Application of an edible coating developed with Andean potato starch 1 and carboxymethyl-cellulose for lipid reduction during frying 2 S.R. Calliope¹, A. Slavutsky², N. Segura, N. C. Samman^{1, \Box} 3 ¹Centro Interdisciplinario de Investigaciones en Tecnologías y Desarrollo Social para el NOA. 4 5 CIITED- CONICET, Facultad de Ingeniería, Universidad Nacional de Jujuy, Ítalo Palanca 10, 6 (PC4600) Jujuy - Argentina 7 ² INIQUI-CONICET, Sede Regional Sur, Universidad Nacional de Salta. Av. Bolivia 5150 (A4408FVY) Salta-Argentina 8 9 ³ Área de Grasas y Aceites, Facultad de Química, UdelaR, Gral. Flores 2124, (PC11800) 10 Montevideo-Uruguay. ^CCorresponding author: normasamman@gmail.com 11 12

13 SUMMARY: This work aimed to search for technological alternatives for the use of different varieties of Andean potatoes (Solanum tuberosum ssp andigenum) reintroduced in north-14 western Argentina. Coatings made with starch (S) extracted from the Runa variety, 15 16 carboxymethyl-cellulose (CMC), and their combination (S/CMC) were studied. These coatings 17 were applied to chips of Waycha variety potatoes before being fried; the effect of prior bleaching of the chips with different media was also evaluated: water, calcium chloride solution, 18 19 and ascorbic acid. The results showed that the type of oil used did not affect their absorption by the chips. The bleaching treatments with calcium chloride and S/CMC coating significantly 20 21 reduced the oil absorption (39.5 $\% \pm 0.7$), delayed its oxidation, and decreased the loss of 22 tocopherols during the frying process. It also contributed to the physical and sensory 23 characteristics of the final product, which presented high acceptability by consumers.

24

25 **KEYWORDS**: Andean potato starch, Andean potato chips, coating, frying, oil absorption

26 **RESUMEN:** Este trabajo tuvo como objetivo buscar alternativas tecnológicas para el 27 aprovechamiento de diferentes variedades de papa andina (Solanum tuberosum ssp andigenum) reintroducidas en el noroeste argentino. Se estudiaron recubrimientos elaborados con almidón 28 29 (S) extraído de la variedad Runa, carboximetilcelulosa (CMC) y su combinación (S/CMC). Estos recubrimientos se aplicaron a chips de papa variedad Waycha antes de ser fritos; también 30 se evaluó el efecto del blanqueo previo de los chips con diferentes medios: agua, solución de 31 32 cloruro de calcio y ácido ascórbico. Los resultados mostraron que el tipo de aceite utilizado no 33 afectó su absorción por los chips. Los tratamientos de blanqueo con cloruro de calcio y 34 recubrimiento S/CMC redujeron significativamente la absorción de aceite (39,5% ±0,7), retrasaron su oxidación y disminuyeron la pérdida de tocoferoles durante el proceso de fritura. 35 36 También contribuyeron a las características físicas y sensoriales del producto final, que presentó alta aceptabilidad por parte de los consumidores. 37

38

39 PALABRAS CLAVE: almidón de papa Andina, hojuelas de papa andinas, recubrimiento, fritura, absorción de aceite 40

ORCID (https://orcid.org/0000-0002-8895-7928), Slavutsky 41 ID: Calliope S Α (https://orcid.org/0000-0002-6240-3281), Segura N (https://orcid.org/0000-0002-9196-1557), 42 Samman N (https://orcid.org/0000-0001-6773-2247) 43 44

45 1. INTRODUCTION

Many strategies have been proposed to reduce oil absorption in food during frying (Crosa et 46 47 al., 2014). The application of hydrocolloid coatings has been one of the most promising methods (Naghavi et al., 2018). These modify the food surface, decreasing its permeability. 48 49 Among the materials used to make coatings are methylcellulose (MC), hydroxypropyl-cellulose (HPC), carboxymethyl-cellulose (CMC) and hydroxypropylmethyl-cellulose (HPMC) (Mai et 50 51 al., 2007). The use of natural polymers in packaging and food additive applications is gaining 52 popularity, due to the prevention of environmental problems. Edible coatings must contain 53 substances that comply with food standards and must also be economical, easy to apply and 54 respectful of the environment. Cellulose is a very abundant natural polysaccharide, it is the 55 structural component of the cell wall of plants, therefore, it is obtained from various natural sources, from food waste, cereal bran and fruit peels. The main reasons for the common use of 56 57 CMC are its viscosity, flocculant property, excellent oil resistance, transparency, non-toxicity, and low price. It has GRAS status from the FDA (Yalsin et al., 2022). Starch, as one of the most 58 59 abundant, sustainable, and low-cost commercial biopolymers, has versatile applications in many 60 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 61 62 genetic effects determine external qualities. The internal ones refer to the chemical composition 63 of tubers that includes the content of sugars, dry matter, and starch, among others. Reducing 64 sugars (fructose and glucose) have a critical role in the industrial process, so the legislation 65 establishes contents lower than 0.25% for French fries' elaboration and less than 0.2% (Colman 66 et al., 2009) for potatoes in flakes. Frying is an operation widely used in the food industry. It is 67 based on the transfer of heat from hot oil to foods, causing water removal and oil absorption. 68 The high consumption of fried products is a risk factor for health due to the high energy density 69 and the possible formation of toxic compounds. The origin and oil composition can influence 70 the food oil absorption during frying process, temperature and frying time, type of food, porosity, and pretreatments applied (Alvis et al., 2015). During the frying occur, reactions 71

72 responsible for taste, color, and texture and also unhealthy components formation such as polar 73 compounds (Jimenez et al., 2017). During repeated use of the frying oil, it degrades and 74 changes its composition, generating a mixture of polar compounds that act as wetting agents 75 that reduce the surface tension between water and oil causing an increase in oil absorption.

76 This paper proposed to search technological alternatives for use of Andean potatoes 77 (solanum tuberosum ssp. andigenum) genotypes reintroduced in northwestern Argentina to 78 revalue these relegated foods. For this purpose, the objective was to study the application of 79 films elaborated with hydrocolloids and starches extracted from Andean potatoes and to study 80 their application in deep frying of chips in order to diminish the oil absorption.

81

82

2. MATERIALS AND METHODS

83

84 **Materials** a.

85 Starch was extracted from Runa Andean potato variety (30% amylose content) (Calliope et al., 2019), carboxymethyl-cellulose (CMC) (food grade, Rettenmaier & Sohne GMBH + Co), 86 87 calcium chloride and ascorbic acid (food grade), were used for coatings formulation. Waycha 88 Andean variety and Spunta high -consumption commercial potato- were used for frying assays. 89 Commercial potato chips were used as control. Sunflower oil and blend oil (sunflower/soybean) 90 were used for frying.

A) Formulation and properties of films 91 b.

92

93 Films formulation

94 The components were used as aqueous solutions in the following concentrations: S(1%); 95 S/CMC (1:05; 1.5%) and CMC (1%); 13 g of each formulation were poured onto 10 cm 96 diameter polystyrene plates and allowed to dry 6 h in forced flow oven at 35 °C and then
97 maintained 15 h at 53% of relative humidity and room temperature.

98 Thickness

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

102 Water Vapour Permeability (WVP)

103 The WVP was determined gravimetrically according to the standard method ASTM E96 104 (2000). Films were conditioned 48 h in a desiccator at 25 °C and 53% relative humidity (RH) 105 using Mg (NO₃)₂ supersaturated solution. The measurements of WPV (quadruplicate) were 106 performed according to Slavutsky and Bertuzzi (2015).

107 The water vapour transmission rate (WVTR) was calculated from equations 1 and 2

108
$$WVTR = \frac{G}{A}$$
 (1) $P = cte \cdot \frac{WVTR \cdot l}{p_{W0} - p_{W2}}$ (2)

Where: G: slope of linear regression; A: area of the exposed film; P: water vapour permeability;
l: film thickness; pw₀: partial pressure of water vapour in the air on the surface of distilled
water; pw₂: partial pressure of water vapour on the surface of the film outside the cup; cte:
constant to satisfy unit conversion.

113 *Solubility*

It was measured as a percentage of dry matter of 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:

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

121 Sorption Isotherms

The films were cut in pieces of approximately 2 cm² and placed 48 h in a desiccator with P2O5. Then, 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 weighing 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 (Eq. 4).

128
$$w_{g} = \frac{w_{0}.C.a_{W}}{(1-a_{W}).(1+(C-1)a_{W})}$$
 (4)

129 Where w_e is the equilibrium moisture content (g water/100g dry film), w_0 is the moisture 130 content in monolayer (g water/100g dry film) and C is adsorption constant of the first layer 131 dependent on temperature. The quality of the fit was assessed through R^2 .

132 Colour

133 The films colour was determined with a colorimeter (Colorquest XE Hunter Lab, USA) 134 versus a standard film (L=94; a=-0.11 and b=3.2). All measurements were performed in 135 triplicate. Total colour difference (ΔE), was calculated as:

136
$$\Delta E = ((L_{\text{standar}} - L_{\text{sample}})^2 + (a_{\text{standar}} - a_{\text{sample}})^2 + (b_{\text{standar}} - b_{\text{sample}})^2)^{1/2}$$
(5)

137 *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 μ L) was dropped on 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.

143

c. B) Potato Chips

144 Analysis of the raw material

145 Reducing sugar content was determined by the spectrophotometric method of 3.5
146 dinitrosalicylic acid; absorbance at 540 nm was measured (Mapada, model UV 6300 PC).
147 Glucose p.a. (Merck) for the standard curve was used.

148 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.

153 *Coating application*

After blanching the potatoes were drained on absorbent paper and immediately immersed in solutions described in section 2.2.1., 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.

158 Frying Process

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

165 *Chip evaluation*

In the first frying cycle, the lipid content (AOAC 920.39) and moisture/solid matter(AOAC 925.09) were determined.

168 To calculate the reduction in oil absorption (% ROA, Equation 6), a commercial potato169 chip was taken as a reference.

170 %
$$RAA = 100 - \left(\frac{\% LChA \times 100}{\% LChC}\right)$$
 (6)

171 % LChA: percentage of lipids of Andean potato chips, scalded with coatings

172 % LChC: percentage of lipids of commercial potato chips, label value: 30.4 g/100 g173 potato.

174 *Colour*

175 It was measured by a Colorimeter (Colorquest XE Hunter Lab, USA). The average of 5 176 readings was calculated. A chip without frying was taken as reference. The measure of colour 177 change was evaluated according to Equation 5. Where L*a*b*standard were the values for fresh 178 potato and L*a*b*sample the values of fried chips.

179 Sensory evaluation

180 Chips samples from the first frying cycle in the two types of oil were used to carry out the 181 sensory analysis with 48 untrained consumers. Six sensory attributes were evaluated using a 5-182 point hedonic scale, where 5 corresponded to the maximum score.

183

d. C) Analysis of fresh and used oils

184 Fatty acid composition

Fatty acid methyl esters (FAMEs) were prepared according to IUPAC 2.301. 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.

189 *Calculated oxidizability (Cox)*

190 The Cox value of oils was calculated by the percentage of unsaturated C18 fatty acids,191 applying the equation 7, proposed by Rossi *et al.* (2013):

192 Cox = [1(oleic acid %) + 10.3(linoleic acid %) + 21.6 (linolenic acid %)]/100 (7)

193 Tocopherols

194 They were determined by AOCS Method Ce8-89. A chromatograph (Shimadzu model 20, 195 Japan) was used, with a fluorescence detector, a Phenomenex C18 silica column (250 × 4.6 mm, 196 5.0 μ m); the mobile phase was acetonitrile, methanol, water with phosphoric acid and 197 isopropanol (the flow rate was kept constant at 1.0 mL/min). Tocopherol isomers (α -, β - γ -, δ -) 198 were identified using standards (Sigma Aldrich). Isopropanol (1 mL) was added to the oil 199 sample (30 mL) and then injected into the HPLC equipment. 200 *Polar Compounds*

They were determined by adsorption chromatography (IUPAC 2.507). 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 were quantified, such as the difference between the initial mass of oil and the eluted non-polar fraction.

206

e. D) Statistical Analysis

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

212

213 3. RESULTS AND DISCUSSION

214

a. Films

216

217 The average results of the measured parameters are shown in Table 1. The water vapor 218 permeability (WVP) of edible films should be as low as possible to control the transfer of moisture between the food and the surrounding atmosphere. S/CMC films showed a 219 220 significantly lower WVP value than CMC films which would be related to the thickness of the 221 film and the intrinsic characteristic of each material (Basiak et al., 2017). The permeation 222 phenomenon depends on three stages: adsorption, diffusion, and desorption. The diffusion stage 223 depends on the thickness of the film, while the other two are independent of it. Starch has a 224 semi-crystalline structure; the amylose is capable of forming a tortuous path that decreases the 225 diffusion of water through the film. The different behavior of starch and CMC films may be due 226 to this. No significant difference was observed between S/CMC and S films. This indicated that 227 in the composite films, permeability was related to the presence of starch. Almasi et al. (2010) 228 postulated that starch forms hydrogen bonds with the hydroxyl groups of the CMC, and this 229 strong structure could reduce the diffusion of water in the material. Therefore, the addition of CMC would improve the water-resistance of the starch matrix. The water solubility of the S 230 231 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 of potato var. Runa used. The combination with CMC 232 233 produced a decrease in solubility of approximately 50%. This behavior was also observed by Ghanbarzadeh et al. (2010). The solubility of the S/CMC composite films was related to the 234 235 behavior observed in the permeability study.

Figure 1 shows the absorption isotherms obtained at 25 °C for the three formulations. 236 237 Curves were typical of polymers with affinity for water. The curves showed a slight relative 238 slope at low aw values, while they were exponential at aw values greater than 0.60. Other 239 authors reported similar behavior in starch-based films (Slavutsky et al., 2015). Experimental 240 data indicated that the CMC film had the lowest water absorption, while the S/CMC film had 241 similar behavior to the S film. The adjustment parameters obtained with the BET model 242 (Equation 4) of each film showed that the constant c influences the sigmoidal shape of the 243 isotherms, particularly in the low range of aw. The values of c would indicate that the moisture 244 absorption of the matrix studied could occur more easily in the upper layers than in the monolayer. These results showed that the stage that controls the water permeability of the S and 245 S/CMC films was diffusion and not the adsorption / desorption of water, so the influence of 246 247 thickness would be less significant. This confirmed that the composite films have lower 248 solubility and water vapor permeability.

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 being lower for the S film. In

parameter a, all the films had a greenish hue being higher for the CMC and in b the films hue was yellow with no significant differences among them. In general, the optical values of 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 had 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 confirming 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 blend oil. This is according to the frying experiments (Table 2 and Fig. 2), in which the chips potatoes 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.

265 b. Chips

266 Andean potato var. Waycha, and Spunta contained 26.38 ± 0.31 and $15.00 \pm 0.20\%$ of dry 267 matter (DM) and 0.18 ± 0.06 and $0.28 \pm 0.08\%$ of reducing sugars (RS) respectively. The 268 appropriate value for the production of potato chips is 25% DM and 0.2% RS (Colman et al., 269 2009). The Waycha potato met both characteristics. The DM content decreased with all the 270 bleaching treatments. Significant differences in DM content were found between chips scalded 271 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 272 273 potato compounds to the bleaching medium. The oil content was significantly affected (p>0.05) 274 by kind of scalding and the type of coating used (Table 2). The oils employed did not 275 significantly influence absorption. Figure 2 a and b, shows the percentages of oil reduction 276 according to the treatments applied taking as reference a commercial potato (label value 30.4 g 277 oil/100g). Control samples scalded in water and without coating showed a slight reduction in oil content (16.1-18.5%), compared to those scaled in calcium chloride with S/CMC coating (39.1-278

279 40.1%). These results indicated that calcium chloride stabilized the structure of the tissue during 280 the frying process. The texture of the potato depends on the presence of pectinic substances, 281 which are part of the intercellular material. Pectinolytic enzymes produce free carboxylic 282 groups, which can react with divalent ions such as calcium and magnesium, creating more rigid 283 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 284 285 (Hernandez et al., 2014), and therefore its structure better resists the frying process. Table 2 and 286 Figure 2 a) and b), shows that the coatings influenced the decrease in oil absorption. The results 287 showed significant differences (p>0.05) between treatments. The one with the greatest effect 288 was the coating of S/CMC (39.5% \pm 0.7) combined with scalding in calcium chloride, while the 289 one with the least effect was the control without coating and scalding in water (17.3% \pm 1.7). 290 This reduction in oil absorption could be attributed to the fact that the starch undergoes 291 structural changes in which the crystals of amylose and amylopectin are reorganized and 292 promote the formation of a gel that functions as a barrier to the entry of oil (Hasbún et al., 293 2009). Varela and Fiszman (2011) and Freitas et al. (2009) postulated that CMC increases water 294 retention capacity and, consequently, prevents the replacement of water with oil. In addition, 295 since the polymer is hydrophilic, it forms a thin layer on the surface of the food that acts as a 296 barrier to the incorporation of oil. Ali et al. (2012) observed that CMC increases surface 297 tension, which facilitates the draining of surface oil. Likewise, calcium chloride is a cross-298 linking agent that forms a fine network, which prevents the migration of oil to the potato during 299 the frying process (Hasbún et al., 2009).

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

Table 3 shows colour change during 40 frying cycles. In the parameters L*a* and b* within the frying cycles with coatings, there were significant differences in L. It was observed with L value for chips with film, as the cycles pass, the product is darkening. 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 last cycles, possibly due to the effect of the coating. While in 306 parameter b, there was greater variation, with the exception of chips without coating fried in 307 blend oil. In the other treatments, the intensity of the yellow colour varied, not finding a defined 308 pattern. In all cases, the yellow/gold colour, typical of fried products, was characteristic. The 309 parameter ΔE was used to evaluate the colour change between the different processes tested; no 310 statistical differences were observed between the treatments since the observed variations were very wide. Table 3 shows the average hedonic classification of sensory attributes. Scalded 311 312 samples with coatings for both types of oils obtained high scores on almost all attributes. The 313 texture and overall acceptability of these samples received higher scores compared to the uncoated sample fried in sunflower oil. The uncoated sample fried in sunflower oil had the 314 315 lowest score for the texture. While the uncoated sample fried in blend oil obtained the lowest 316 taste score. The flavours described by consumers were "bitter, burned and taste oily." These 317 indicated that the coating contributed to eliminating these perceptions. Garcia et al. (2002) 318 reported that edible coatings with CMC affected the colour of potato chips samples but did not 319 change the texture characteristic. In this study, the coating with S/CMC did not affect the colour 320 and gave a better "crunchy" texture to the fried chips in both types of oils used.

321 The sample with coating and fried in sunflower had a significantly greater acceptance, the322 texture being notable for its high crunchiness.

During the frying, the oil is exposed to high temperatures in 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 colour and changes in its composition (Navas *et al.*, 2007).

327

c. 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 too. 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. This probably is related to the temperature/time of oil use. Cis to Trans isomerization begins when the frying temperature is higher than 150 °C (Bhardwaj *et al.*, 2016). However, the TFA content of oils with 40 frying cycles was less than the maximum established (5%) by Argentine legislation.

337 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. 338 339 Table 3 shows the content of the different types of tocopherols of SO and OB fresh and after 340 being used in 40 frying cycles. The tocopherols content was significantly higher in the OB than 341 in SO, both fresh. When both were used in 40 frying the total tocopherols content decreased 342 significantly; this was less noticeable when covered chips were frying. Rossi et al. (2017) 343 reported that frying potato chips in eight different types of vegetable oils, including sunflower 344 pure and mixture, tocopherols decreased rapidly after the third hour of continuous use of the 345 oils. In this study, the frying cycles exceeded 3 hours of oil use. The mechanism of the reaction 346 to eliminate radicals of tocopherols requires that they lose their mobile hydrogen atom in the 347 hydroxyl group, forming more stable free radicals than fatty acids, it follows that rapid 348 oxidation of tocopherols corresponds to greater antioxidant power. However, if all other 349 fractions are taken into account, it could be assumed that, in the case of oils containing higher 350 levels of PFA, the double bond that determines unsaturation competes with tocopherols as 351 substrates for oxidation, determining a less rapid decrease of these antioxidants. In contrast, in 352 the case of low polyunsaturated oils, tocopherols would constitute the substrates that react more 353 easily with oxygen. In fact, it was reported in the literature that, in the propagation phase of the 354 reaction, peroxy fatty acid-free radicals preferentially react with the phenolic hydrogen of the 355 tocopherol molecule (Rossi et al., 2017). The PC concentrations of fresh oils were for OB 5.9 \pm 356 3.7% and 5.3 \pm 2.5% for SO, which are within the reported values (Ramírez Botero et al., 357 2012). After 40 frying, the PC content increased to 13.0 ± 0.7 and 10.5 ± 1.4 in SO and to 14.5 358 \pm 1.4 and 11.9 \pm 0.5% in OB when chips with and without coating were fried, respectively. The 359 higher PC content in the frying 40 in OB with film (p>0.5), is probably due to the oil 360 composition since SO has greater stability against oxidation due to its lower degree of361 unsaturation.

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 that have their content legislated. For example, Spain, France, Italy, and Chile accept as maximum value 25% of polar compounds content, while Germany accepts 24% and Austria and Switzerland up to 27% (Suaterna Hurtado, 2009).

367 4. CONCLUSIONS

368 The Waicha variety was suitable to obtain potato chips because dry matter and reducing369 sugars content meet the conditions established for that use.

The coating formulated with starch extracted of Runa variety combined with CMC, applied to chips scalded in calcium chloride contributed to decreasing the oil absorption during the frying process. This formulation delayed oil oxidation and decreased loss of tocopherols during the frying process. It also contributed to improving the physical and sensory characteristics of the final product, which had high acceptability by consumers.

These results confirm two technological applications for Andean potatoes that can be used to contribute to a healthy diet. Additionally, 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.

379

380 ACKNOWLEDGMENTS

381 This work was supported by the University National of Jujuy, CIITED-CONICET, University

382 of Republic - Montevideo, University of Salta INIQUI-CONICET.

383

384 **REFERENCES**

14

- Ali, H., Abdel-Razek, A., Kamil, M. 2012. Effect of pre-frying treatments of french-
- fried potatoes to achieve better oil uptake reduction for health and technological aspects.

387 Journal of Applied Sciences Research, 8(10), ISSN: 1819-544X.
388 https://www.researchgate.net/publication/285956246 Effect of pre-

- frying_treatments_of_french_fried_potatoes_to_achieve_better_oil_uptake_reduction_f
- 390 or_health_and_technological_aspects>
- 391 Almasi, H., Ghanbarzadeh, B., Entezami, A. 2010. Physicochemical properties of

392 starch-CMC-nanoclay biodegradable films. International Journal of Biological

393 *Macromolecules*, **46(1)**, pp. 1–5. DOI: 10.1016/j.ijbiomac.2009.10.001

- Alvis, A., González, A., Arrázola, G. 2015. Efecto del Recubrimiento Comestible en las
- 395 Propiedades de Trozos de Batata (*Ipomoea Batatas Lam*) Fritos por Inmersión. Parte 2:
- 396 Propiedades Termofísicas y de Transporte. Información Tecnológica, 26(1), pp. 103-

397 116. DOI: 10.4067/S0718-07642015000100012. In Spanish.

- 398 AOAC. 2016. Official methods of analysis of association of official analytical chemists
- 399 (20th ed.). Arlington, USA: Association of Official Analytical Chemists International.
- 400 Brand Williams, W., Cuvelier, M. E., & Berset, C. (1995). Use of a free radical method
- 401 A. O. C. S. Ce 8-89. 1993. Determination of tocopherols and tocotrienols in vegetable
- 402 oils and fats by HPLC, Urbana: *AOCS official Method*.
- 403 ASTM-E96. 2000. Standard test methods for water vapor transmission of materials.
- 404 Philadelphia: Standards American Society for Testing and Materials.

- Basiak, E., Lenart, A., Debeaufort, F. 2017. Effect of starch type on the physicochemical properties of edible films. *International Journal of biological macromolecules*, 98, pp. 348-356. DOI: 10.1016/j.ijbiomac.2017.01.122.
- 408 Bhardwaj, S., Passi, S., Misra, A., Pant, K., Anwar, K., Pandey, R., Kardam, V. 2016.
- 409 Effect of heating/reheating of fats/oils, as used by Asian Indians, on trans fatty acid
- 410 formation. *Food Chemistry*, **212**, pp. 663-670. DOI: 10.1016/j.foodchem.2016.06.021
- Calliope, S., Wagner, J., Samman, N. 2019. Physicochemical and Functional
 Characterization of Potato Starch (Solanum Tuberosum ssp. Andigenum) from the
 Quebrada De Humahuaca, Argentina. *Starch-Stärke*, 72(1-2), pp.1900069. DOI:
 10.1002/star.201900069
- Colman, S., Monti, C., Divito, S., Digilio, A., Feingold, S. 2009. Marcadores
 funcionales asociados al endulzamiento inducido por frío en papas nativas de Argentina. *Revista Latinoamericana de la Papa*, 15(1), pp. 61-65. DOI: 10.37066/ralap.v15i1.155.
 In Spanish.
- 1
- 419 Crosa, M., Skerl, V., Cadenazzi, M., Olazábal, L., Silva, R., Suburú, G., Torres, M.
- 420 2014. Changes produced in oils during vacuum and traditional frying of potato chips.
- 421 *Food Chemistry*, **146**, pp. 603–607. DOI: 10.1016/j.foodchem.2013.08.132.
- 422 Freitas, D., García, S., Prati, P., Fakhouri, F., Collares, F., Vicente, E. 2009. Reducing
- 423 of fat uptake in cassava product during deep-fat frying. *Journal of Food Engineering*,
- 424 **94**, 390-394. DOI: 10.1016/j.jfoodeng.2009.04.005
- 425 García, M., Ferrero, C., Bertola, N., Martino, M., Zaritzky, N. 2002. Edible coating
- 426 from cellulose derivatives to reduce oil uptake in fried products. *Innovative food science*
- 427 & emerging technologies, **3**, pp. 391-391. DOI: 10.1016/S1466-8564(02)00050-4

- Ghanbarzadeh, B., Almasi, H., Entezami, A. 2010. Physical properties of edible
 modified starch/carboxymethyl cellulose films. *Innovative food science & emerging technologies*, 11(4), pp. 697-702. DOI: 10.1016/j.ifset.2010.06.001
- Hasbún J., Esquivel P., Brenes A., Alfaro I. 2009. Propiedades físico-químicas y
 parámetros de calidad para uso industrial de cuatro variedades de papa. *Agronomía Costarricense*, 33(1), pp.77-89, ISSN: 0377-9424
 https://www.redalyc.org/articulo.oa?id=43612054007
- Hernández, A., Márquez Cardozo, J., Restrepo Flores, C., Cano Salazar, J., Patiño
 Gómez, J. 2014. Aplicación de tratamiento térmico, recubrimiento comestible y baño
 químico como tratamientos poscosecha para la conservación de hortalizas recién
 cortadas. *Acta Agronómica*, 63 (1), pp. 1-10. DOI: 10.15446/acag.v63n1.40149. In
 Spanish,
- IUPAC-2.301. 1987. Preparation of fatty acid methyl ester. Blackwell, Oxford:
 International Union of Pure and Applied Chemistry. *Standard Methods for Analysis of Oils, Fats and Derivatives.*
- Jiménez, P., García, P., Bustamante, A., Barriga, A., Robert, P. 2017. Thermal stability
 of oils added with avocado (Persea americana cv. Hass) or olive (Olea europaea cv.
 Arbequina) leaf extracts during the french potatoes frying. *Food Chemistry*, 221, pp.
 123-129. DOI: 10.1016/j.foodchem.2016.10.051
- Mai Tran T., Dong Chen X., Southern C. 2007. Reducing oil content of fried potato
 crisps considerably using a 'sweet' pre-treatment technique. *Journal of Food Engineering*, 80, pp. 719–726. DOI: 10.1016/j.jfoodeng.2006.06.031

- Naghavi, E., Dehghannya, J., Ghanbarzadeh, B. 2018. Effect of hydrocolloid type on
 transfer phenomena during deep-fat frying of coated potato strips: Numerical modelling
 and experimental analysis. *Computers and electronics in agriculture*, **154**, pp. 382-399.
- 453 DOI: 10.1016/j.compag.2018.09.024
- Navas J., Tres A., Bou R., Codony R., Guardiola F. 2007. Optimization of analytical 454 455 methods for the assessment of the quality of fats and oils used in continuous deep fat 456 frying. Grasas Aceites, 48(2), 148-153, ISNN: 0017-3495. y pp. http://diposit.ub.edu/dspace/handle/2445/32267 457
- 458 Ramírez Botero, C., Gómez Ramírez, B., Suaterna Hurtado, A., Martínez Galán, J.,
- 460 aceites de cocina previo uso más vendidos en Medellín (Colombia). *Perspectivas en*

Cardona Zuleta, L., Rojano, B. 2012. Contenido de compuestos polares totales en

- 461 *Nutrición Humana*, **14**, pp. 59-69. DOI: 10.17533/udea.penh. In Spanish,
- 462 Rimac-Brnčić S., Lelas V., Rade D., Šimundić B. 2004. Decreasing of oil absorption in
- 463 potato strips during deep fat frying. Journal of Food Engineering, 64, pp. 237–241.
- 464 DOI: 10.1016/j.jfoodeng.2003.10.006

459

- Rossi, M., Alamprese, C., Ratti, S. 2017. Tocopherols and tocotrienols as free radicalscavengers in refined vegetable oils and their stability during deep-fat frying. *Food Chemistry*, **102(3)**, pp. 812-817. DOI: 10.1016/j.foodchem.2006.06.016
- 468 Slavutsky, A., Bertuzzi, M. 2015. Formulation and characterization of nanolaminated
- 469 starch-based film. LWT-Food Science and Technology, 61(2), pp. 407-413. DOI:
- 470 10.1016/j.lwt.2014.12.034
- 471 Spiess, W., Wolf, W. 1983. The results of the COST 90 project on water activity.
- 472 R. Jowitt, F. Escher, B. Hallstrom, H.F.Th. Meffert, W.E.L. Spiess, G. Vos (Eds.), Phys

- *ical properties of foods*, Applied Science Publishers, Elsevier Science Publishing
 Company, London, NY, pp. 65-91. ISBN 1-85166-124-7.
- 475 Suaterna Hurtado, A. 2009. La fritura de los alimentos: el aceite de fritura. *Perspectivas*
- 476 *en nutrición humana*, **11(1)**, pp. 39-53. DOI: 10.17533/udea.penh. In Spanish,
- 477 Varela, P., Fiszman, S. 2011. Hydrocolloids in fried foods. A review. Food
- 478 *Hydrocolloids*, **25**, pp. 1801-1812. DOI: 10.1016/j.foodhyd.2011.01.016
- 479 Yildirim-Yalcin, M., Tornuk, F., Toker, O. S. 2022. Recent advances in the
- 480 improvement of carboxymethyl cellulose-based edible films. Trends in Food Science &
- 481 *Technology*. **129**, pp. 179 193. DOI: <u>10.1016/j.tifs.2022.09.022</u>
- Zdanowicz, M., Johansson, C. 2016. Mechanical and barrier properties of starch-based
 films plasticized with two-or three component deep eutectic solvents. *Carbohydrate*
- 484 *polymers*, **151**, pp. 103-112. DOI: 10.1016/j.carbpol.2016.05.061

Parameters		S	СМС	S/CMC
Thickness (μ m) 10 ⁻⁵		$6.42\pm0.20^{\rm c}$	4.86 ± 0.07^{a}	$5.63\pm0.08^{\text{b}}$
Barrier properties water vapour permeability (10 ⁻¹⁰ g m ⁻¹ s ⁻¹ Pa ⁻¹)		2.12 ± 0.23^{ab}	2.73 ± 0.21^{b}	$1.94\pm0.29^{\mathtt{a}}$
Solubility in water	(%)	$26.24\pm6.66^{\text{b}}$	$9.25\pm2.23^{\rm a}$	13.06 ± 1.34^{a}
BET	\mathbf{W}_0	$3.09\pm0.13^{\text{b}}$	$2.00\pm0.10^{\rm a}$	$3.23\pm0.15^{\text{b}}$
	с	$15.87\pm2.58^{\text{b}}$	$5.01\pm4.50^{\rm a}$	$6.15\pm5.36^{\rm a}$
	\mathbb{R}^2	0.9292	0.9388	0.9240
Colour	L	$92.98\pm0.09^{\rm a}$	$93.32\pm0.06^{\text{b}}$	$93.24\pm0.17^{\text{b}}$
	а	$\textbf{-0.33} \pm 0.03^{c}$	$\textbf{-0.57} \pm 0.02^{a}$	$\textbf{-}0.52\pm0.02^{b}$
	b	3.60 ± 0.19^{a}	3.90 ± 0.27^{a}	$3.47\pm0.87^{\rm a}$

 $1.11\pm0.15^{\text{b}}$

 $15.80\pm1.20^{\mathrm{a}}$

 18.80 ± 4.10^{a}

 1.08 ± 0.22^{ab}

 18.90 ± 3.90^{ab}

 16.80 ± 1.80^{a}

 0.91 ± 0.15^{a}

 20.60 ± 3.90^{b}

 19.10 ± 3.10^{a}

Table 1. Parameters measured in the developed films

486 w_0 : monolayer moisture content, c: constant related to the heat sorption for monolayer,

487 R²: coefficient of determination. θ (OB): contact angle of blend oil; θ (SO): contact 488 angle of sunflower oil; colour parameters (L, a, b). Values having the same letter for a

489 parameter within the same row are not significantly different at p level > 0.05.

AE

Surface properties

 θ (OB)

 θ (SO)

490 S: starch; CMC: carboxymethyl-cellulose; S/CMC: combination starch with carboxymethyl-491 cellulose

492

493

494