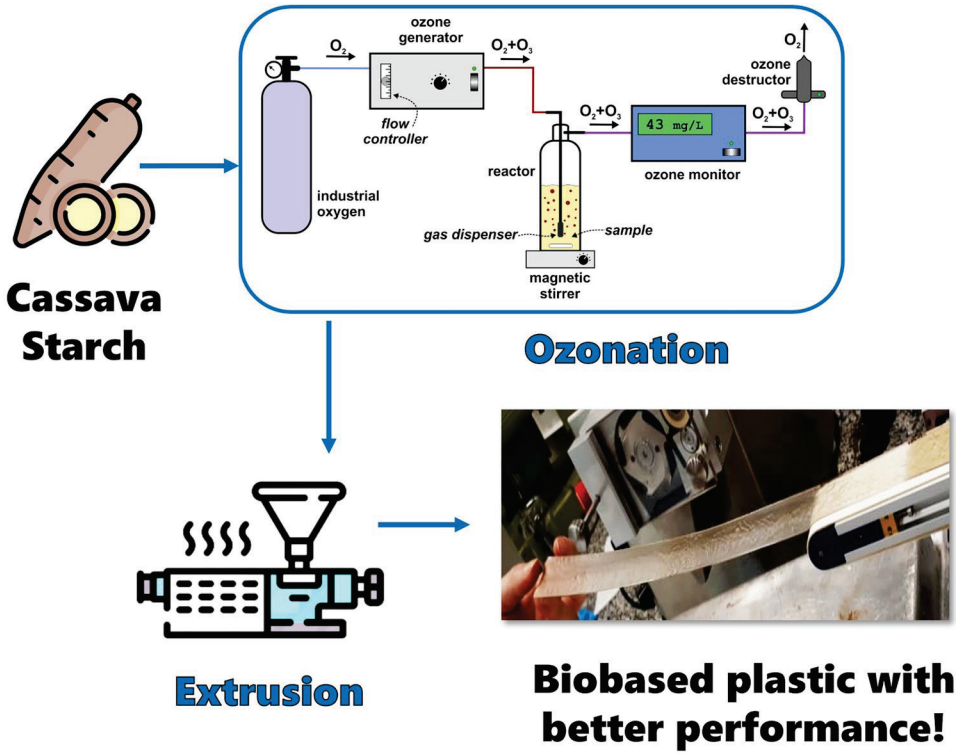
Graphical Abstract



Keywords Biodegradable plastics · Ozonation · Green technologies · Starch modification

List of Symbols

A	Area (m^2)
E	Young's modulus (MPa)
p	Pressure (kPa)
RC	Relative crystallinity
t	Time (h)
TS	Tensile strength (MPa)
WVP	Water vapor permeability (g mm/m^2 day kPa)
x	Thickness (mm)
Y	Opacity (%)

Subscripts

b	Black standard
w	White standard

Greek

ε	Elongation at break (%)

Introduction

Starch-based plastics have been developed as an alternative to petroleum-based ones, being cassava starch an interesting raw material for this application [1]. However, starch-based plastics can show lower performance when compared with traditional plastic, such as worse mechanical properties, low transparency, and high-water absorption [2, 3] mainly due to the hydrophilic character of this polymer [4].

Different modification techniques can be used to overcome those issues, being the so-called "green technologies" interesting approaches to enhance performance for attaining sustainability. The ozonation process (i.e., processing using the ozone gas) is considered an environmentally friendly technology that promotes three main modifications in starch molecules, achieving different properties: partial depolymerization, oxidation of hydroxyl groups into carbonyl and carboxyl groups [5]. In fact, ozonation was able to enhance the performance of the bio-based plastics of cassava [6, 7] and potato [8] bio-based plastics produced by the casting technique.

However, although casting is an interesting technology to understand the polymeric interactions with some other compounds or process conditions, as a first approach, it is a laboratory-scale technique, difficult to apply on an industrial scale. Extrusion technology is widely used in the polymer industry [2], but studies on starch-based plastics are still scarce in the literature. The extrusion technique has many

advantages, being a continuous and low time-consuming process, and efficient to produce viscous materials [9, 10].

When both processes are compared (casting vs. extrusion), drying conditions are quite different. Casting plastics are slowly dried (~ 12 h) at low temperatures and rest (i.e., at negligible stress), while extruded plastics are quickly dried at high temperatures and high shear stress, resulting in a different matrix conformation and recrystallization ability [11, 12]. These differences affect the mechanical, barrier, and physical properties of the material, highlighting the importance of this research.

Therefore, in this study, ozonation, a "green emerging technology", was used to modify cassava starch before bioplastic production. Ozonated starch-based plastics were produced by extrusion, reported for the first time in the literature. Those new plastics were characterized by correlating their mechanical, barrier, physical and thermal characteristics with the starch modification process.

Materials and Methods

Materials and Ozonation Process

Native cassava starch (Amilogill 1500; 28.94 g/100 g of amylose) provided by Cargill Agrícola—Brazil, glycerol P.A. grade (Sigma-Aldrich, Brazil), and Milli-Q water were used to produce the ozonated starch-based plastics.

The ozonation process and the full characterization of cassava starch were described in a previous study [13]. Briefly, a rich stream was produced with a gas flow of 1 L min^{-1} with an ozone concentration of 41 mg O_3 L^{-1} going through the samples for 15 or 30 min at 25 ± 1 °C, which resulted in the ozone doses (consumption during the reaction) of 78.9 and 145.3 mg O_3/g starch, respectively (and hereafter called O78.9 and O145.3, respectively). This was followed by decantation, centrifugation, and air-drying in a circulation oven (Marconi, MA 035, Brazil) for ~ 12 h at 35 °C, until reaching a moisture content of ~ 12 g/100 g w.b. The O78.9 and O 145.3 samples resulted in carbonyl, carboxyl, and amylose content of (0.080; 0.020) groups/100 glucose units, 25.85 g/100 g and (0.12; 0.040) groups/100 glucose units, 23.79 g/100 g, respectively [13].

Bio-Based Plastic Production

Premixes of starch, glycerol (43.1 g/100 g of starch), and water (25.9 g/100 g of starch) [14] were homogenized in a mixer (Kitchen Aid, 525, Brazil) and then extruded in a corotating twin-screw extruder (Thermo Fisher Scientific, Process 11, Germany) L/D 40, and 11-mm screw diameter to produce pellets. The premixes were fed through a double screw feeder (Brabender, Volumetric Minitwin Process 11, Germany) at 0.05 kg/h and a thread speed of 80 rpm. The temperature profile to obtain pellets from the feed zone (1) to the extrudate outlet (zone 8) was based on Vedove et al. [14], being: 60, 75, 90, 100, 110, 110, 105, and 100 °C. The cylindrical material obtained was then cut to 2 mm to obtain the pellets.

Those pellets were fed from a conical type feeder (Brabender, Kulturstrasse 55–73, Germany), with a feed flow of 0.2 kg/h to the same co-rotating twin-screw extruder. The sheets were obtained by the extrusion process using the same temperature profile, the die (3 cm × 1 mm) with the mold to form the sheets at 105 °C and the thread speed at 80 rpm.

For each level of ozone applied to cassava starch (78.9 and 145.3 mg O_3/g starch), the pellets and their respective sheets were produced by extrusion in duplicate. The pellets and sheets were also produced from native cassava starch (no ozonated) for comparison.

Bio-Based Plastic Characterization

The materials were conditioned for 7 days in desiccators (75% RH) at room temperature (~ 25 °C) and then evaluated according to their morphological, structural, mechanical, barrier, physical, and thermal characteristics.

Morphology

The morphology of the bio-based plastics was visualized by a scanning electron microscope (SEM). The specimens were coated with 10-nm platinum and observed using the microscope (FEI, model Quanta 600FEG, Netherlands) at 15 kV and the magnification ranged from 1500× (surface) to 150× (cross-section) images.

Relative Crystallinity

The crystallinity of the materials was analyzed by an X-ray diffractometer (PANalytical, model X'Pert PRO, Netherlands) at 45 mA and, 40 kV. The scanning rate was 0.02°/s with 2θ angles from 2° to 40°. The Origin 2020 software was used for data analysis (OriginLab Corporation, Massachusetts, USA).

Fourier-Transform Infrared (FTIR) Analysis

Sheet spectra were investigated by Fourier transform infrared spectroscopy (Pekin Elmer Frontier IR-4700, USA) in attenuated total reflectance (ATR) mode using a diamond ATR crystal in a wavenumber range from 540 to 4000 cm^{-1}; 32 scans were recorded per sample. The software Origin 2020 was employed for data obtained from the spectra (OriginLab Corporation, Massachusetts, USA).

Mechanical Properties

Plastic thickness was determined at five random positions using a digital micrometer (precision 0.001 mm) (MITUTOYO, Japan). Their mechanical properties were evaluated using a uniaxial tensile assay according to the ASTM D882-12 standard method [15] on a texture analyzer (Stable Micro Systems, TAXT2i, UK). Tensile strength (*TS*) and elongation at break (ε) were evaluated for ten strips (100 mm x 25 mm) using the A/TGT self-tightening roller grips at a speed of 1 mm s^{-1} and grip separation of 50 mm. Young's modulus (*E*) was calculated as the slope of the initial linear portion of the stress *versus* strain curve.

Barrier Properties

Water vapor permeability (*WVP*) was determined through the gravimetrical method according to the ASTM E96/E96M-16 Standard Method [16], in triplicate. The specimens were placed in circular permeation cells containing silica gel and then in a desiccator (75% RH) in a climate chamber (TIRACLIMA, model TCC 7034, Germany) at a temperature of 25 °C. The weight gain was recorded at intervals of 1 h. The *WVP* was 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}); *A* is the film area exposed to permeation ($4.9 \cdot 10^{-4}$ m^2); *x* is the film thickness (mm); Δp is the difference in vapor pressure (kPa) of the atmosphere over silica gel and pure water.

Wettability

The wettability of the bio-based plastic surface was determined by the contact angle with Milli −Q water, according to ASTM D7334 08 standard methods [17] through an optical system (Dataphysiscs, OCA 15, Germany). The water contact angle was determined in six small specimens per sample. Angle measurements were quickly carried out to avoid water vaporization.

Solubility and Moisture Content

The bio-based plastic solubility in water was evaluated in triplicate with discs (diameter of 20 mm) immersed in water at 25 °C, being agitated at 120 rpm for 24 h, according to Gontard et al. [18]. The solubility was calculated according to 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 mass of the discs (g), respectively.

Moisture of bio-based plastics was determined in triplicate, according to Gontard et al. [18] in an oven (Marconi, M030/2057, Brazil) at 105 ºC, until constant mass.

Opacity and Light Transmittance

The transmission of UV to visible light of the materials was measured with a spectrophotometer from 200 to 800 nm (FEMTO, model 700.Plus, Brazil). The bio-based plastics opacity was determined, in triplicate, using a colorimeter (HUNTERLAB, model ColorQuest XE, USA) using Eq. (3).

$$Y = \frac{Y_b}{Y_w} \quad (3)$$

wherein: Y_b is the opacity on the black standard and, Y_w is the opacity on the white standard.

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis was performed in duplicate using a thermal analyzer (TA Instrument, model TGA-Q500 V20.13, EUA), using ~ 10 mg of samples, which were heated from 25 to 700 °C, at a rate of 10 °C/min under nitrogen flow. The sample mass was continuously measured to describe its reduction over temperature.

Statistical Analyses

All data were evaluated by the Analysis of Variance (ANOVA), applying Tukey's test ($p < 0.05$) using the Statgraphics Centurion XV software (StatPoint, Inc., USA).

Results and Discussion

Figure 1 presents the visual aspect of the bio-based plastics produced by extrusion, which were classified as "sheets" due to their thickness (> 0.250 mm) according to the standard terminology of ASTM D882-18 [15].

Different performances were achieved in each treatment, while the ozonation conditions resulted in a hormetic pattern (increasing performance at low doses and decreasing it at high doses) for some properties. This indicates there is an interesting range of starch molecular modification levels from which the ozonation process becomes deleterious to the bio-based plastic—therefore highlighting the importance of the present evaluation.

For instance, while the sheet produced with cassava starch ozonated at 78.9 mg O_3/ g starch seems more homogenous and thinner, with adequate transparency to be used as

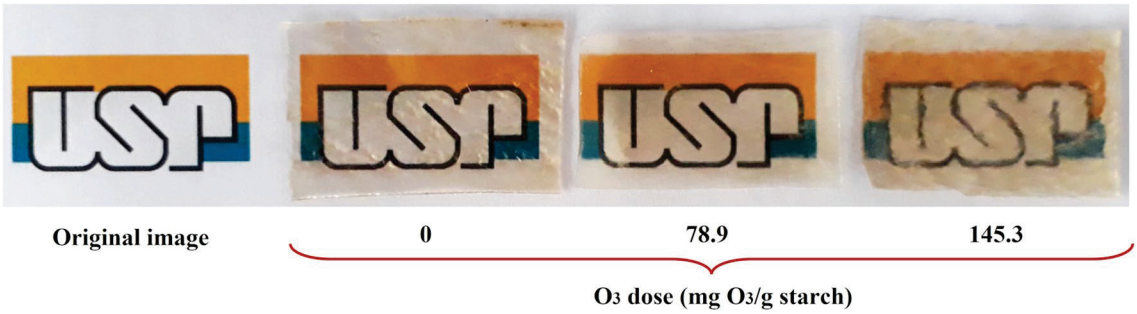


Fig. 1 Images of bio-based plastics produced with native and ozonated cassava starch by extrusion

packaging material, the plastics produced with the native and 145.3 mg O_3/g ozonated starches were rougher and heterogeneous—the latter (145.3 mg O_3/g starch) presented higher opacity. More details are discussed in the following.

Morphology

Figure 2 presents the morphology of the sheets obtained. In general, the 15-min ozonated sheets present a compact and smooth structure on the surfaces and cross section, while for the O145.3, some irregularities are visualized. Higher heterogeneity and roughness are observed in the sheet produced from native cassava starch, which could be attributed to the formation of bubbles/drops in the extruder exit section [19]. A smoother surface for ozonated cassava films in comparison to native films produced by casting was reported by La Fuente et al. [6]. According to Biduski et al.[20], the oxidation of hydroxyl groups allows a higher penetration of the plasticizer in the starch chains, improving the interactions between molecules. However, in this study, it is important to highlight the difference in the drying process, which can affect the final conformation of the matrix. Actually, extrusion drying favors the organization of the molecules in the flow direction [21], while in casting, molecules can be entangled due to slow drying under steady conditions, resulting in morphology with different characteristics.

The presence of micro-voids and cracks in extruded bio-based plastics is associated with the accelerated drying process [22, 23], as well as the formation of bubbles/droplets at the exit of the die, due to the pressure and temperature drop [19].

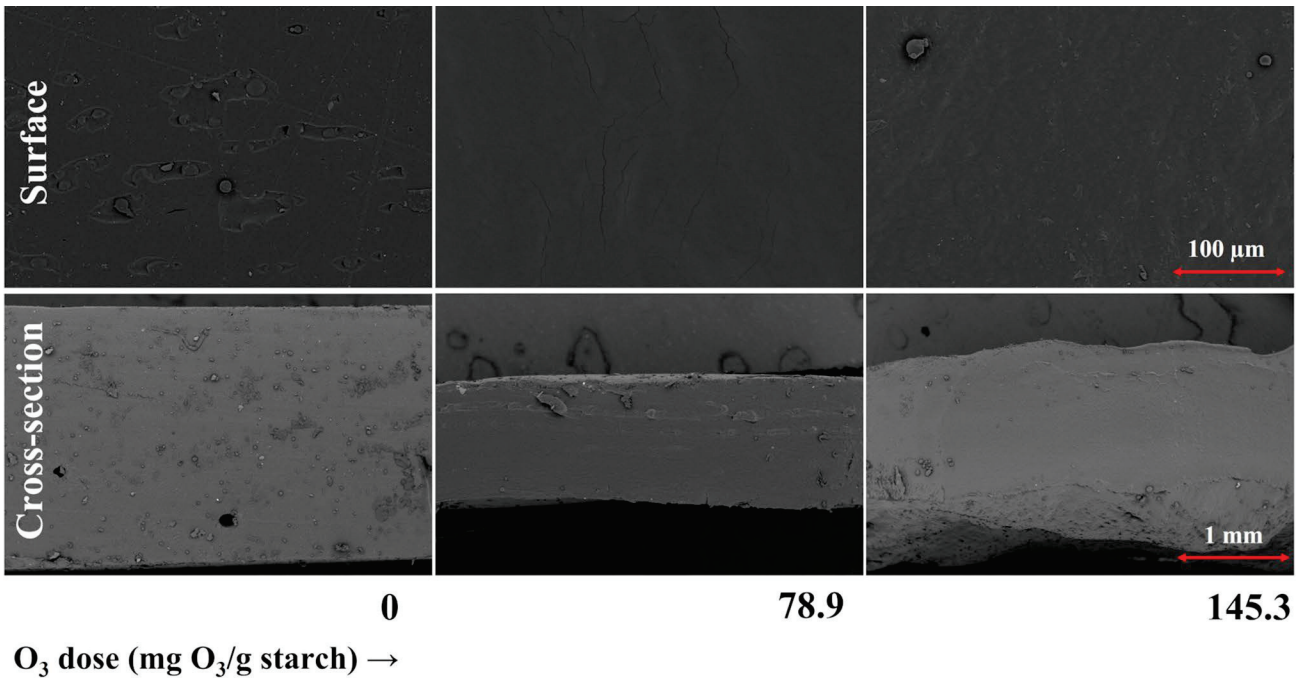


Fig. 2 Morphology of native and ozonated cassava starch plastics observed by scanning electron microscopy (SEM)

Crystallinity and Fourier-Transform Infrared (FTIR) Spectra

Figure 3A shows the X-ray diffractograms for the native and ozonated cassava sheets, in which peaks were observed at 5.1°, 17.0°, 20.0°, 22.0°, 31.0°, and 33.9° (2θ), indicating a type-B crystalline structure. The peaks at 5.1°, 17.0°, 20.0°, and 22.0° were also observed by La Fuente [6] in ozonated cassava starch films produced by casting, while Valencia [24] also observed peaks near 31.0 ° in native cassava films produced by casting. Vedove [14] observed peaks near 20.0° and 22.3° in native cassava starch sheets produced by extrusion, under conditions similar to those applied in this study.

Ozonated sheets presented higher values of relative crystallinity (Table 1) in comparison with the native starch, the same behavior was observed in ozonated potato [8] and cassava [6] starch films produced by casting. This suggests that depolymerization occurred during ozonation and the partial replacement of the hydroxyl groups by carbonyl and carboxyl groups [5, 13], resulting in molecules with better organization, increasing the crystalline regions.

Figure 3B presents the FTIR spectra of the sheets obtained. In general, the spectra showed a typical behavior for cassava starch films plasticized with glycerol [25–27]. The absorbance at 3300 cm^{-1} is attributed to O–H stretching, while C–H stretching appeared at 2922 cm^{-1}. The band near 1650 cm^{-1} is assigned to the water adsorbed by starch molecules [5, 26], near 1455 cm^{-1} to C–H bending, near 1242 cm^{-1} to C–O stretching, or the C–OH stretching [25]. Then, at 1000 cm^{-1} to the C–O stretching, while near 925 cm^{-1} designated to the C–O and the C–H stretching [25, 26].

Satmalawati et al. [28] observed a difference in the peak sharpness at 1780–1680 cm^{-1} between native and ozonated cassava starch, which they attributed to the carbonyl groups due to the ozone oxidation process. However, no difference in this region among samples was visualized in Fig. 3. Vicentini et al. [27] discussed that different molecular changes

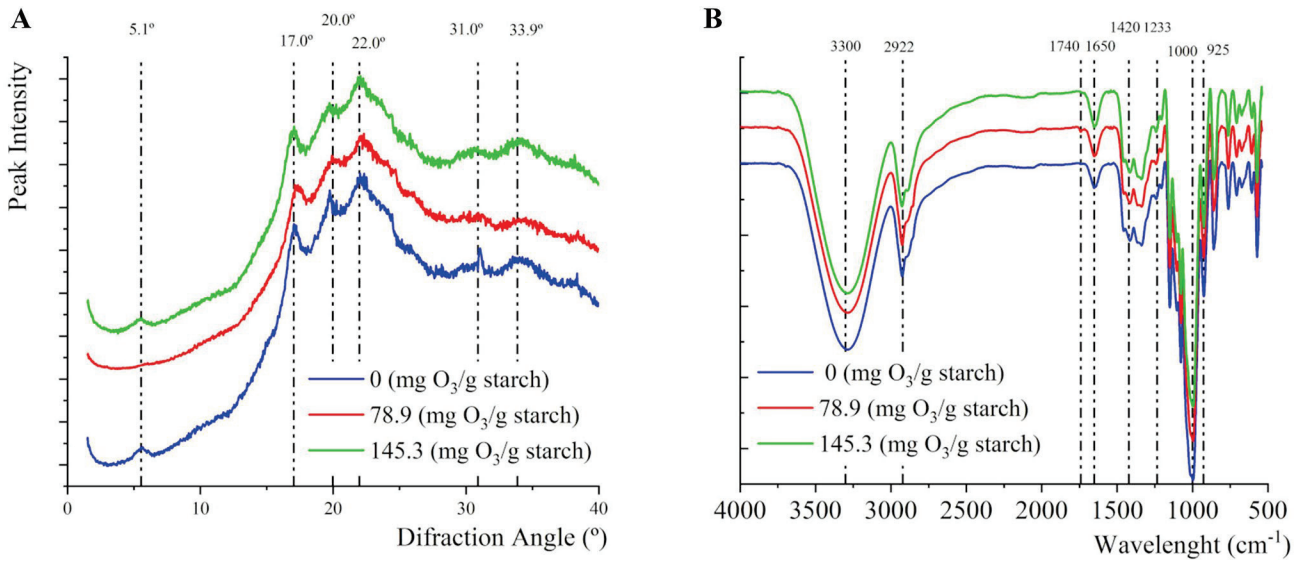


Fig. 3 **A** X-ray diffraction patterns and **B** FTIR spectra of native and ozonated cassava starch sheets

Table 1 Relative crystallinity, thickness, tensile strength, elongation at break, Young modulus's, moisture content, and opacity of native and ozonated cassava starch sheets

Ozone dose (mg O_3/g starch)	*RC* (%)	Thickness (mm)	Tensile strength (MPa)	Elongation at break (%)	Young modulus (MPa)	Moisture (g/100 g)	Opacity (–)
0	3.81 ± 0.59^{a}	1.19 ± 0.00^{b}	1.13 ± 0.11^{b}	38.82 ± 1.32^{b}	5.23 ± 0.70^{a}	20.47 ± 0.35^{a}	49.33 ± 1.15^{a}
78.9	5.68 ± 0.17^{a}	0.96 ± 0.10^{a}	1.29 ± 0.09^{b}	29.84 ± 4.39^{a}	7.50 ± 0.46^{b}	19.65 ± 0.29^{a}	79.33 ± 1.53^{b}
145.3	5.69 ± 0.81^{a}	1.17 ± 0.01^{b}	0.88 ± 0.08^{a}	29.41 ± 2.36^{a}	4.90 ± 0.61^{a}	19.23 ± 1.22^{a}	93.33 ± 0.58^{c}
Tukey HSD*	2.46	0.15	0.26	7.46	1.50	0.02	2.90

The means with different letters in the column are significantly different ($p < 0.05$)

*Tukey's honestly significant difference (HSD)

could occur in other regions, which probably explains why carboxyl and carbonyl groups were not visualized.

According to the literature [5, 26, 27], starch shows a fingerprint region within 1200–900 cm^{-1} bands, which is attributed to changes in starch structure. However, once again, no differences were visualized in this region among samples. At this point, it is important to note that, in ATR spectra (mode used in this study), the penetration depth of infrared light in the sample is about 15 µm and, probably, the higher thickness of the sheets (Table 1) could interfere with visualization of this functional groups in all ranges studied herein.

Mechanical Properties

Table 1 presents the mechanical properties of the materials. Similar values have been reported for native cassava sheets [14]. As shown, there was no significant variation ($p > 0.05$) in tensile strength between the native and the O78.9 cassava sheet, while for the O145.3 sheet, this property was ~20% lower. Similarly, the elongation at break was ~25% lower for ozonated starch sheets compared to the plastic produced with the native starch. Table 1 allows verifying that the Young Modulus follows the same behavior as the tensile strength, as expected. It increased by 43% for O78.9 in comparison to the O145.3 and native cassava sheets, indicating that O78.9 increased the mechanical properties, while for O145.3 this property is similar to that of native starch.

The increase in stiffness and the decrease in the elongation of cassava sheets, depending on the process conditions, can be interesting since we could produce materials with unique characteristics according to the market demand. This behavior can be attributed both to the new matrix conformation obtained after determining the ozonation process and to the drying conditions in the extruder. Probably, the higher degree of depolymerization of this material (O145.3 cassava starch), in combination with higher temperatures and shear stress during extrusion, was drastic enough to weaken the polymeric matrix, thus resulting in the lower values of Young Modulus, while for the O78.9 material, the degree of depolymerization reached, in combination with the extrusion process (temperature and shear stress) was good enough to increase the toughness of the polymeric matrix.

Barrier and Physical Properties

As shown in Fig. 4, there is no statistical difference in water vapor permeability between native and the ozonated cassava sheets. In addition, an increase of 13% in the solubility of the O78.9 sheet can be observed compared to the other materials. The values are similar to those reported by Pérez-Vergara et al. [29] for native cassava starch films.

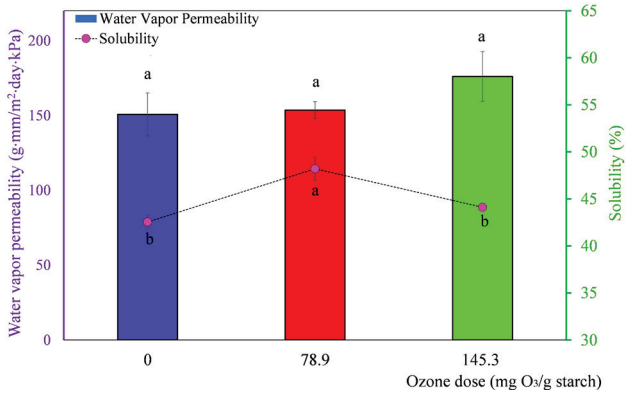


Fig. 4 Water vapor permeability and solubility of native and ozonated cassava starch sheets produced by extrusion

Although a decrease in water vapor permeability was expected due to the decrease in hydroxyl groups, leading to a decrease in hydrophilic properties [30], this did not occur. A possible explanation may be the carboxyl groups formed as a result of ozonation, which are electronegatively charged, change the polarity of the polymeric matrix, increasing the repulsive forces, favoring the mobility of water, as Biduski et al. [20] exposed. In fact, an increase in the water vapor permeability was observed in cassava [6] and potato [8] ozonated starch films produced by casting. These electrostatic repulsion forces could also be responsible for the increase in the solubility of the O78.9 sheets. However, for O145.3 sheets, the greater ozonation might cause the opposite behavior. Additionally, it is also possible that the intense shear stress and high temperature during the extrusion process resulted in a molecular conformation that reduces the effect of these repulsive forces, without affecting the water vapor permeability or the solubility.

Figure 5 presents the water contact angle formed with the first drop of water released onto the surface of the material, indicating the hydrophobicity or hydrophilicity of the surface of the material. According to Chimonyo et al. [31], hydrophobic interactions occur when non-polar starch groups escape from the water to interact with a hydrophobic surface. In this sense, the ozonated cassava sheet for O78.9 could be considered a hydrophobic material with an increase of 37% in contact angle in comparison to the native cassava starch sheet. On the contrary, we observed a decrease in the contact angle for the O145.3 sheet, which could be attributed to the strong polarization and resonance stabilization of the carboxyl-OH bonds formed (higher for the O145.3 starch), which enhances the level of polarity on the polymeric matrix [31], resulting in the decrease in the water contact angle.

There was no statistical difference in the moisture content of the bio-based plastics (Table 1), showing that ozonation did not interfere with this parameter, being the the values similar to those reported for native cassava sheets [14].

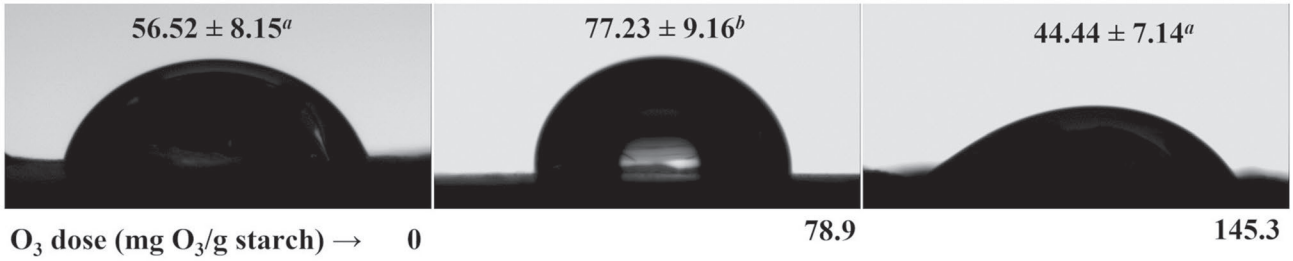


Fig. 5 The water contact angle of native and ozonated cassava starch sheets produced by extrusion

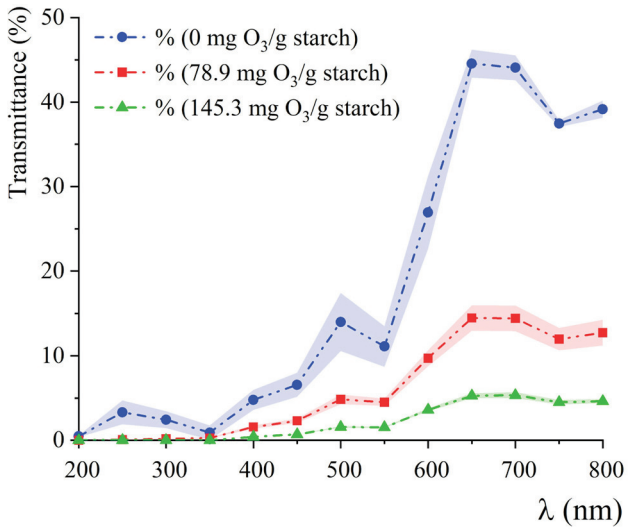


Fig. 6 Transmittance of native and ozonated cassava starch sheets produced by extrusion

Opacity and Transmittance

As shown in Table 1, the native cassava starch sheet showed lower values of opacity in comparison to the O78.9 sheet, similar to those reported by La Fuente et al. [6, 7] for ozonated cassava films produced by casting. However, for the O145.3 material, while the films obtained by casting were less opaque [6] the sheets were more opaque. This could be attributed to several factors, such as the thickness of the material (Table 1), different molecules' conformation due to the extrusion process, and also the bubbles/droplets formation, which could interfere with the measurement of this property. Figure 6 presents the spectra of transmittance of the sheets, confirming that the ozonated sheets presented less transmission from 200 to 800 nm. Specifically, in the UV region (200–400 nm), considerably lower transmittance values can be observed, which means the starch ozonation treatment on starch improves the ability of films to protect against UV light. Note that this is important for different applications, such as for food packaging. Other studies reported this achievement but after the addition of other compounds, such as nano-encapsulated lycopene, β-carotene, or blueberry and pomace extracts [32, 33]. It is worth highlighting that the ozonated starch sheets do not need the addition of any components to achieve this good behavior. This result can be a consequence of the new polymeric matrix formed by ozonation, which, according to Fakhouri et al. [22], can also be related to the high relative crystallinity of these sheets (Table 1).

Thermogravimetric Analysis (TGA)

The thermogravimetric analyzes and their respective differential thermogravimetric (DTG) profiles are presented in Fig. 7, where different profile slopes can be observed. According to Medina-Jaramillo et al. [34], the first stage (100–150 °C) is related to the evaporation of water and/or volatiles. The second stage (180–260) °C is correlated with the decomposition of the glycerol-rich phase, which also holds starch; and the third stage (250–350 °C) is related to the degradation of the components of the starch. As observed in Fig. 7A–C, no differences are observed between sheets of (350–500 ºC), which implies that ozonation did not interfere with starch degradation. Finally, the region from (350–500) ºC corresponds to carbon burning [35].

From the weight loss profile (Fig. 7D), faster degradation of native and O78.9 cassava starch sheets can be observed within the step from (100–150) °C to (250–350) °C. According to Medina-Jaramillo et al. [34], the degradation at lower temperatures suggests a reduction in the molecular interactions between starch-starch chains and strengthening of hydrogen bonding interactions between hydroxyl groups and other molecules. Therefore, ozonation could reduce the molecular interactions between the starch–starch chains and favor the interactions between the hydroxyl groups of the starch and carbonyl and carboxyl groups, thus resulting in a decrease in the degradation temperature for the O78.9 sheet. This was not observed for the O145.3 sheet, probably due to the higher degree of ozonation, which can promote other interactions between the hydroxyl, carbonyl, and carboxyl

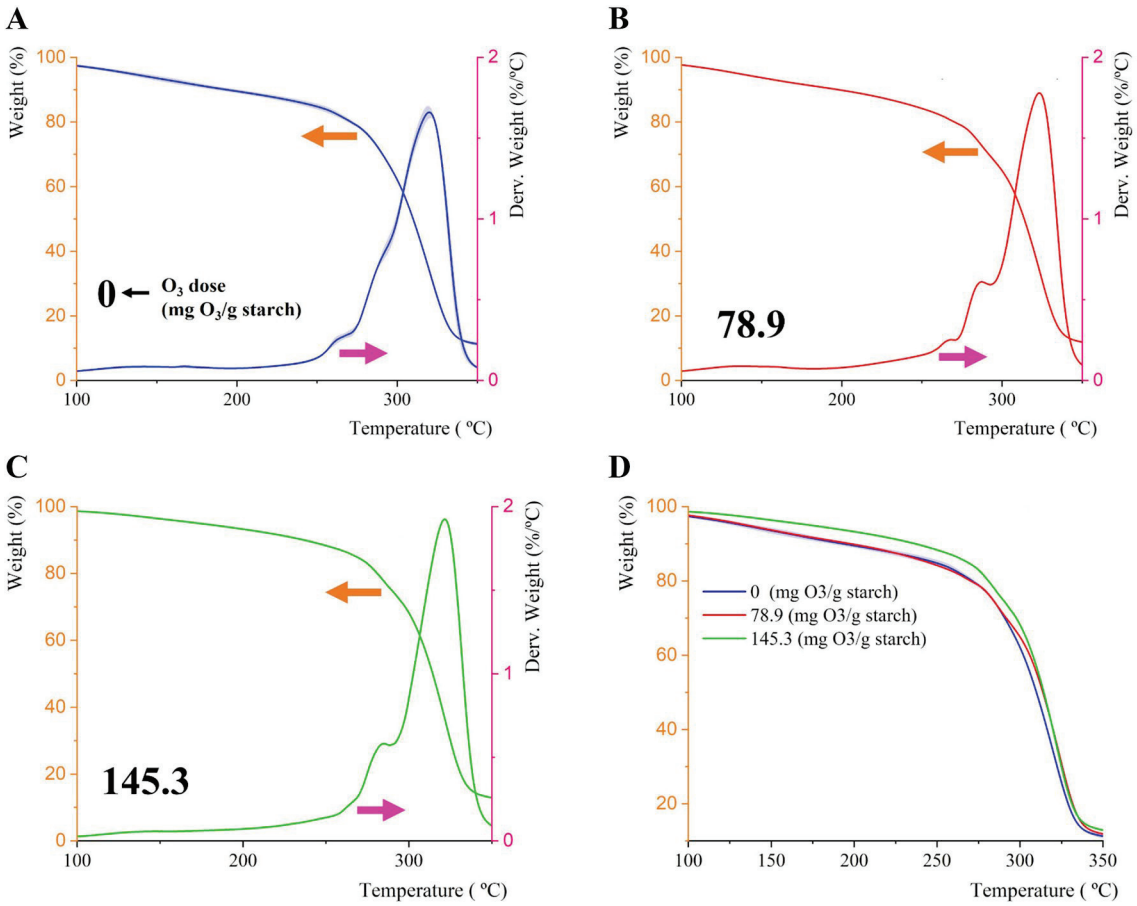


Fig. 7 Thermo gravimetrical analysis of native (**A**) and ozonated (**B**) and **C** cassava starch sheets produced by extrusion. **D** Comparatives profiles

groups, as well as the different molecular size distribution (molecular depolymerization).

Conclusions

The starch ozonation process resulted in the formation of the carbonyl and carboxyl groups, as well as partial molecular depolymerization of the amylose and amylopectin molecules. Consequently, a polymeric matrix with different molecular size distribution, charge distribution, and thus, packing properties, was achieved.

In this work, first reported in the literature, it was possible to produce cassava sheets with unique characteristics, from ozonated starch processed by the extrusion process. The level of ozone processing was shown to be a key factor in selecting the desired properties.

The sheet produced with ozonated starch for O78.9 resulted in a homogeneous structure, with improved mechanical behavior (increased Young Modulus of 43% and decreased elongation at break of 23%), increase hydrophobicity (37%), without interfering with the water vapor permeability. Furthermore, a lower transmittance was achieved in the UV-region (200 to 400 nm) was achieved.

Conversely, for the O145.3 starch sheet, the higher degree of ozonation in combination with the conditions of the extrusion process did not improve the mechanical properties, the water vapor permeability, or the wettability characteristics. This behavior could be attributed to the combination of the molecular modification during the pre-treatment with ozone, and the network formation under the shear-temperature conditions during extrusion. Therefore, an adequate combination of ozonation and extrusion processes yields materials with specific characteristics, with a wide range of applications for starch-based bioplastic production.

We suggest future studies including other starch sources, processing conditions, formulations, and a combination of processes to obtain bio-based plastics with better performance.

Acknowledgements The authors acknowledge the São Paulo Research Foundation (FAPESP) for the postdoctoral fellowship of CIA La Fuente

(2017/05307-8), the Ph.D. scholarship of L Siqueira (2019/21700-7), and the project EMU 2016/12385-2; and the National Council for Scientific and Technological Development (CNPq, Brazil) for funding the project of CIA La Fuente (429043/2018-0) and the productivity grants of PED Augusto (310839/2020-3) and CC Tadini (309548/2021).

Author Contributions CIALF: conceptualization, methodology, validation, formal analysis, investigation, resources, data curation, writing—original draft, writing—review and editing, project administration. LVS: methodology, formal analysis, investigation, data curation, writing—original draft, writing—review and editing. PEDA: conceptualization, methodology, formal analysis, writing—review and editing, supervision, project administration, funding acquisition. CCT: conceptualization, methodology, formal analysis, resources, writing—review and editing, supervision, project administration, funding acquisition.

Declarations

Conflict of interest A patent related with this work was filed (BR1020190112166).

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