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Application of an edible coating developed with Andean potato starch and carboxymethyl-cellulose for lipid reduction during frying

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SUMMARY: This work aimed to search for alternative uses for different varieties of Andean potatoes (*Solanum tuberosum ssp andigenum*) which have been reintroduced in north-western Argentina. Specifically, the development of simple and compound films made with hydrocolloids such as carboxymethyl-cellulose (CMC) and starch (S) extracted from Andean potatoes var. Runa, and its application as a cover in the deep frying of Andean potato chips var. Waycha was studied to minimize oil absorption. The effect of prior bleaching of the chips with different media was also evaluated: water, calcium chloride solution, and ascorbic acid. The coatings were applied to potatoes chips before being fried. The results showed that the type of oil used did not affect absorption by the chips. The bleaching treatments with calcium chloride and coating with S/CMC, showed a significant reduction in oil absorption (39.5 % ± 0.7), delayed its oxidation, and decreased the loss of tocopherols during the frying process. It also contributed to the physical and sensory characteristics of the final product, which presented high acceptability by consumers.

KEYWORDS: *Andean potato chips; Andean potato starch; Coating; Frying; Oil absorption*

RESUMEN: ***Aplicación de un recubrimiento comestible desarrollado con almidón de papa andina y carboximetilcelulosa para la reducción de lípidos durante la fritura.*** Este trabajo tuvo como objetivo buscar alternativas de uso para diferentes variedades de papas andinas (*Solanum tuberosum ssp andigenum*) reintroducidas en el noroeste argentino. Específicamente, el desarrollo de películas simples y compuestas elaboradas con hidrocoloides como la carboximetilcelulosa (CMC) y el almidón (S) extraído de papa andina variedad Runa, y su aplicación como cobertura en frituras de papas andinas var. Waycha fue estudiado para minimizar la absorción de aceite. También se evaluó el efecto del blanqueo previo de las hojuelas con diferentes medios: agua, solución de cloruro de calcio y ácido ascórbico. Los recubrimientos se aplicaron a patatas fritas antes de freírlas. Los resultados mostraron que el tipo de aceite utilizado no afectó su absorción por parte de las hojuelas. Los tratamientos de blanqueo con cloruro de calcio y recubrimiento con S/CMC, mostraron una reducción significativa en la absorción de aceite (39,5 % ± 0,7), retrasaron su oxidación y disminuyeron la pérdida de tocoferoles durante el proceso de fritura. También contribuyó a las características físicas y sensoriales del producto final, que presentó alta aceptabilidad por parte de los consumidores.

PALABRAS CLAVE: *Absorción de aceite; Almidón de papa andina; Fritura; Hojuelas de papas andinas; Recubrimiento*

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1. INTRODUCTION

Many strategies have been proposed to reduce oil absorption in food during frying (Crosa *et al.*, 2014). The application of a hydrocolloid coatings has been one of the most promising methods (Naghavi *et al.*, 2018). These modify the food surface, decreasing its permeability. Among the materials used to make coatings are methylcellulose (MC), hydroxypropyl-cellulose (HPC), carboxymethyl-cellulose (CMC) and hydroxypropylmethyl-cellulose (HPMC) (Mai Tran *et al.*, 2007). The use of natural polymers in packaging and food additive applications is gaining popularity, due to the prevention of environmental problems. Edible coatings must contain substances that comply with food standards and must also be economical, easy to apply and respectful of the environment. Cellulose is a very abundant natural polysaccharide, it is the structural component of the cell wall of plants, and therefore, it is obtained from various natural sources, such as food waste, cereal bran and fruit peels. The main reasons for the common use of CMC are its viscosity, flocculant property, excellent oil resistance, transparency, non-toxicity, and low price. It has GRAS status from the FDA (Yaldirim–Yalcin *et al*., 2022). Starch, as one of the most abundant, sustainable, and low-cost commercial biopolymers, has versatile applications in many industries (e.g., food, paper, packaging, etc.). Potato varieties to produce fried products at the industrial level must meet external and internal quality characteristics. Environmental and genetic effects determine external qualities. The internal ones refer to the chemical composition of tubers which includes the content of sugars, dry matter, and starch, among others. Reducing sugars (fructose and glucose) play a critical role in the industrial process, so the legislation establishes contents lower than 0.25% for the elaboration of French fries and less than 0.2% (Colman *et al.*, 2009) for potatoes in flakes. Frying is an operation widely used in the food industry. It is based on the transfer of heat from hot oil to foods, causing water removal and oil absorption. The high consumption of fried products is a risk factor for health due to the high energy density and the possible formation of toxic compounds. The origin and oil composition can influence the absorption of oil into food during the frying process, as well as temperature and frying time, type of food, porosity, and pretreatments applied (Alvis *et al.*, 2015). During frying, reactions responsible for taste, color, and texture occur and unhealthy components are formed such as polar compounds (Jimenez *et al.*, 2017). During repeated use of the frying oil, it degrades and changes its composition, generating a mixture of polar compounds that act as wetting agents which reduce the surface tension between water and oil, causing an increase in oil absorption.

This paper proposed to search technological alternatives for use of Andean potato *(Solanum tuberosum ssp. andigenum*) genotypes which have been reintroduced in northwestern Argentina to revalue these relegated foods. For this purpose, the objective was to study the application of films elaborated with hydrocolloids and starches extracted from Andean potatoes var. Runa and to study their application in the deep frying of chips of the var. Waycha, in order to reduce oil absorption.

2. MATERIALS AND METHODS

2.1. Materials

Starch extracted from the Runa Andean potato variety (30% amylose content) (Calliope *et al.*, 2019), carboxymethyl-cellulose (CMC) (food grade, Rettenmaier & Sohne GMBH + Co), calcium chloride and ascorbic acid (food grade) were used for the formulation of coatings. The Andean variety Waycha was used for frying assays. Commercial potato chips were used as reference to calculate the relative reduction in oil absorption. Sunflower oil and an oil blend (soybean/sunflower, ratio: 94/6) were used for frying.

2.2. Formulation and properties of films

Starch Extraction. Healthy tubers of the Andean potato var. Runa were used to extract starch. They were cut into cubes of 2–3 cm, submerged in sodium bisulfite (1.2 $g \cdot L^{-1}$) and then crushed in an Omni Mixer. The obtained mixture was filtered; and the residue was washed repeatedly with a sodium bisulfite solution. The filtrate was centrifuged and the starch obtained was washed with alcohol, dried at 40 °C, and packaged until analysis (Calliope *et al.*, 2019).

Formulation of films. The concentrations of the components were: S (1%); S/CMC (1:0.5; 1.5%), and CMC (1%), which were dispersed in distilled water, heated (S) at 80 °C and (CMC) at 100 °C for 1 h and cooled to room temperature (25 °C). 13 g of each formulation were poured onto 10 cm diameter polystyrene plates and allowed to dry for 6 h in a forced-flow oven at 35 °C and then maintained for 15 h at 53% relative humidity in room temperature.

Thickness. The film thickness was measured with an analog micrometer (Digimess, Argentina, sensibility 0.0001mm); the measurement was evaluated with the average of 5 different points of the film.

Water Vapour Permeability (WVP). The WVP was determined gravimetrically according to the standard method ASTM E96 (2000). The films were conditioned for 48 h in a desiccator at 25 °C and 53% relative humidity (RH) using a supersaturated solution of Mg $(NO_3)_2$. The measurements of WPV (quadruplicate) were performed according to Slavutsky and Bertuzzi (2015).

The water vapor transmission rate (WVTR) was calculated from equations 1 and the water vapor permeability (P) was calculated from equation 2

$$WVTR = \frac{G}{A} \quad \text{(Eq. 1)}$$

$$P = cte \cdot \frac{WVTR \cdot l}{P_{w0} - P_{w2}} \quad \text{(Eq. 2)}$$

Where: G: slope of linear regression; A: area of the exposed film; l: film thickness; P_{w0}: partial pressure of water vapor in the air on the surface of distilled water; P_{w2}: partial pressure of water vapor on the surface of the film outside the cup; cte: constant to satisfy unit conversion.

Solubility. Solubility was measured as a percentage of dry matter in the film solubilized in water for 24 h immersion. The samples, previously dried in an oven at 105 °C, were weighed (1 g) and placed in a beaker with 50 mL of distilled water at 30 °C, with constant stirring. The non-solubilized material was then separated by centrifugation (Sigma 4K10, Germany) and dried to determine the weight of the dry matter. The tests were performed in triplicate and the solubility was calculated as follows:

$$solubility = \frac{Initial\ dry\ weight - final\ dry\ weight}{Initial\ dry\ weight} x\ 100 \quad \text{(Eq. 3)}$$

Sorption isotherms. The films were cut into pieces of approximately 2 cm^2 and placed in a desiccator with P_2O_5 for 48 h. After that, they were placed in containers with controlled relative humidity using different supersaturated saline solutions (range of aw: 0.10 to 0.90) (Spiess and Wolf, 1983). The weight of the samples was recorded until the difference between the two consecutive weighings was less than 1 mg. Absorption tests were performed in triplicate at each aw. The data obtained were adjusted by the sorption model of BET (Equation 4).

$$W_e = \frac{W_0 \cdot C \cdot a_w}{(1 - a_w) \cdot (1+(C - 1)a_w)} \quad \text{(Eq. 4)}$$

Where W_e is the equilibrium moisture content (g water/100g dry film), W_0 is the moisture content in monolayer (g water/100g dry film) and C is adsorption constant of the first layer dependent on temperature. The quality of the fit was assessed through R^2.

Color. The color of the films was determined with a colorimeter (Colorquest XE Hunter Lab, USA) versus a standard film (L=94; a=−0.11 and b=3.2). All measurements were performed in triplicate. Total color difference (ΔE), was calculated according to Equation 5:

$$\Delta e = ((L_{standar}-L_{sample})^2 + (a_{standar}-a_{sample})^2 + (b_{standar}-b_{sample})^2)^{1/2} \quad \text{(Eq. 5)}$$

Contact angle. To evaluate the wettability of the oils to the different surfaces, the contact angles were measured using a goniometer (Standard Goniometer with DROP image model 200-00, Ramé-Hart Instrument Co., USA). The oil (10 µL) was dropped onto the surface of the film, using a micro-syringe. The contact angle was measured in 5 points on each film (Zdanowicz and Johansson, 2016). Each analysis was performed in sextuplicate at 25 °C.

2.3. Potato Chips

Analysis of the raw material. Reducing sugar content was determined according to the dinitrosalicylic (DNS) acid method (Miller, 1959). The DNS reagent contained 10 g/L 3,5-dinitrosalicylic acid, 16 g/L NaOH and 300 g/L sodium potassium tartrate (Rochelle salt). 3 mL DNS reagent and 1 mL supernatant sample were mixed in a test tube and heated in a boiling water bath for 5 min. Subsequently, they were placed in a cold water bath for 2 minutes, shaken and left to rest for 10 minutes. The reacted mixture was measured for absorbance at 540 nm in a spectrophotometer (Mapada, model UV 6300 PC). Glucose p.a. (Merck) was used for the standard curve.

Blanching treatments. The potatoes were washed and cut without peeling in the form of chips (2.5 mm thick); then three scalding processes were applied: 1) water boiling for 5 min, 2) aqueous solution of calcium chloride (0.5%), and 3) ascorbic acid solution (1%), with the same temperature/time conditions.

Coating application. After blanching, the potatoes were drained on absorbent paper and immediately immersed in the solutions described in section 2.2.2., at 25 °C for 2 min, then the potatoes were drained and the surface moisture was removed in a convection oven at 40 °C for 20 min. An uncoated sample was used as control.

Frying process. The potatoes (150 ± 5 g) were fried in 3 L of oil in a domestic fryer without reposition. The temperature/time conditions were 180 ± 10 °C/3 min. The fried chips were drained for 2 min in the fryer basket and stored for 24 h until analysis. The oil absorption of the chips with different blanching and coatings was studied in the first frying cycle. To determine the behavior of the oils concerning the tested coatings, 40 frying cycles were performed for each type of oil; 10 g of oil was taken in cycles 1, 20, 40, and stored at -20 °C until analysis.

Chip evaluation. In the first frying cycle, the lipid content and moisture/solid matter were determined (AOAC, 2016).

To calculate the reduction in oil absorption (% ROA, Equation 6), a commercial potato chip was taken as a reference.

$$\%ROA = \left(\frac{\%LChA \times 100}{\%LChC}\right) \quad \text{(Eq. 6)}$$

% LChA: percentage of lipids of Andean potato chips, scalded with coatings
% LChC: percentage of lipids of commercial potato chips, label value: 30.4 g/100 g potato.

Color. It was measured by a Colorimeter (Colorquest XE Hunter Lab, USA). The average of 5 readings was calculated. A chip without frying was taken as reference. The measure of color change was evaluated according to Equation 5. Where L*a*b*standard were the values for fresh potatoes and L*a*b*sample were the values for fried chips.

Sensory evaluation. Chip samples from the first frying cycle in the two types of oil were used to carry out the sensory analysis with 48 untrained consumers (Sullivan, 2017). Four different samples were put on a colorless plate and arranged according to the master sheet. The consumers evaluated sensory attributes of color, odor, flavor, acceptability and, texture. The consumers assessed the samples using a 5- point hedonic scale where 5-very pleasant, 4-pleasant, 3-neither like nor dislike, 2-unpleasant, 1-very unpleasant. Four-digit random numbers were used to identify each sample.

2.4. Analysis of fresh and used oils

Fatty acid composition. Fatty acid methyl esters (FAMEs) were prepared according to IUPAC (1987). The FA were quantified in a gas chromatograph model 2014 (Shimadzu, Japan) equipped with column SP 2560 (100 mm x 0.25 mm). A mixture of FAME (Supelco FAME Mix C4-C24 18919) was employed as standard.

Calculated oxidizability (Cox). The Cox value of the oils was calculated by the percentage of unsaturated C18 fatty acids, applying Equation 7, as proposed by Rossi *et al.* (2013):

$$\text{Cox} = [1(\text{oleic acid }\%) + 10.3(\text{linoleic acid }\%) + 21.6\ (\text{linolenic acid }\%)]/100 \quad \text{(Eq. 7)}$$

Tocopherols. They were determined by the AOCS Method Ce8-89. A chromatograph (Shimadzu model 20, Japan) was used, with a fluorescence detector, a Phenomenex C18 silica column (250 × 4.6 mm, 5.0 μm); the mobile phase was acetonitrile, methanol, water with phosphoric acid and isopropanol (the flow rate was kept constant at 1.0 mL/min). Tocopherol isomers (α-, β-γ-, δ-) were identified using standards (Sigma Aldrich). Isopropanol (1 mL) was added to the oil sample (30 mL) and then injected into the HPLC equipment.

Polar compounds. They were determined by adsorption chromatography. Stationary phase Silica gel (Merck) particle size 0.063-0.200 mm was used as the mobile phase for non-polar compounds ethyl ether/petroleum ether 10:90 v/v, and diethyl ether for the polar fraction. Polar compounds (PC) were quantified, such as the difference between the initial mass of oil and the eluted non-polar fraction (IUPAC, 1987).

2.5. Statistical analysis

The means were analyzed by analysis of Variance. Differences among samples were analyzed according to Tukey's test. Differences among treatments were considered significant at ($p < 0.05$). To determine the influence of the scalding solution, coating addition, and oil absorption during frying, the 3-way interaction method was applied. Software Infostat 2017 and Graph pad prism version 5.01 were used.

3. RESULTS AND DISCUSSION

3.1. Films

The average results of the measured parameters are shown in Table 1. The water vapor permeability (WVP) of the edible films should be as low as possible in order to control the transfer of moisture between the food and the surrounding atmosphere. S/CMC films showed a significantly lower WVP value than CMC films, which would be related to the thickness of the film and the intrinsic characteristic of each material (Basiak *et al.*, 2017). The permeation phenomenon depends on three stages: adsorption, diffusion, and desorption. The diffusion stage depends on the thickness of the film and the tortuous path which hinder the passage of water molecules through the film matrix, while the other two are independent of it. Starch has a semi-crystalline structure; the amylose is capable of forming a tortuous path that decreases the diffusion of water through the film. The different behavior of starch and CMC films may be due to this. No significant difference was observed between S/CMC and S films. This indicated that in the composite films, permeability was related to the presence of starch. Almasi *et al.* (2010) postulated that starch forms hydrogen bonds with the hydroxyl groups of the CMC, and this strong structure could reduce the diffusion of water into the material. Therefore, the addition of CMC would improve the water-resistance of the starch matrix. The water solubility of the S films was high and higher than that reported by Basiak *et al.* (2017). This would be related to the higher amylose content of the starch in the potato var. Runa used. The combination with CMC produced a decrease in solubility of approximately 50%. This behavior was also observed by Ghanbarzadeh *et al.* (2010).

Table 1. Parameters measured in the developed films

Parameters		S	CMC	S/CMC
Thickness (µm) 10^{-5}		6.42 ± 0.20^{c}	4.86 ± 0.07^{a}	5.63 ± 0.08^{b}
Barrier properties water vapor permeability (10^{-10} g· m^{-1}·s^{-1}·Pa^{-1})		2.12 ± 0.23^{ab}	2.73 ± 0.21^{b}	1.94 ± 0.29^{a}
Solubility in water (%)		26.24 ± 6.66^{b}	9.25 ± 2.23^{a}	13.06 ± 1.34^{a}
BET	w_0	3.09 ± 0.13^{b}	2.00 ± 0.10^{a}	3.23 ± 0.15^{b}
	c	15.87 ± 2.58^{b}	5.01 ± 4.50^{a}	6.15 ± 5.36^{a}
	R^2	0.9292	0.9388	0.9240
Color	L	92.98 ± 0.09^{a}	93.32 ± 0.06^{b}	93.24 ± 0.17^{b}
	a	-0.33 ± 0.03^{c}	-0.57 ± 0.02^{a}	-0.52 ± 0.02^{b}
	b	3.60 ± 0.19^{a}	3.90 ± 0.27^{a}	3.47 ± 0.87^{a}
	AE	1.11 ± 0.15^{b}	1.08 ± 0.22^{ab}	0.91 ± 0.15^{a}
Surface properties	θ (OB)	15.80 ± 1.20^{a}	18.90 ± 3.90^{ab}	20.60 ± 3.90^{b}
	θ (SO)	18.80 ± 4.10^{a}	16.80 ± 1.80^{a}	19.10 ± 3.10^{a}

S: starch; CMC: carboxymethyl-cellulose; S/CMC: combination starch with carboxymethyl-cellulose.
w0: monolayer moisture content, c: constant related to heat sorption for monolayer, R^2: coefficient of determination. θ (OB): contact angle of oil blend; θ (SO): contact angle of sunflower oil; color parameters (L, a, b). Values are the average ± SD of triplicate samples.
Values having the same letter for a parameter within the same row are not significantly different at p level > 0.05 according to the Tukey test.

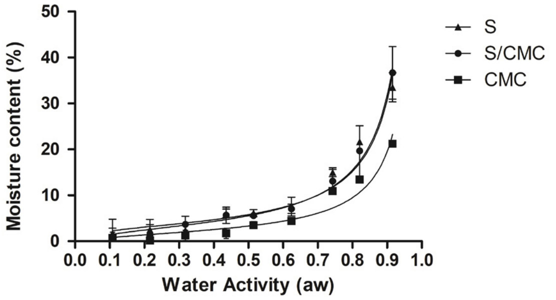

Figure 1. Moisture Absorption Isotherms Of Films. Coating: Starch (S); Carboxymethyl-cellulose (CMC); combination starch with carboxymethyl-cellulose (S/CMC). Continuous line: BET model.

Figure 1 shows the absorption isotherms obtained at 25 °C for the three films formulated. The curves were typical of polymers with affinity for water. The curves showed a slight relative slope at low a_w values, while they were exponential at aw values greater than 0.60. Other authors reported similar behavior in starch-based films (Slavutsky and Bertuzzi, 2015). The experimental data indicated that the CMC film had the lowest water absorption, while the S/CMC film showed similar behavior to the S film. The adjustment parameters obtained with the BET model (Equation 4) of each film showed that the constant c influenced the sigmoidal shape of the isotherms, particularly in the low range of a_w. The values for c would indicate that the moisture absorption of the matrix studied could occur more easily in the upper layers than in the monolayer. These results showed that the stage that controlled the water permeability of the S films was diffusion and not the adsorption/desorption of water. Instead, the stage that controlled the water permeability phenomena for CMC films depended on the absorption/desorption phenomena. This was probably due to the lower water sorption capacity of these films. However, S/CMC films presented a similar value to the S films for the water permeability and sorption isotherm, but the solubility in water was similar to CMC films. This was probably due to the influence of the semi-crystalline structure of starch and the interaction through hydrogen bonds between both polymers.

Starch films showed greater opalescence, which could be explained by their greater thickness, which was probably due to the higher amylose content (Basiak *et al.*, 2017). Regarding color, parameter L showed significant differences which were lower for the S film. In parameter a, all the films had a greenish hue, which was higher for the CMC, and in b the film, hue was yellow with no significant differences between them. In general, the optical values for the films presented good transparency. Ghanbarzadeh *et al.* (2010) observed in a study conducted with S/CMC composite films that the CMC aggregate produced clearer films. These changes can be further described with the ΔE function, which showed a significant decrease ($p < 0.05$) when CMC was added.

The contact angle was used as an indicator of the degree of interaction between the oils and the surface of the films. The three films had surfaces with moisturizing properties which confirmed their hydrophilicity. An increase in the contact angle between the oil and the film indicates a lower affinity between both materials. The highest value (20.6°) was obtained for S/CMC films in the oil blend. This is accordance with the frying experiments (Table 2 and Figure 2), in which the potato chips with the lowest oil content were those covered by S/CMC. The contact angles of the CMC and S films were smaller, indicating surfaces with greater affinity to oils.

3.2. Chips

Colman *et al.* (2009) reported that the minimum values for the dry matter (DM) and reducing sugar (RS) content for a potato to be suitable for frying are 25 and 0.2%, respectively. The Andean potato var. Waycha, contains 26.38 ± 0.31 DM and 0.18 ± 0.06 RS. Therefore, the Waycha potato variety meets both conditions. It is also larger than other varieties, which would indicate that it could be suitable for use in the production of fried potato chips. The DM content decreased with all the bleaching treatments. Significant differences in DM content were found among chips scalded with water (observed decrease from 26.4 to 23.8%), with respect to treatments with ascorbic acid (22.6%) and calcium chloride (22.1%). This could be due to different migrations of soluble potato compounds to the bleaching medium. The oil content was significantly affected ($p > 0.05$) by the kind of scalding and the type of coating used (Table 2). The oils employed did not significantly influence absorption. Figures 2a and 2b, show the percentages of absorbed oil reduction according to the treatments applied, taking as reference a commercial potato chip (Label value 30.4 g oil/100g). Control samples scalded in water and without coating showed

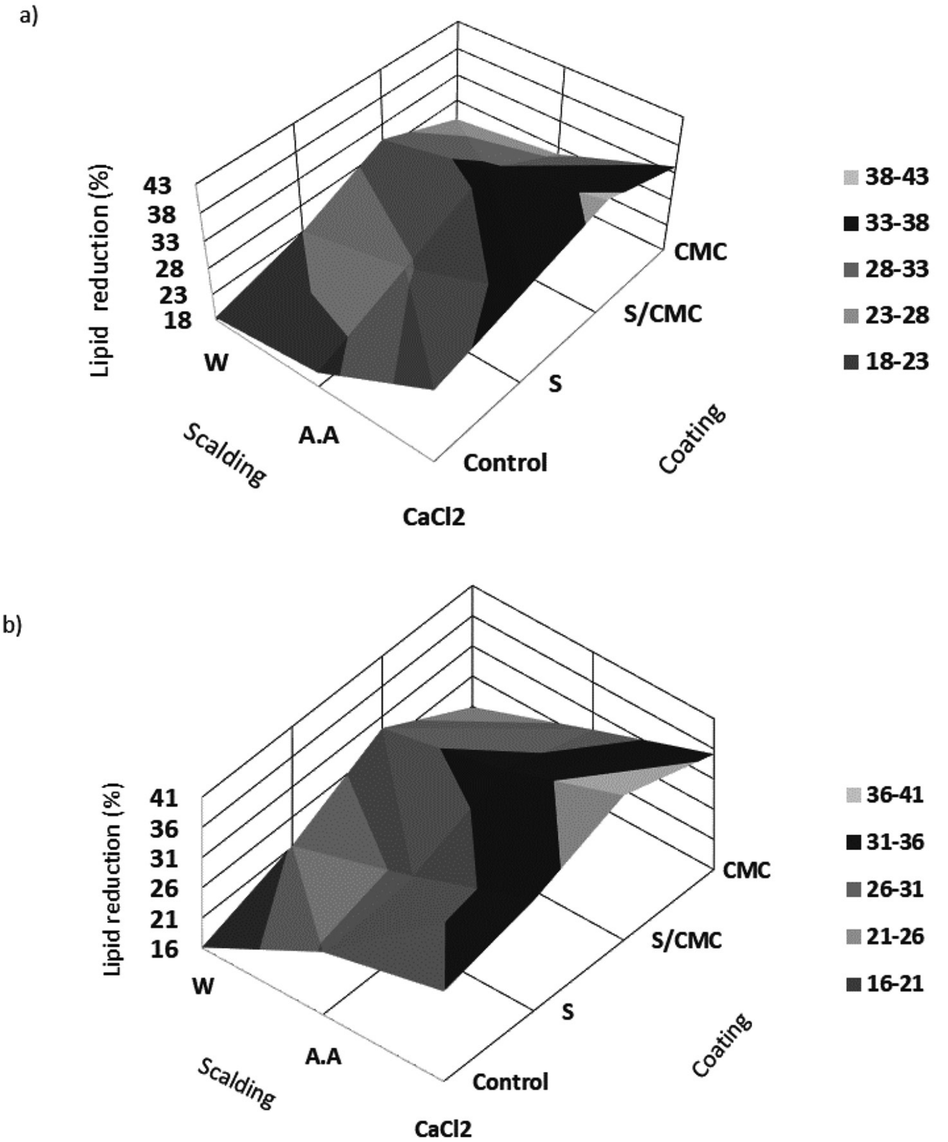

Figure 2. Reduction in fat content in Andean potato chips vs. commercial chips, according to treatments applied. a) Frying oil: sunflower, b) Frying oil: blend (Sunflower/soybean).
Coating: Starch (S); Carboxymethyl-cellulose (CMC); combination starch with carboxymethyl-cellulose (S/CMC). Scalding: Water (W), Ascorbic acid (A.A); Calcium chloride (CaCl2).

a slight reduction in oil content (16.1-18.5%), compared to those scalded in calcium chloride with S/CMC coating (39.1–40.1%). These results indicated that calcium chloride stabilized the structure of the tissue during the frying process. The texture of the potato depends on the presence of pectin substances, which are part of the intercellular material. Pectinolytic enzymes produce free carboxylic groups, which can react with divalent ions such as calcium and magnesium, creating more rigid structures and increasing firmness. The formation of these calcium/pectin complexes causes the reaffirmation of the cell wall and increase the stiffness of the medium of the laminar cell wall (Hernandez *et al.*, 2014), and therefore its structure better resists the frying process. Table 2 and Figures 2a and 2b show that the coatings influenced the decrease in oil absorption. The results showed significant differences ($p > 0.05$) among treatments. The one with the greatest effect was the coating of S/CMC (39.5% ± 0.7) combined with scalding in calcium chloride; while the one with the least effect was the control without coating and

Table 2. Oil content in Waycha potato chips (g/100 g) with different treatments

Treatment	Sunflower oil				Oil Blend				Mean (o*b)
	Coating				Coating				
Blanching	Control	S	S/CMC	CMC	Control	S	S/CMC	CMC	
Water	24.79±0.18^{l}	23.40±0.26^{ij}	21.25±0.09^{def}	23.05±0.09^{i}	25.50±0.13^{m}	23.93±0.09^{jk}	21.57±0.10^{efg}	24.06±0.24^{jk}	23.44±1.47^{b}
AA (1%)	24.08±0.21^{k}	22.07±0.08^{gh}	19.95±0.16^{b}	22.30±0.15^{h}	22.37±0.06^{h}	22.12±0.04^{gh}	20.33±0.17^{bc}	21.85±0.11^{fgh}	21.88±1.28^{b}
CaCl2 (0.5%)	20.83±0.16^{cd}	19.68±0.11^{b}	18.52±0.13^{a}	20.03±0.08^{b}	20.99±0.45^{cde}	19.97±0.65^{b}	18.24±0.07^{a}	19.72±0.17^{b}	19.75±0.97^{a}
Mean (o*f)	23.23±1.80^{c}	21.72±1.61^{b}	19.91±1.17^{a}	21.79±1.34^{b}	22.95±1.98^{c}	22.01±1.72^{b}	20.05±1.44^{a}	21.88±1.85^{b}	

References: Control: Uncoated, AA: ascorbic acid. Mean (o*b): interaction oil*blanching; Mean (o*f): interaction oil*film. Letters inside box are the interaction of (o*b*f). Each value in the table is the mean of three replicates. Means with a common letter are not significantly different ($p > 0.05$) according to the Tukey test.

scalding in water (17.3% ± 1.7). This reduction in oil absorption could be attributed to the fact that the starch undergoes structural changes in which the crystals of amylose and amylopectin are reorganized and promote the formation of a gel that functions as a barrier to the entrance of oil (Hasbún *et al.*, 2009). Varela and Fiszman (2011) and Freitas *et al.* (2009) postulated that CMC increases water retention capacity and, consequently, prevents the replacement of water with oil. In addition, since the polymer is hydrophilic, it forms a thin layer on the surface of the food which acts as a barrier to the incorporation of oil. Ali *et al.* (2012) observed that CMC increased surface tension, which facilitated the draining of surface oil. Likewise, calcium chloride is a cross-linking agent which forms a fine network which prevents the migration of oil to the potato during the frying process (Hasbún *et al.*, 2009).

The results showed that the type of oil had no significant influence on absorption ($p > 0.05$).

Table 3 shows color changes during 40 frying cycles. In the parameters L* a* and b* within the frying cycles with coatings there were significant differences in the L values. It was observed that chips with coating darkened as the cycles continued. For parameter a, the potatoes with coatings in both oils showed significant differences between the first and the last frying, with an increase in redness in the last cycles, possibly due to the effect of the coating. While in parameter b, there was greater variation, with the exception of chips without coating fried in the oil blend. In the other treatments, the intensity of the yellow color varied, and a defined pattern was not found. In all cases, the yellow/gold color, typical of fried products, was characteristic. The parameter ΔE was used to evaluate the color change between the different processes tested. The mean values for color L*a*b (Table 3) show that the potatoes with coating, fried in sunflower oil, presented statistical differences with respect to those without coating. It is also observed that the highest ΔE corresponded to the treatments with edible coating, due to the parameters *b followed by *a. This could be due to the presence of the coating and the type of oil. However, the sensory attributes of acceptability and texture for fried coated potatoes in sunflower oil presented a favorable statistical difference compared to those without coating in the same type of oil. The re-

Table 3. Color parameters and preference scores for sensory attributes of Waycha coated potato chips with S/CMC and scalding with calcium chloride. Tocopherol content in fresh and used oils

Properties	Variable	SO		OB	
		without coating	with coating	without coating	with coating
*Chips Color L*a*b*	L(St)	80.37±0.23	80.37±0.23	80.37±0.23	80.37±0.23
	L(1)´	78.85±1.28^{a}	78.82±1.24^{a}	77.49±0.88^{a}	77.42±1.01^{a}
	L(20)´	74.18±1.50^{a}	75.05±0.49^{ab}	78.52±3.52^{a}	72.48±2.78^{ab}
	L(40)´	70.63±4.72^{a}	69.44±2.07^{c}	73.25±2.39^{a}	63.07±2.59^{b}
	a(St)	1.04±0.15	1.04±0.15	1.04±0.15	1.04±0.15
	a(1)´	1.46±1.12^{a}	1.72±0.58^{b}	4.17±0.61^{a}	4.87±0.78^{b}
	a(20)´	5.75±2.13^{a}	2.27±0.40^{b}	3.92±3.43^{a}	4.96±1.77^{b}
	a(40)´	5.79±4.52^{a}	6.23±0.14^{a}	5.71±0.82^{a}	14.65±1.39^{a}
	b(St)	31.39±0.53	31.39±0.53	31.39±0.53	31.39±0.53
	b(1)´	38.37±3.29^{ab}	41.29±0.77^{a}	36.93±1.14^{a}	37.18±0.63^{bc}
	b(20)´	42.97±2.75^{a}	32.42±1.80^{b}	40.58±2.27^{a}	40.75±1.37^{ab}
	b(40)´	38.10±5.60^{ab}	41.48±1.14^{a}	41.08±2.51^{a}	41.56±1.19^{a}
	ΔE(1)´	7.15	10.04	6.99	7.54
	ΔE(20)´	13.95	5.56	9.81	12.85
	ΔE(40)´	12.74	15.13	12.9	24.25
**Sensory attributes of fried chips 1° cycle with film and blanching (calcium chloride)	Color	4.0±0.4^{a}	4.2±0.4^{a}	3.8±0.8^{a}	4.0±0.6^{a}
	Odor	3.5±0.5^{ab}	4.0±0.4^{b}	3.4±0.7^{ab}	3.3±0.8^{a}
	Flavor	3.7±0.9^{b}	4.3±0.5^{b}	2.7±0.7^{a}	3.6±0.9^{b}
	Acceptability	3.8±0.8^{a}	4.7±0.5^{b}	3.5±0.9^{a}	4.0±1.0^{ab}
	Texture	2.9±0.9^{a}	4.4±0.9^{c}	3.0±0.9^{ab}	3.9±0.8^{bc}
	Mean	3.6±0.4^{a}	4.3±0.3^{b}	3.3±0.4^{a}	3.8±0.3^{ab}
***Tocopherol Content in oils (ppm)	α (fresh)	650.5±1.0^{c}		88.0±1.4^{a}	
	F40	530.5±1.0^{a}	548.9±2.6^{b}	91.5±1.2^{ab}	97.5±0.7^{b}
	β–ϒ (fresh)	121,5±2.5^{c}		2059.2±2.7^{c}	
	F40	106.8±0.9^{a}	114.6±1.1^{b}	1688.4±2.4^{a}	1899.1±0.9^{b}
	δ- (fresh)	22.2±0.3^{a}		647.8±1.6^{b}	
	F40	21.9±1.1^{a}	25.6±1.2^{a}	621.6±1.1^{a}	766.6±0.4^{c}
	Total (fresh)	794.1±1.1^{c}		2795.0±5.7^{c}	
	Total F40	659.1±1.3^{a}	688.2±2.6^{b}	2401.5±0.1^{a}	2763.2±1.1^{b}

*Standard (St): raw potato; SO: Sunflower oil; OB: Oil blend. Number of frying cycles; coating combined starch/ carboxymethyl-cellulose: S/CMC; the number in brackets is the number of frying cycles. * Different letters (a, b, c) indicate significant differences among results in columns ($p < 0.05$). **The ratings are based on a 5-point hedonic scale where 1=very unpleasant, 5=very pleasant; Means with one common letter per row are not significantly different ($p > 0.05$). *** Comparison of means between fresh potatoes and frying cycle 40 (F40) with and without coatings. Each observation is a mean of 10 replicate experiments. Different letters for fraction (α- βɤ- δ) indicate significant differences ($p < 0.05$).

sults of this study show that the coating with S/CMC did not affect the color and provided a better "crunchy" texture to the fries in the two types of oils used; while the attributes described for the product without coating were "bitter taste, burnt and oily". This indicates that the coating contributed to eliminating these perceptions. García *et al.* (2002) reported that CMC edible coatings affected the color of potato chip samples, but did not change the characteristic texture.

The coating not only impacted the reduction in the oil content but also slightly improved the sensory attributes of the fries. During frying, the oil is exposed to high temperatures in the presence of air and humidity, which generates oxidation, hydrolysis and polymerization reactions (Rimac-Brnčić *et al.*, 2004). This is why the oil usage times are reflected in the color and changes in its composition (Navas *et al.*, 2007).

3.3. Analysis of fresh and used oils

Figure 3 shows the fatty acid fractions: saturated (SFA), monounsaturated (MFA), polyunsaturated (PFA), and Trans (TFA) of fresh oils and after being used in 40 frying cycles. The SO had a lower content of polyunsaturated fatty acids (5.6%) than the OB (7.03); so, its calculated oxidability was different as well. There was an increase in the SFA content in OB with increasing frying cycles, and in TFA when potato chips were uncoated. In the SO the MFA fraction increased and TFA were generated when uncoated chips were fried. It is known that TFA has been related to temperature and times the same oil is used. In this study, the temperature was maintained at 180 °C, but the times of frying changed, which explains the increase of TFA in cycle frying 40 in both cases. Also, the increase in TFA has been related to the kind of food and the fatty acid composition of the oil. The food varied due to the presence of the coating, which favored a lower increase of TFA, apparently acting as a protective agent against it. The higher amount of TFA observed in the oil blend was probably due to its composition related to less oxidative stability compared to sunflower oil. Cis to Trans isomerization begins when the frying temperature is higher than 150 °C (Bhardwaj *et al.*, 2016). However, the TFA content in the oils with 40 frying cycles was less than the maximum established (5%) by Argentine legislation.

Tocopherols are natural components of oils with a protective effect against oil oxidation. During the processing, storage, and use of oils there are partial losses of these components. Table 3 shows the content of the different types of tocopherols in fresh SO and OB and after being used in 40 frying cycles. The tocopherol content was significantly higher in the OB than in SO, both fresh. When both were used in 40 frying cycles, the total tocopherol content decreased significantly, which was less noticeable when covered chips were fried. Rossi *et al.* (2017) reported that frying potato chips in eight different types of vegetable oils, including pure and blended sunflower oil, tocopherols decreased rapidly after the third hour of

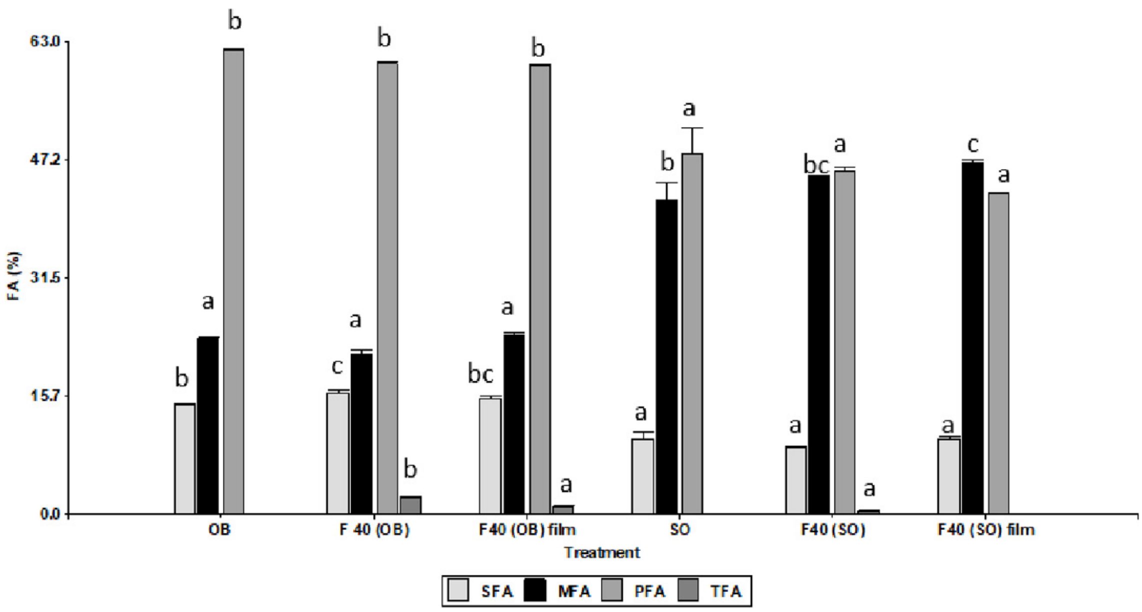

Figure 3. Fatty acid fraction of fresh oils and those used for frying

OB: oil blend (Sunflower/soybean); F40 (OB): Frying cycle 40 in oil blend; F40 (OB) film: Frying cycle 40 in oil blend chips with film; SO: sunflower oil; F40 (SO): Frying cycle 40 in sunflower oil; F40 (SO) film: frying cycle 40 in sunflower oil with film. Fatty acids: saturated (SFA), monounsaturated (MFA), polyunsaturated (PFA), and trans (TFA). Different letters indicate significant differences by the Tukey test ($p < 0.05$) among the same fatty acid fraction with different treatments.

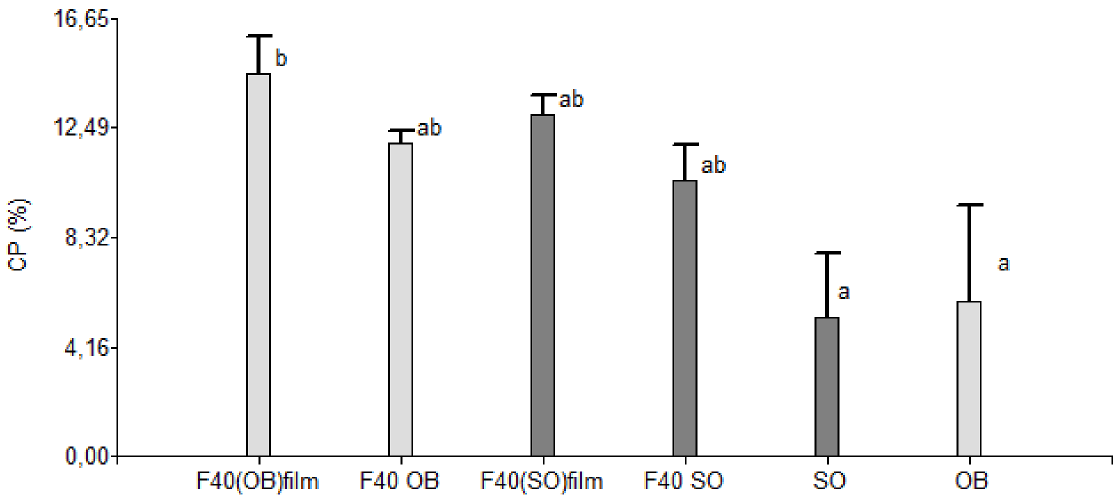

FIGURE 4. Polar compounds in fresh oils (OB and SO) and used in 40 frying cycles (F40) of potatoes with and without coating

Each observation is an average of 6 replicates. The same letter for the same parameter is not significantly different at $p > 0.05$ according to the Tukey test.

continuous use of the oils. In this study, the frying cycles exceeded 3 hours of oil use. The mechanism of the reaction to eliminate radicals of tocopherols requires that they lose their mobile hydrogen atom in the hydroxyl group, forming more stable free radicals than fatty acids. It follows that the rapid oxidation of tocopherols corresponds to greater antioxidant power. However, if all other fractions are taken into account, it could be assumed that, in the case of oils containing higher levels of PFA, the double bond that determines unsaturation competes with tocopherols as substrates for oxidation, resulting in a less rapid decrease in these antioxidants. In contrast, in the case of low polyunsaturated oils, tocopherols would constitute the substrates that react more easily with oxygen. In fact, it was reported in the literature that in the propagation phase of the reaction, peroxy fatty acid-free radicals preferentially react with the phenolic hydrogen of the tocopherol molecule (Rossi *et al.*, 2017). The initial concentrations of PCs in the fresh oils were within the reported values (Ramírez Botero *et al.*, 2012). After 40 frying cycles (Fig. 4), the PC content increased, but there were no statistically significant differences due to the application of the coating. In this study, it can be inferred that the changes in the increase in polar compounds are related to the amount of frying cycles carried out. In addition, the fatty acid profile of the oils is an important factor which contributes to the generation of polar compounds, consequently, the oil blend, with a higher degree of unsaturation, presents more polar compounds than sunflower oil. It was also possible to observe that sunflower oil was more resistant to oxidative deterioration during frying, probably due to containing more monounsaturated fatty acids (Jadhav *et al.*, 2022). These results indicated that under the conditions used in this study, CP content was not generated in concentrations higher than the limits established by countries which have their content legislated. For example, Spain, France, Italy, and Chile accept a maximum value of 25% of polar compound content, while Germany accepts 24% and Austria and Switzerland up to 27% (Suaterna Hurtado, 2009).

CONCLUSIONS

The Waycha variety is suitable for producing potato chips because the contents of dry matter and reducing sugars meet the conditions established for that purpose.

The coating formulated with starch extracted from the Runa variety combined with CMC and applied to chips scalded in calcium chloride contributed to decreasing oil absorption by 39.5% during the frying process. This formulation did not increase the formation of polar compounds. In addition, it contributed to a reduction in the loss of tocopherols during the frying process and improved the physical and sensory characteristics of the final product, which had high acceptability by consumers.

These results confirm two technological applications for Andean potatoes which can be used to contribute to a healthy diet. In addition, both materials used in the preparation of edible coatings are ecological and respectful of the environment since they will contribute to the recycling of waste from food and other industries.

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