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Additional Information

1 **Effect of the citric acid addition on the properties and ageing time of starch-**
2 **polycaprolactone based films**

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10
11 **ABSTRACT**

12
13
14 **1. INTRODUCTION**

15 The packaging films, made of synthetic polymers, cause serious ecological problems
16 due to their non-biodegradability. The increase of the consumers' conscience for the
17 environmental protection is causing the intensification in research about biodegradable
18 packaging materials (Fajardo, Martins, Fuciños, Pastrana, Teixeira, & Vicente, 2010).
19 The development of biodegradable materials designed to maintain or improve the shelf
20 life of food is very important today (García, Pinotti, Martino, & Zaritzky, 2004). In last
21 decade, many research about materials for food packaging has been brought out, these
22 research have had in common the work with economically viable natural sources.
23 Among these materials, the starch is known for its low cost, its renewability and its
24 processability by mean of traditional techniques (Yoon, Chough & Park, 2006;
25 Ghanbarzadeh, Almasi & Entezami, 2011).

26 Starch represents more than 60% of cereal grains produced in the world and it is
27 relatively easy separate it from other chemicals compounds (Lourdin, Della Valle &
28 Colonna, 1995). It has great importance in the packaging industry compared to other
29 biopolymers by its technical characteristics. The starch based films are continuous,
30 homogeneous, odourless and colourless and its oxygen permeability is very low (Dole,
31 Joly, Espuche, Alric, & Gontard, 2004; Liu, 2005; Ortega-Toro, Jiménez, Talens &
32 Chiralt, 2014a). However, starch films have some disadvantages such as high
33 hydrophilicity (water sensitivity) and poor mechanical properties compared to
34 conventional synthetic polymers (Averous & Boquillon, 2004). Furthermore, the
35 temperature and relative humidity (RH) during storage, have an effect on the
36 crystallinity of the films and therefore on its physical properties (Rindlava, Hulleman, &
37 Gatenholma, 1997; Bergo, Sobral & Prison, 2010). For improve or maintain their
38 properties, is necessary to add plasticizers, fillers and cross-linking agents. The most
39 common plasticizer in the starch based films is the glycerol. This polyol reduces the
40 intermolecular attractive forces in the native starch and increases the flexibility and the
41 resistance to fracture (Mali, Grossmann, García, Martino & Zaritzky, 2005).

42 On the other hand, the polycaprolactone (PCL) is a biodegradable thermoplastic
43 polymer obtained by chemical synthesis from crude oil (Flieger, Kantorová, Prell,
44 Rezanka & Votruba, 2003). It has some interesting characteristics like it is waterproof
45 and has great flexibility (Averous, Moro, Dole, & Fringant, 2000). Several authors have
46 shown that blends of polycaprolactone and starch are readily biodegradable and
47 processible by conventional methods (Matzinos, Tserki, Gianikouris, Pavlidou, &
48 Panayiotou, 2002; Rosa, Lopes & Calil, 2005; Calil, Gaboardi, Bardi, Rezende & Rosa,
49 2007). However these mixtures are chemically incompatible and therefore have a phase

50 separation as occurs with other polymers (Annable, Fitton, Harris, Philips, & Williams,
51 1994; Mathew & Abraham, 2008; Ortega-Toro, Talens & Chiralt, 2015)

52 In previous works, Ortega-Toro *et al.* (2015) have observed the separation between
53 these two polymers by mean of Scanning Electron Microscopy and Atomic Force
54 Microscopy, concluding that it is necessary the incorporating of a compatibilizer
55 compound to improve the blends. One way to increase the number of interactions
56 between polymers is the addition of cross-linking agents. An appropriate compatibilizer
57 could be the citric acid (CA) because is a cheap organic acid and widely used in the
58 food industry as a cross-linking agent (Ghanbarzadeh, Almasi, & Entezami, 2010;
59 Ortega-Toro, Jiménez, Talens & Chiralt, 2014b). The CA use is interesting due to the
60 three carboxyl groups in its structure which can interact with the hydroxyl groups of the
61 starch molecules through the formation of esters. According to other works, the
62 esterification reaction using polycarboxylic acids occur with the polymer's hydroxyl
63 groups, at high temperatures (about 160 °C), through the formation of anhydride groups
64 (Reddy & Yang, 2010; Ortega-Toro *et al.*, 2014b). This blend can improve the water
65 vapour barrier properties, due to the reduction of available hydroxyl groups (Borredon,
66 Bikiaris, Prinos & Panayiotou, 1997) through the formation of strong hydrogen bonds
67 (carboxyl- hydroxyl) in order to decrease the crystallization and retrogradation (Shi,
68 Zhang, Liu, Han, Zhang, Chen, & Tian, 2007). However, the action mechanisms of the
69 CA are not clear and it can to act like compatibilizer, plasticizer and depolymerization
70 agent over different polymers according to processing conditions (Chabrat, Abdillahi,
71 Rouilly, & Rigal, 2012).

72 The aim of this work was to study the influence of the citric acid addition, and the effect
73 of the storage time, on the structural, thermal and physicochemical properties of starch-
74 polycaprolactone based films obtained by compression molding.

75

76 **2. MATERIALS AND METHODS**

77 **2.1. Materials**

78 Corn starch was purchased from Roquette (Roquette Laisa España, Benifaió, Spain).

79 Glycerol was obtained from Panreac Química, S.A. (Castellar del Vallès, Barcelona,

80 Spain). Polycaprolactone (pellets ~3 mm, average M_n 80.000, impurities <1.0% water)

81 was provided by Fluka (Sigma–Aldrich Chemie, Steinheim, Germany). Citric acid was

82 provided by Fisher (Scientific Afora, Valencia, Spain). Phosphorus pentoxide (P_2O_5)

83 and Magnesium nitrate-6-hydrate ($Mg(NO_3)_2$) were obtained from Panreac Química,

84 S.A. (Castellar Vallés, Barcelona).

85 NaOH and phenolphthalein was provided by ???

86 **2.2. Film preparation**

87 Eleven formulations based on starch and PCL, with and without CA, were prepared.

88 Starch:PCL ratios were 100:0, 90:10, 80:20, 70:30, 60:40 and 0:100, and starch:CA

89 ratio was 1:0.01. A 30% of glycerol was added respect to the starch content. . Firstly,

90 native starch and glycerol were dispersed in water. Afterwards, PCL was added to the

91 aqueous mixture of starch-glycerol. The blends were named as: S, S-CA, S90, S90-CA,

92 S80, S80-CA, S70, S70-CA, S60, S60-CA and PCL. The controls used were starch-

93 glycerol (S) and pure PCL (PCL).

94 The formulations were gradually mixed on a two-roll mill (Model LRM-M-100,

95 Labtech Engineering, Thailand) at 160 °C and 8 rpm for 30 min until a homogeneous

96 paste sheet was obtained. The CA was added to the formulations 10 min before the

97 homogenization. Paste sheet formed was conditioned at 25 °C and 53% RH using

98 $Mg(NO_3)_2$ oversaturated solutions for 48 h.

99 The films were obtained by compression molding (Model LP20, Labtech Engineering,
100 Thailand). Four grams of the paste were put onto steel sheets and preheated on the
101 heating unit for 5 min. The films were performed at 160 °C for 2 min at 30 bars,
102 followed by 6 min at 130 bars; thereafter a cooling cycle was applied for 3 min. The
103 films obtained were conditioned at 25 °C and 53% RH for 1 and 5 weeks for the initial
104 and final time characterization.

105

106 **2.3. Film characterization**

107 2.3.1. Film thickness and extensibility

108 The film thickness was measured with a Palmer digital micrometer (Palmer–Comecta,
109 Spain, +/- 0.001 mm) at six random positions around the film. The extensibility was
110 calculated by the relation between the surface and the weight of films with known
111 dimensions. This parameter was expressed in cm²/g of film.

112

113 2.3.2. Structural properties

114 The surface morphology of the samples, conditioned for 5 weeks at 25 °C and 53% RH
115 , was analyzed using an Atomic Force Microscope (AFM) (Multimode 8, Bruker AXS,
116 Santa Barbara, USA) with a NanoScope[®] V controller electronics. Measurements were
117 taken using the PeakForce QNM[®] mode (Quantitative Nanomechanical Mapping). The
118 statistical parameters: average roughness (Ra: average of the absolute value of the
119 height deviations from a mean surface), root-mean-square roughness (Rq: root-mean-
120 square average of height deviations taken from the mean data plane), and roughness
121 factor (r: ratio between the three-dimensional surface and two-dimensional area
122 projected onto the threshold plane), were calculated according to the method [ASME](#)

123 B46.1 (ASME, 1995). The DMT Modulus mode, derived from PeakForce QNM, was
124 considered. Three replicates for each formulation were taken to obtain these parameters.
125 The microstructural analysis of cross-sections of films was carried out by using a
126 Scanning Electron Microscope (SEM) (JEOL JSM-5410, Japan). The film samples were
127 maintained in desiccators with P₂O₅ for 2 weeks at 25 °C and the measurements were
128 taken in duplicate for each formulation. Pieces about 0.5 cm² were cut from films and
129 mounted on copper stubs perpendicularly to their surface. Samples were gold coated
130 and observed, using an accelerating voltage of 10 kV.

131 A diffractometer (XRD, Bruker AXS/D8 Advance) was used for obtained X-ray
132 diffraction patterns. All samples (equilibrated for 1 and 5 weeks) were analyzed at 25
133 °C and 53% RH, between 2 θ : 5° and 30° using K α Cu radiation (λ : 1.542 Å), 40 kV and
134 40 mA with a step size of 0.05°. For this analysis, the samples were cut into 4 cm².

135

136 2.3.3. Thermal properties

137 A Differential Scanning Calorimeter DSC 1 Star^e System (Mettler-Toledo Inc.,
138 Switzerland) was used to analyze the thermal properties. Weighted amounts of samples
139 were placed into aluminum pans, sealed and drilled to promote moisture loss during the
140 heating. The thermograms were obtained using a triple scan. First, a scan from -80 °C to
141 160 °C at a rate of 50 °C/min was used for obtaining the PCL melting temperature (T_m)
142 and to eliminate the bonded water in the film. The initial and final weights of the pans
143 were registered to assess water loss during the first heating Then, the temperature was
144 lowered to -80 °C at a rate of 50 °C/min. In this cooling step the PCL crystallization
145 temperature (T_c) was obtained. Finally, samples were heated to 160 °C at a rate of 20
146 °C/min in order to analyze the starch glass transition and the second melting
147 temperature of PCL..

148

149 2.3.4. Physicochemical properties

150

151 The film water content was determined conditioning the samples at 53% RH and dried
152 for 24 h at 60 °C using a convection oven (J.P. Selecta, S.A. Barcelona, España).
153 Afterwards, the samples were placed in a desiccator at 25 °C with P₂O₅ for 2 weeks.
154 This assay was realized for triplicate.

155 The film solubility was determined holding the sample in bidistilled water for 48 h. The
156 film:water ratio was 1:10. These samples were transferred to a convection oven (J.P.
157 Selecta, S.A., Barcelona, Spain) for 24 h at 60 °C to remove free water and then were
158 transferred to a desiccator with P₂O₅ at 25 °C for 2 weeks to remove the linked water.
159 The initial and final weights were registered for calculating the solubility in water.
160 Three replicates were analyzed from each formulation Bonded citric acid in the film,
161 was determined using the water solution of the solubility assay.. Free CA was assumed
162 to dissolve in the aqueous phase and was determined by titration of an aliquot of the
163 solution with NaOH (0.1 N), using phenolphthalein as indicator. Three replicates were
164 considered for each formulation.

165 An universal test machine (TA.XTplus model, Stable Micro Systems, Haslemere,
166 England) was used to determine the tensile strength (TS), the elastic modulus (EM), and
167 the elongation (E) of the films, according to the ASTM standard method D882 (ASTM,
168 2001). 2.5 cm wide and 5 cm long equilibrated samples were mounted in the film-
169 extension grips of the testing machine and stretched at 50 mm min⁻¹ until breaking. Ten
170 replicates were analyzed from each formulation.

171 The ASTM E96-95 (ASTM, 1995) gravimetric method was used for determining the
172 Water Vapour Permeability (WVP) of the films, considering the modification proposed

173 by McHugh, Avena-Bustillos & Krochta (1993).. Distilled water was placed in Payne
 174 permeability cups (3.5 cm diameter, Elcometer SPRL, Hermelle/s Argenteau, Belgium)
 175 to expose the film to 100% RH on one side. Each cup was placed in a cabinet
 176 equilibrated at 25 °C and 53% RH, with a fan placed on the top of the cup in order to
 177 reduce the resistance to water vapor transport, thus avoiding the stagnant layer effect in
 178 this exposed side of the film. The relative humidity of the cabinet (53%) was held
 179 constant using Mg(NO₃)₂ oversaturated solutions. The cups were weighed periodically
 180 (0.0001 g) and the water vapor transmission (WVTR) was determined from the slope
 181 obtained from the regression analysis of weight loss data versus time. From WVTR
 182 data, the vapor pressure on the film's inner surface (p₂) was obtained with eq. (1),
 183 proposed by McHugh *et al.* (1993) to correct the effect of concentration gradients.

184

$$185 \quad WVTR = \frac{P \cdot D \cdot L_n [P - p_2 \setminus P - p_1]}{R \cdot T \cdot \Delta z} \quad (1)$$

186

187 where P, total pressure (atm); D, diffusivity of water through air at 25 °C (m² /s); R, gas
 188 law constant (82.057 x 10⁻³ m³ atm kmol⁻¹ K⁻¹); T, absolute temperature (K); Δz, mean
 189 stagnant air gap height (m), considering the initial and final z value; p₁, water vapor
 190 pressure on the solution surface (atm); and p₂, corrected water vapor pressure on the
 191 film's inner surface (atm). Water vapor permeance was calculated using eq. (2) as a
 192 function of p₂ and p₃ (pressure on the film's outer surface in the cabinet).

193

$$194 \quad permeance = \frac{WVTR}{p_2 - p_3} \quad (2)$$

195

196 The permeability was calculated by multiplying the permeance by film thickness. This
 197 study was carried out for triplicate.

198 The Oxygen Permeability (OP) of the films was determined using an OX-TRAN Model
199 2/21 ML (Mocon Lippke, Neuwied, Germany) according to the ASTM Standard
200 Method D3985–05 (2010). Three samples conditioned at 53% RH and 25 °C for each
201 formulation were studied. The transmission values were determined every 20 min until
202 to reach the equilibrium. The area used for the tests was 50 cm². The film thickness was
203 considered in all cases for obtaining the OP.

204 The transparency, using the Kubelka-Munk theory for multiple scattering (Hutchings,
205 1999) and the gloss, at 85° angle from normal to the surface, according to the ASTM
206 standard D523 method (ASTM, 1999) were determined on the films. The surface
207 reflectance spectrum was determined from 400 to 700 nm with a spectro-colorimeter
208 CM- 3600d (Minolta Co., Tokyo, Japan) on both a white and a black background. As
209 light passes through the film, it is partially absorbed and scattered, which is quantified
210 by the absorption (K) and the scattering (S) coefficients. Internal transmittance (Ti) of
211 films was determined using eq. (3).

212

$$213 \quad T_i = \sqrt{(a - R_0)^2 - b^2} \quad (3)$$

214

215 where R_0 is the reflectance of the film on an ideal black background. The parameters a
216 and b were calculated by eqs. (4) and (5).

217

$$218 \quad a = \frac{1}{2} \left(R + \frac{R_0 - R + R_g}{R_0 R_g} \right) \quad (4)$$

219

$$220 \quad b = \sqrt{a^2 - 1} \quad (5)$$

221

222 where R is the reflectance of the sample layer backed by a known reflectance R_g . Three
223 replicates were used for each formulation. For the analysis was considered a wavelength
224 of 650 nm.

225 The gloss was determinate using a flat surface gloss meter (Multi.Gloss 268, Minolta,
226 Germany). Three films of each formulation were considered taken three measurements
227 in each sample. All results are expressed as gloss units (GU), relative to a highly
228 polished surface of black glass standard with a value near to 100 GU.

229

230 2.3.5. Statistical analysis

231 Statgraphics Plus for Windows 5.1 (Manugistics Corp., Rockville, MD) was used for
232 carrying out statistical analyses of data through analysis of variance (ANOVA). Fisher's
233 least significant difference (LSD) was used at the 95% confidence level.

234

235 **3. RESULTS**

236 **3.1. Thickness and extensibility**

237 According to Chabrat *et al.*, 2012, in blends of starch and PCL processed at high
238 temperature, the use of citric acid could act like a compatibilizer (esterification,
239 hydrogen bonds), as a starch plasticizer and/or as a depolymerization agent for starch
240 and PCL.

241 Table 1 shows the thickness and extensibility of the studied films. The PCL films had
242 lower thickness, and greater extensibility (area per mass unit in the compression
243 molding) than the other formulations. By contrast, the thickness tends to increase when
244 increase the amount of starch in the matrix, due to their reduced ability to flow. On the
245 other hand, the plasticizer effect of citric acid was masked with the high plasticity of
246 PCL.

247

248 **3.2. Structural analysis**

249 Atomic Force Microscopy on mode PeakForce QNM was used to acquire the images of
250 the Figure 1. For the study of the nano-mechanical properties of the material the DMT
251 modulus was considered. The control formulations (S and PCL) did not presented
252 marked changes in its structure, showing more homogeneous colors than the starch-PCL
253 blends. When the PCL was added to the starch matrix, the heterogeneity of the material
254 was higher and the DMT modulus values were greater than control formulations. The
255 blends exhibit dark and light zones corresponding to amorphous and crystalline
256 fragments (Baker, Miles & Helbert, 2001; Ortega-Toro *et al.*, 2014b). Regarding the
257 effect of citric acid, in the S formulation, a hardening on the surface of films was
258 observed when citric acid was added. The same effect was observed for blends that had
259 high content of starch. This phenomenon suggests an effect of cross-linking or an
260 increasing in the hydrogen bonds in the structure of polymeric matrix (Ortega-Toro *et*
261 *al.*, 2014b), which is masked when the content of PCL is higher.

262 Figure 2 shows SEM micrographs of the cross-section of the studied films, with or
263 without citric acid, conditioned at 25 °C and 53% RH for one week. S and PCL
264 formulations have a continuous and homogeneous structure; the PCL showed
265 deformations caused by the cryo-fracture with liquid nitrogen. When the PCL was
266 added to the starch matrix, the films were more heterogeneous, manifesting the
267 immiscibility of the polymers. In the formulations with less PCL (S90-S80) the
268 distribution of PCL was more effective. When the proportion of PCL was increased
269 (S70 and S60) zones rich in PCL and zones rich in starch were observed.

270 The addition of citric acid provoked changes in the polymers interaction's. . The S
271 formulation has a continuous matrix with some cracks when the CA was added (S-CA).

272 This suggests the formation of a matrix with less deformation capacity. However, the
273 S-CA formulation was more homogeneous than the S formulation, caused by citric acid
274 which can promote the fragmentation and dissolution of the native starch granules (Yu,
275 Wang, & Ma, 2005; Ma, Chang, Yu, & Stumborg, 2009). On the other hand, in the
276 formulations with less PCL (S80-CA and S90-CA), the CA promotes a change in the
277 PCL structure doing the PCL more thin and with better distribution. Similar results were
278 reported by Chabrat *et al.*, 2012, in blends of starch and PCL in presence of citric acid.
279 In the formulations S70-CA and S60-CA the changes were less marked because the
280 high amount of PCL could mask the citric acid effect. These phenomena may be due to
281 the depolymerization effect on the PCL; this could induce to better affinity between the
282 polymers (Reddy & Yang, 2010; Chabrat *et al.*, 2012).

283 Figure 3 shows the X-ray diffraction patterns of the films stored for 1 and 5 weeks at
284 controlled conditions. In all formulations which contain starch, the typical crystalline
285 forms of amylose V type at 2θ : 7° , 14° and 20° were observed (Lesmes, Cohen, Shener,
286 & Shimoni, 2009). When the amount of PCL increased the peaks were less marked and
287 the peak at 2θ : 14° was the only observed. Thinnest peaks and more intense were
288 observed in the PCL diffractogram due to crystalline zones biggest at 2θ : 22° and 24°
289 (Mark, 1999). On the other hand, the amorphous zones were less pronounced with the
290 PCL increasing. In the formulations containing PCL, the peaks intensity were smaller
291 with the storage time because of the reduction of the polymeric matrix crystallinity.
292 Regarding the citric acid effect, the displacement of peaks were observed, which
293 suggest polymorphisms in the polymeric matrix (Reddy & Yang, 2010), and a decrease
294 in the peaks intensity with the citric acid presence was observed on both the initial and
295 the final time of storage. These phenomena are interesting because this could suggest
296 the partial inhibition of starch retrogradation. These results are in accordance with other

297 authors demonstrating that the CA can protect the thermoplastic starch from
298 retrogradation (Yu *et al.*, 2005; Ortega-Toro *et al.*, 2014b). During the process, the CA
299 penetrates the starch granule and replaces partially the intermolecular hydrogen bonds
300 of starch. This causes the crystallinity reduction of the thermoplastic starch (Xie, Liu, &
301 Cui 2006; Ma *et al.*, 2009)

302

303 **3.3. Thermal analysis**

304 Table 2 shows the thermal properties of the studied films conditioned for 1 and 5 weeks.
305 Two heating scans and one cooling scan were performed. In the first heating scan the
306 melting temperature (T_m) of PCL was determined as the peak temperature of the
307 endotherm. In the first scan, the T_m and ΔH_m of the initial and the final storage time
308 were considered. During cooling, the crystallization temperature (T_c) of PCL was
309 determined as the peak temperature of the exotherm. Finally, during the second heating
310 scan another fusion temperature value was taken (PCL crystallized during cooling) and
311 the glass transition temperature (T_g) of starch at the midpoint was determined. The
312 values of enthalpy of fusion (ΔH_m) and crystallization (ΔH_c) are also shown in Table 2.
313 The T_g of starch decreased significantly ($p < 0.05$) with the PCL incorporation (S90).
314 This decrease only was promoted with the addition of 10% of PCL. When the amount
315 was bigger than 10%, the effect was not progressive and the values were almost
316 constants. On the other hand, the ΔC_p increased with the PCL addition in concordance
317 with a decrease in average molecular weight or a higher molecular mobility in the
318 polymeric matrix.

319 Moreover, the T_c values of the PCL was about 12 °C with ΔH_c about 52 J/g PCL, and
320 among the formulations were not observed significant differences. Besides, the T_m
321 value of PCL in the first scan was approximately 63°C and ΔH_m was observed about

322 72 J/g of PCL. Similar results have been reported by other authors (Averous *et al.*,
323 2000; Matzinos, *et al.*, 2002; Kweon, Kawasaki, Nakayama & Aiba, 2003). With the
324 storage time, a slight increase in T_m and ΔH_m were observed, which suggests that it is
325 necessary an amount bigger of energy for melt the crystals formed during the storage
326 and the interactions among the PCL molecules could be stronger. Additionally, the T_m
327 and ΔH_m on the second scan were lower than the values obtained in the first scan,
328 according with other authors for pure PCL (Koenig & Huang, 1995); the ΔH_m values
329 on the second scan were very close to ΔH_c values, this suggests that the crystals formed
330 during the cooling cycle can melt completely during the second heating cycle (Campos,
331 Marconcini, Martins-Franchetti & Mattoso, 2012).

332 Regarding the citric acid, the principal effects were on the T_g and ΔC_p of starch. The T_g
333 value of starch was decreased significantly ($p < 0.05$) when the CA was added in the S
334 formulation; and also decreased the T_g values in the films containing PCL until about
335 101 °C, remaining constant among these formulations. Meanwhile, the ΔC_p values were
336 lower with the CA addition in every case; perhaps the interactions among starch and
337 PCL were more effective with the citric acid at least when the PCL was in less amount,
338 as was observed in the SEM micrographs. Furthermore it is possible to observe that the
339 T_m and ΔH_c decreased slightly when the CA was added, this may be caused by the
340 decrease in the interactions among the starch molecules, suggesting a possible
341 hydrolysis or a plasticizer effect.

342

343 **3.4. Physicochemical properties**

344 Figure 4 shows the tensile properties of studied films stored under controlled conditions
345 for 1 and 5 weeks. When the starch is blend with PCL, EM is bigger than the control
346 formulations (S and PCL) except for the S90 formulation, where EM is significantly

347 smaller ($p < 0.05$). The blend between starch and PCL could improve the elastic
348 modulus of the resulting material (Avella, Errico, Laurienzo, Martuscelli, Raimo &
349 Rimedio, 2000). In general, TS decreased when the PCL was added, and the elongation
350 at break point was smaller than the S formulation except in the S90. These results, in
351 accordance with the thermal properties and the structural properties, suggest that the
352 interaction between starch and PCL is better when the PCL is presented in low
353 proportion in the polymer blend. .

354 Figure 5 shows the typical stress-strain curves of the PCL films at initial storage time.
355 Pure PCL films presented permanent deformation after the first break. The tensile
356 strength (18.17 ± 1.06 MPa) and deformation ($13 \pm 4\%$) at the yield point were
357 determined. Pure PCL is a ductile polymer so it can be deformed until 1100% in
358 agreement with other authors (Ishiaku, Pang, Lee, & Mohd, 2002). In the present work,
359 the universal test machine used was unable to register the maximum deformation (only
360 150% was possible).

361 The CA effect caused in elongation was especially remarkable; when the citric acid was
362 added, the elongation had a significant increase ($p < 0.05$) for S90-CA and S80-CA but
363 decreased for the S formulation, which suggested a plasticizer effect of the citric acid
364 unbound (Ghanbarzadeh *et al.*, 2011). Regarding EM and TS, the citric acid promoted
365 the increased in these parameters for the S formulation, especially with the storage time,
366 and a decreased in formulations containing less PCL, although in most cases the
367 changes were slight.

368 On the other hand, the formulations showed two trends with the storage time, when the
369 PCL was in low proportion, the EM and TS parameters increased and the elongation
370 decreased. The changes were not marked when the amount of PCL was high (S70, S70-

371 CA, S60 and S60-CA); perhaps, high amount of PCL limited the molecular
372 reorganization and therefore the retrogradation during storage.

373 Table 3 shows the values and standard deviation of water content, film solubility and
374 bonded citric acid of studied films conditioned under controlled conditions at initial and
375 final storage time. The water content (X_w) decreased with the increasing of PCL due to
376 its hydrophobic character. In general, the formulations with citric acid presented
377 significantly less ($p < 0.05$) water content than the CA-free films. This phenomenon
378 indicates a possible esterification of the hydroxyl groups of starch; during the process of
379 films formation (blend in roll mills and compression molding), the temperature used
380 was high ($160\text{ }^\circ\text{C}$) and therefore the matrix was in absence of water and, the citric acid
381 had the adequate conditions for take the anhydrous form, it could lead to esterification
382 reactions described by Reddy & Yang (2010). Cross-linking of starch reinforces the
383 intermolecular binding by introducing covalent bonds, which strengthen natural
384 intermolecular hydrogen bonds, so as to improve the water uptake resistance (Yu *et al.*,
385 2005; Krumova, Lopez, Benavente, Mijangos & Perena, 2000; Ghanbarzadeh *et al.*,
386 2011). Besides, a significant increased ($p < 0.05$) in X_w during the storage time was
387 observed in every case, except in S70 and pure PCL.

388 Regarding the film solubility, a significant decrease ($p < 0.05$) with the PCL addition
389 was observed compared with the S formulation; however, were not observed differences
390 among the formulations containing PCL. On the other hand, the film solubility
391 increased when CA was added, except for the formulations with higher PCL content
392 (S60 and S60-CA). The increase in this parameter suggests partial hydrolysis of starch
393 molecules caused by the presence of citric acid, resulting in the increase of linear and
394 smaller fragments of starch compared to the native starch (Carvalho, Zambon, da Silva
395 Curvelo, & Gandini 2005; Wang, Yu, Chang, & Ma, 2007; Ortega-Toro *et al.*, 2014b).

396 Other works reported similar results for starch-polyvinyl based films in presence of
397 citric acid (Yoon *et al.*, 2006), as also in modified starch-based films in combination
398 with polyvinyl alcohol and citric acid like plasticizer (Lee, Youn, Yun & Yoon, 2007;
399 Yun, Wee, Byun & Yoon, 2008). Other authors reported similar results for
400 thermoplastic starch co-plasticized with citric acid/glycerol (Shi *et al.*, 2007).

401 The values of bonded CA ratio with respect to the amount in the film did not present
402 marked differences among the formulations. Considering that the proportions between
403 the starch and CA were equal, maybe the CA does not act directly with the PCL and/or
404 the PCL presence does not affect the reactions between the CA and the starch
405 molecules.

406 Table 4 presents the water vapor permeability (WVP) and oxygen permeability (OP) of
407 studied films conditioned at 53% RH and 25 °C for 1 and 5 weeks. In food packaging
408 applications, the WVP should be as low as possible. The addition of PCL promoted a
409 significant decreased ($p < 0.05$) in the WVP of studied films due its hydrophobic
410 character. The effect of PCL was more marked than the citric acid effect, however, the
411 addition of CA promotes a slight decreased in the values of this parameter. The CA
412 trend has been observed for other authors (Ma *et al.*, 2009; Reddy & Yang, 2010;
413 Ghanbarzadeh *et al.*, 2011; Olivato, Grossmann, Yamashita, Eiras, & Pessan, 2012),
414 which could attribute to the hydrophilic OH groups substitution with hydrophobic ester
415 groups, and probably introduced a tortuous path for water molecules to pass through
416 with hydrophobic ester groups. Significant differences were not observed through the
417 storage time.

418 The OP values for S and PCL formulations were not presented because the S
419 formulation had very low OP and the pure PCL presented high OP and it was out of
420 range of the equipment used (OX-TRAN Model 2/21 ML Mocon). The values of OP

421 increased significantly ($p < 0.05$) with the PCL, and the CA addition did not present a
422 considerable effect. Regarding the storage time, the changes were very slight.

423 Table 5 presents the values and standard deviation of roughness parameters, internal
424 transmittance at 650 nm and gloss at 85° of studied films conditioned under controlled
425 conditions for 1 and 5 weeks. In general, the roughness parameters did not present
426 marked differences, and showed a slight trend to decrease with the PCL addition. As
427 expected, the pure PCL showed the less roughness (Ra and Rq) than the other
428 formulations. On the other hand, a slight trend to decrease with the CA addition was
429 observed because the acidity of citric acid promotes the fragmentation and dissolution
430 of starch granules (Yu *et al.*, 2005; Wang, Zhang, Han, & Bai, 2009; Chabrat *et al.*,
431 2012). In the analysis of this parameter it is necessary to take into account that the
432 compression molding could affect the surface roughness and mask the effect caused by
433 the components of the polymeric matrix.

434 The gloss of the films was related with the roughness (Sánchez-González, Cháfer,
435 Chiralt, González-Martínez, 2010) and therefore the obtaining process could have an
436 influence in it, in general, the gloss is proportional to the smoothness of the material.
437 The pure PCL and S90-CA have showed the higher values of gloss and the formulation
438 S80-CA has showed the least value of gloss, according to Ra and Rq parameters
439 obtained by AFM.

440 On the other hand, the internal transmittance has trended to decrease with the PCL
441 incorporation, which indicated higher heterogeneity and therefore with a higher opacity.
442 Also is possible to observe that the incorporation of CA to S90 promoted a higher
443 transmittance and a contrary effect was presented for the other blends. This suggests a
444 highest effect of CA when the PCL is less in the formulation, such as occur in the tensil
445 properties and thermal properties.

446 Is possible to deduce that the interaction between the starch and PCL is stronger when
447 the PCL is least in the formulation, and the CA could interact with these polymers and
448 improve the blends although its effect could be masked when the PCL have high
449 proportion.

450

451 **4. CONCLUSIONS**

452

453

454 **ACKNOWLEDGEMENTS**

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609 Figure captions

610 Figure 1. - AFM images of starch:PCL films without (a) and with (b) citric acid at initial time of storage
611 at 53% relative humidity and 25 °C.

612 Figure 2. -SEM micrographs of starch:PCL films without (a) and with (b) citric acid at initial time of
613 storage at 53% relative humidity and 25 °C.

614 Figure 3. -X-Ray diffraction patterns of starch:PCL films without (a) and with (b) citric acid at initial and
615 final time of storage at 53% relative humidity and 25 °C.

616 Figure 4.- Mean values of elastic modulus and stress and strain at break for the different films stored for 1
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618 level) for each mean value are shown.

619 Figure 5.-Typical stress-strain curves of PCL at initial time.

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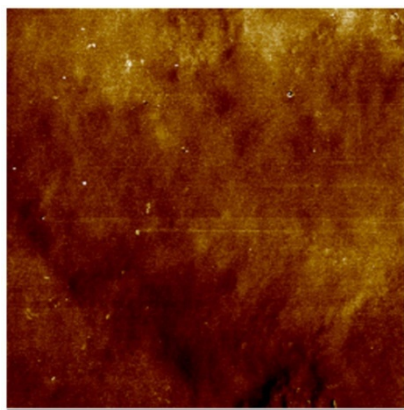
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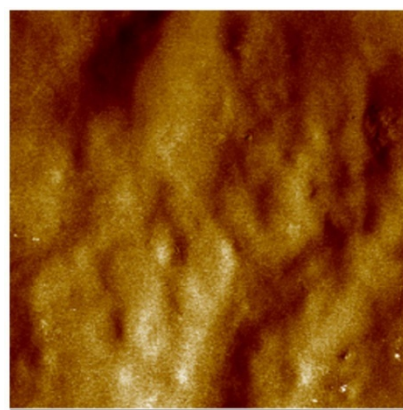
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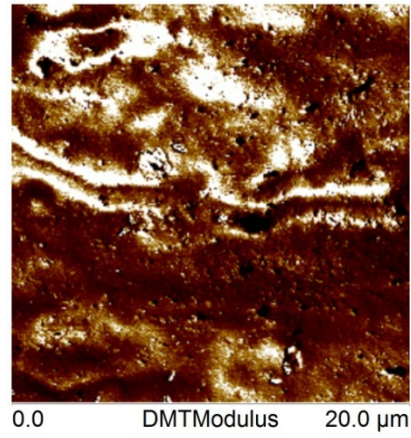
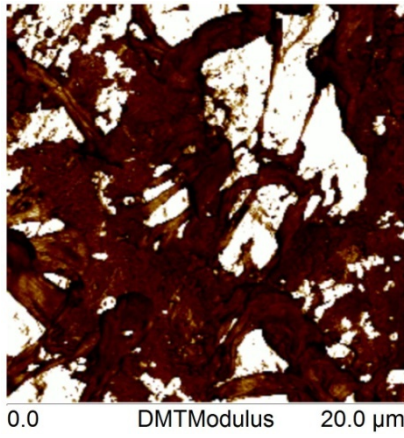
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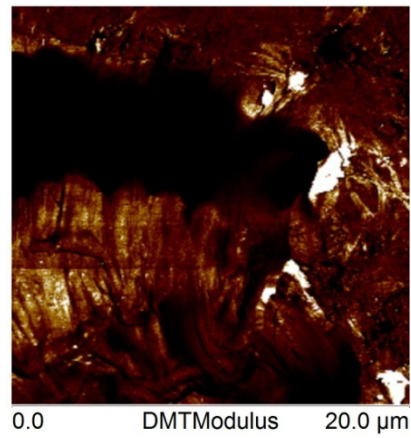
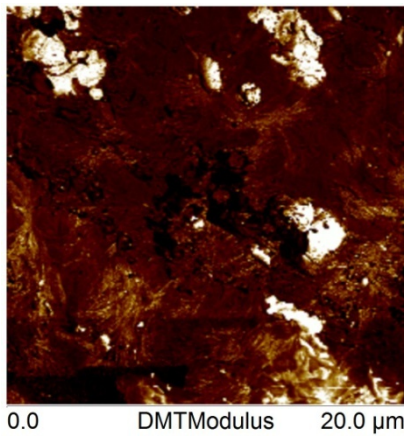
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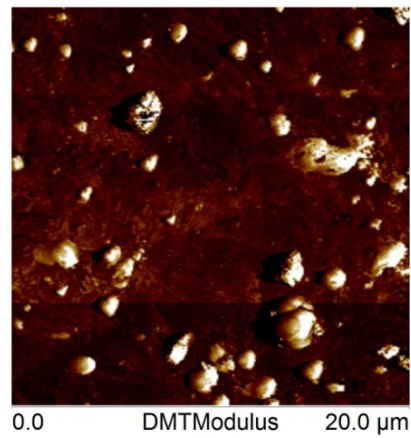
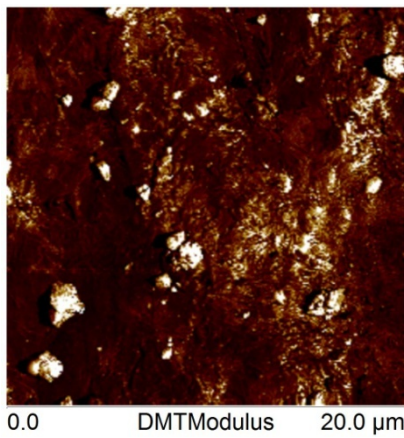
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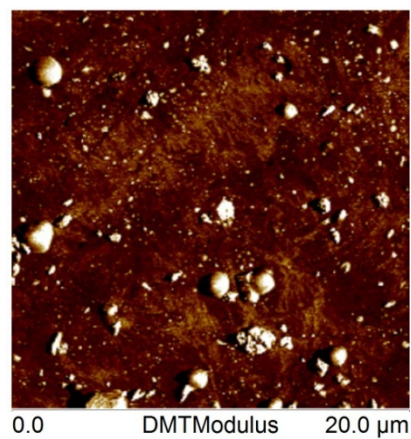
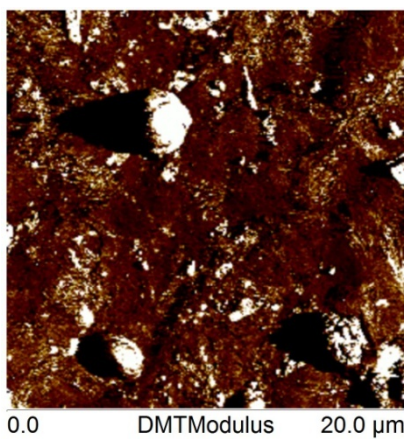
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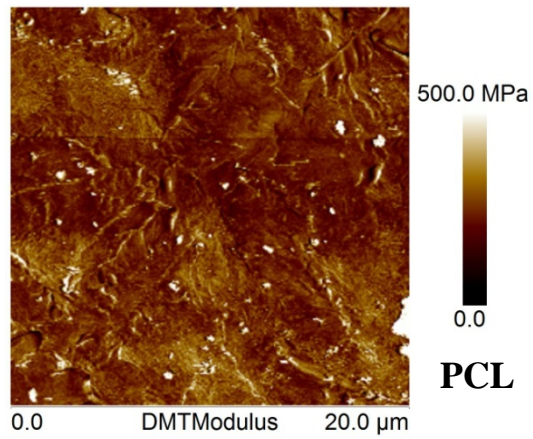


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640 Figure 1. - AFM images of starch:PCL films without (a) and with (b) citric acid at initial
 641 time of storage at 53% relative humidity and 25 °C.

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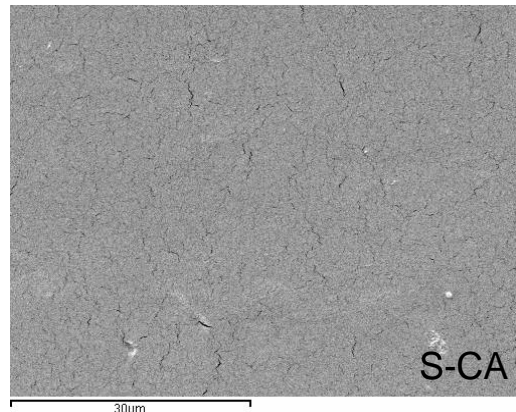
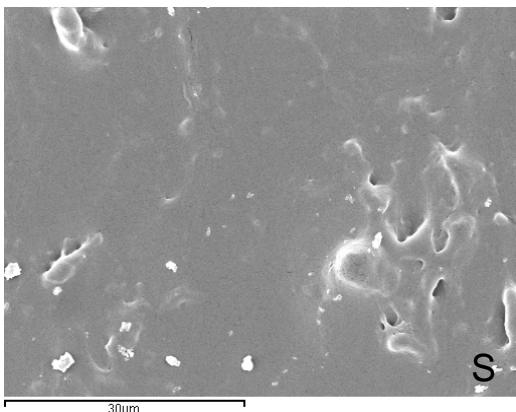
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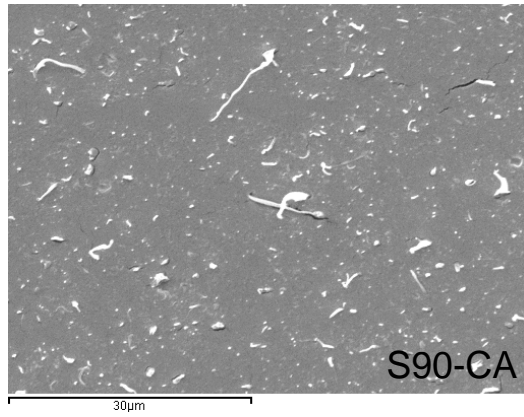
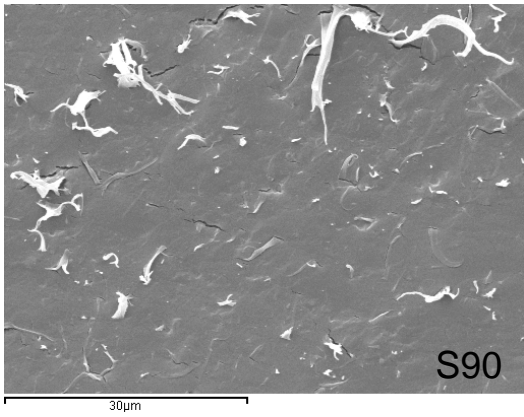
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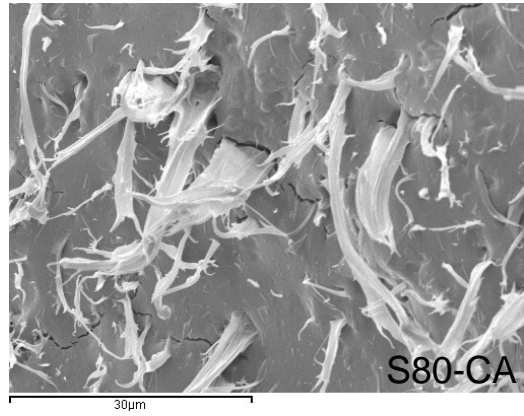
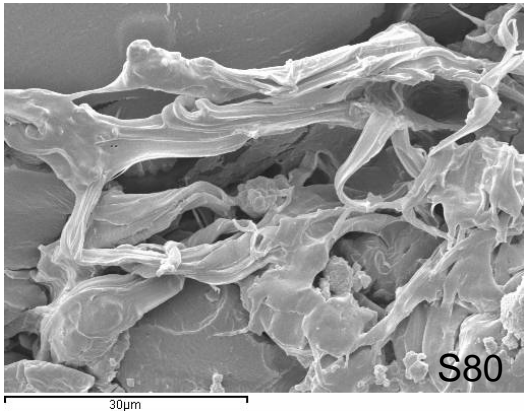
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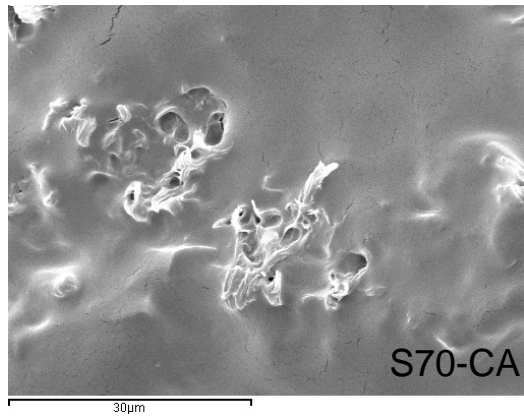
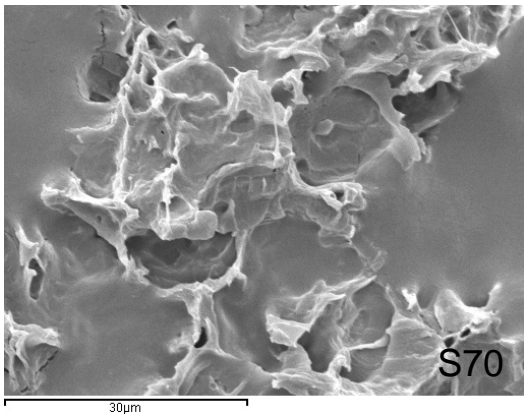
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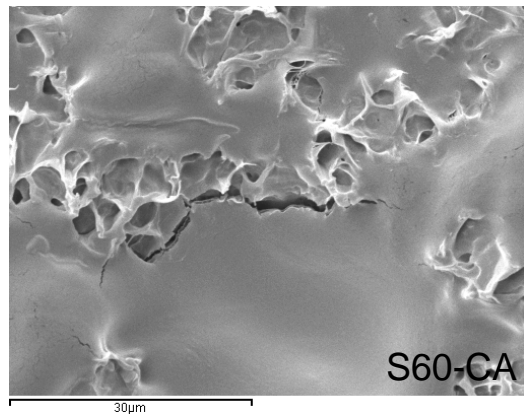
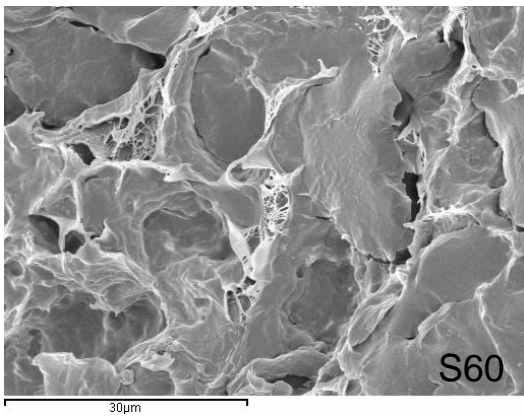
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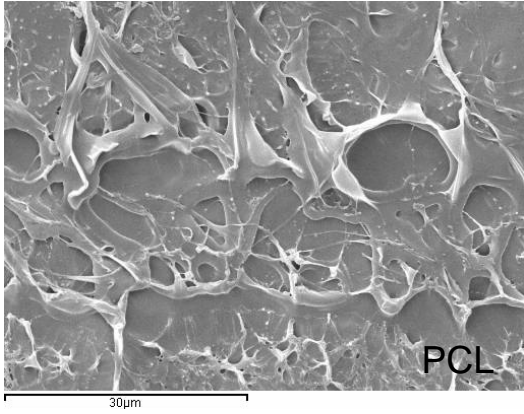
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655 Figure 2. -SEM micrographs of of starch:PCL films without (a) and with (b) citric acid
656 at initial time of storage at 53% relative humidity and 25 °C.

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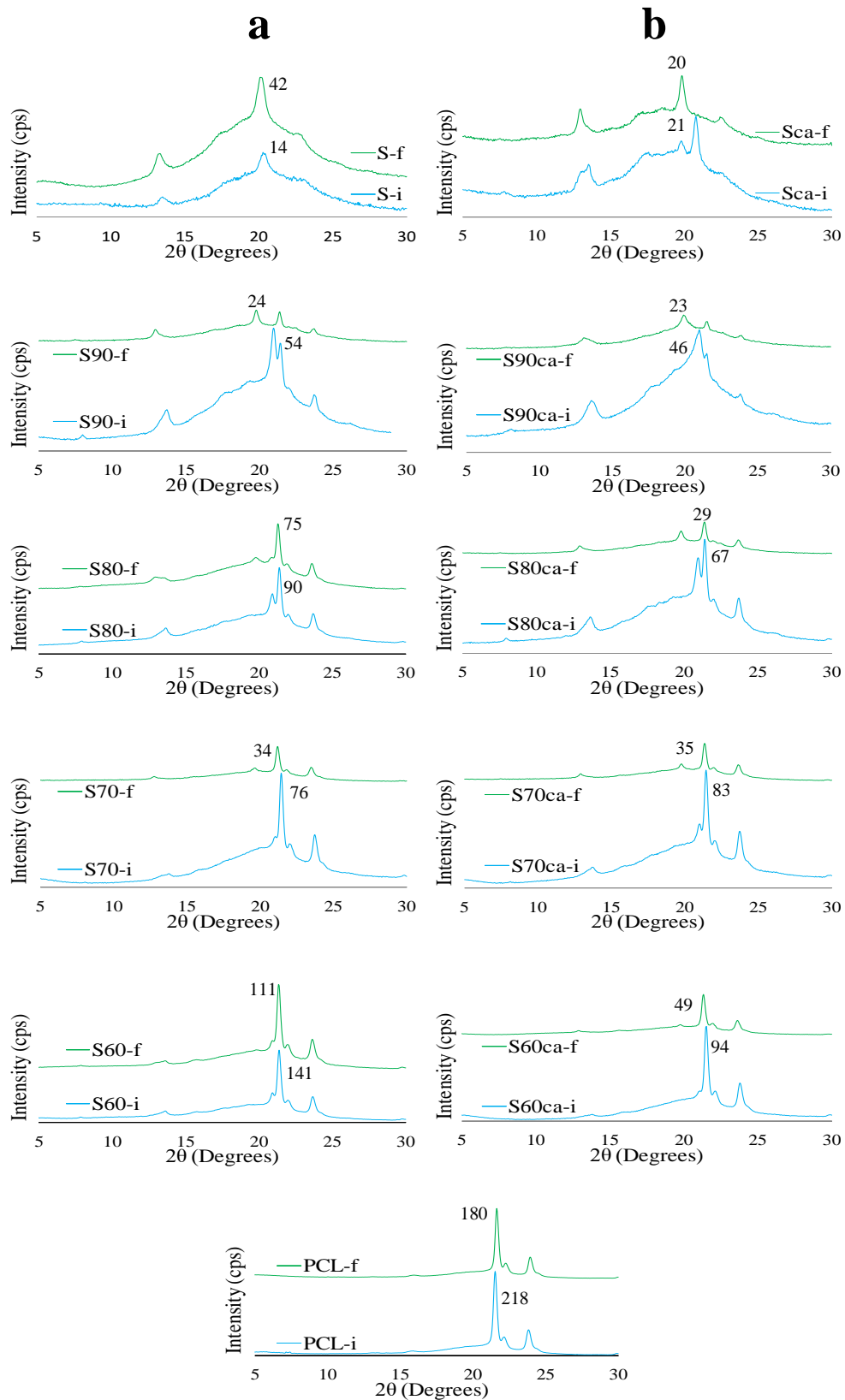
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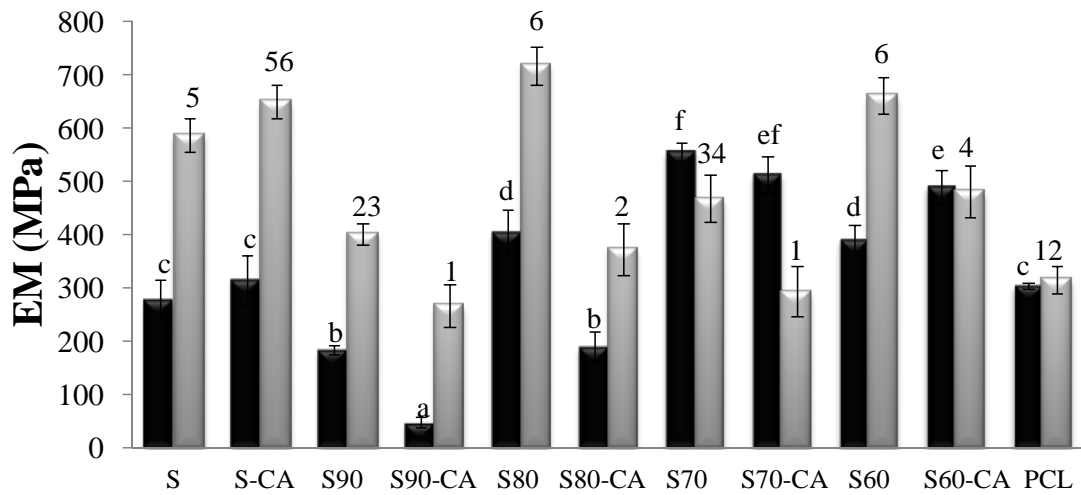
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674 Figure 3. -X-Ray diffraction patterns of starch:PCL films without (a) and with (b) citric
 675 acid at initial and final time of storage at 53% relative humidity and 25 °C.

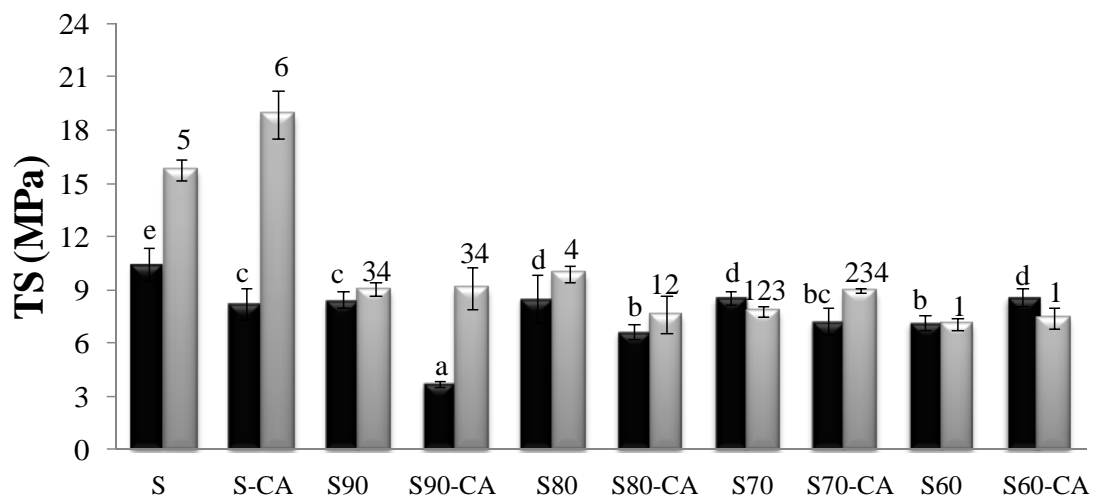
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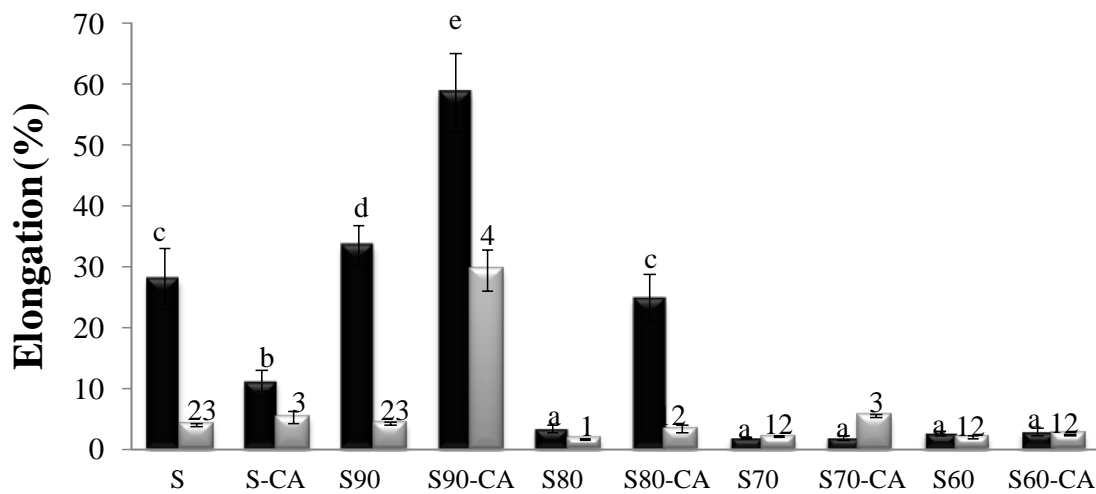
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Figure 4.- Mean values of elastic modulus and stress and strain at break for the different

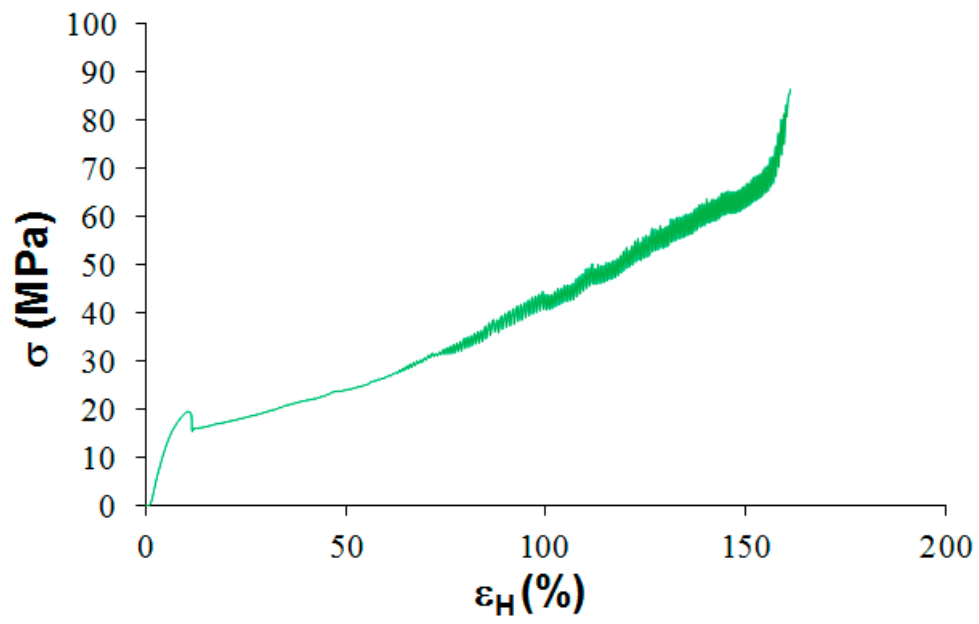
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films stored for 1 (black bars) and 5 (grey bars) weeks at 53% relative humidity and 25

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°C. LSD intervals (95% confidence level) for each mean value are shown.

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688 Figure 5.-Typical stress-strain curves of PCL at initial time.

689 Table 1. Mean values and standard deviation of thickness and extensibility of the different films stored at 53% relative humidity and 25 °C.
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| Films | Thickness (µm) | Extensibility (cm ² /g) |
|--------|------------------------|------------------------------------|
| S | 268 (22) ^e | 23.9 (1.1) ^a |
| S-CA | 217 (22) ^c | 32 (4) ^{bc} |
| S90 | 232 (17) ^{cd} | 28 (2) ^{abc} |
| S90-CA | 293 (27) ^f | 23.7 (0.7) ^a |
| S80 | 221 (9) ^{cd} | 32 (2) ^c |
| S80-CA | 239 (17) ^d | 27 (2) ^{ab} |
| S70 | 224 (9) ^{cd} | 31.1 (1.1) ^{bc} |
| S70-CA | 227 (11) ^{cd} | 29.8 (0.6) ^{bc} |
| S60 | 168 (13) ^b | 45 (6) ^d |
| S60-CA | 172 (14) ^b | 41 (2) ^d |
| PCL | 149 (17) ^a | 57 (9) ^e |

691 Different superscript letters within the same column indicate significant differences among formulations (p < 0.05).
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706 Table 2. Mean values and standard deviation of thermal properties of the starch:PCL films equilibrated at 53% relative humidity and 25 °C
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| Films | Glass transition | | Crystallization | | Fusion on the first scan | | | | Fusion on the second scan | |
|--------|----------------------------|-------------------------------|----------------------------|---------------------------|----------------------------|---------------------------|----------------------------|---------------------------|-----------------------------|---------------------------|
| | Tg midpoint | ΔC_p | Tc peak | ΔH_c (J/g PCL) | Initial | | Final | | Tm peak | ΔH_m (J/g PCL) |
| | | | | | Tm peak | ΔH_m (J/g PCL) | Tm peak | ΔH_m (J/g PCL) | | |
| S | 126.0 (0.3) ^d | 0.112 (0.002) ^b | --- | --- | --- | --- | --- | --- | --- | --- |
| S-CA | 113.0 (0.7) ^b | 0.054 (0.009) ^a | --- | --- | --- | --- | --- | --- | --- | --- |
| S90 | 114.5 (0.7) ^c | 0.17 (0.02) ^d | 12.0 (0.2) ^a | 51.4 (0.9) ^{bc} | 62.4 (0.7) ^{bc} | 72.4 (0.4) ^a | 63.9 (0.6) ^b | 81.9 (1.0) ^{ab} | 55.18 (0.05) ^{bcd} | 51.8 (1.3) ^a |
| S90-CA | 101.6 (0.2) ^a | 0.112 (0.008) ^b | 12.10 (0.14) ^a | 49.2 (0.9) ^a | 61.1 (0.9) ^a | 72.1 (0.5) ^a | 63.84 (0.08) ^b | 79.7 (0.5) ^a | 54.0 (0.2) ^a | 50 (2) ^a |
| S80 | 114.31 (0.05) ^c | 0.1280 (0.0014) ^{bc} | 12.5 (0.6) ^{ab} | 52.3 (0.3) ^c | 62.9 (0.6) ^c | 72.3 (1.3) ^a | 63.29 (0.11) ^{ab} | 82.3 (0.7) ^b | 55.4 (0.3) ^d | 51.2 (1.3) ^a |
| S80-CA | 101.2 (0.2) ^a | 0.131 (0.010) ^{bc} | 12.6 (0.4) ^{ab} | 49.3 (0.9) ^a | 60.97 (0.12) ^a | 72.2 (0.4) ^a | 63.92 (0.11) ^b | 81.0 (1.5) ^{ab} | 54.11 (0.05) ^a | 50.5 (0.9) ^a |
| S70 | 114.35 (0.13) ^c | 0.139 (0.013) ^c | 12.3 (0.3) ^{ab} | 52.0 (0.6) ^c | 62.32 (0.62) ^{bc} | 72.1 (0.3) ^a | 63.32 (0.04) ^{ab} | 81.7 (0.9) ^{ab} | 54.9 (0.2) ^{bc} | 51.4 (1.4) ^a |
| S70-CA | 101.53 (0.13) ^a | 0.052 (0.014) ^a | 12.95 (0.07) ^b | 50.7 (1.1) ^{abc} | 61.55 (0.03) ^{ab} | 72.4 (0.4) ^a | 63.39 (0.11) ^{ab} | 79.9 (0.6) ^a | 54.8 (0.4) ^b | 49.9 (1.1) ^a |
| S60 | 114.8 (0.2) ^c | 0.126 (0.004) ^{bc} | 12.33 (0.07) ^{ab} | 52.2 (0.8) ^c | 63.0 (0.2) ^c | 72.5 (0.6) ^a | 63.3 (0.2) ^{ab} | 81.9 (1.0) ^{ab} | 55.13 (0.04) ^{bcd} | 51.0 (1.3) ^a |
| S60-CA | 100.9 (0.5) ^a | 0.041 (0.004) ^a | 12.3 (0.3) ^{ab} | 50.3 (0.2) ^{ab} | 61.51 (0.02) ^{ab} | 72.2 (0.4) ^a | 63.07 (0.04) ^a | 79.8 (0.4) ^a | 54.88 (0.14) ^b | 49.7 (1.0) ^a |
| PCL | --- | --- | 12.6 (0.6) ^{ab} | 52.4 (0.3) ^c | 63.5 (0.6) ^a | 72.8 (1.4) ^a | 63.7 (0.6) ^a | 82.2 (1.5) ^b | 55.4 (0.4) ^{cd} | 51.0 (1.2) ^a |

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 709 Different superscript letters within the same column indicate significant differences among formulations (p < 0.05).
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723 Table 3. Mean values and standard deviation of water content (g water/g dried film), film solubility (g solubilised film/g initial dried film) and
 724 bonded citric acid (ratio with respect to amount in the film) of the different films stored at 53% relative humidity and 25 °C.
 725

| Films | Xw | | Film solubility | | Bonded citric acid |
|--------|---------------------------------|---------------------------------|---------------------------------|-------------------------------|--------------------------|
| | Initial | Final | Initial | Final | |
| S | 0.0613 (0.0006) ^{h1} | 0.079 (0.004) ^{g2} | 0.19 (0.07) ^{d1} | 0.24 (0.05) ^{d1} | --- |
| S-CA | 0.059 (0.002) ^{gh1} | 0.076 (0.002) ^{fg2} | 0.35 (0.03) ^{f1} | 0.371 (0.012) ^{f1} | 0.80 (0.03) ^a |
| S90 | 0.0664 (0.0004) ⁱ¹ | 0.074 (0.003) ^{ef2} | 0.120 (0.009) ^{bc1} | 0.138 (0.002) ^{b2} | --- |
| S90-CA | 0.0543 (0.0007) ^{ef1} | 0.0713 (0.0005) ^{e2} | 0.328 (0.005) ^{f1} | 0.331 (0.005) ^{e1} | 0.84(0.03) ^a |
| S80 | 0.0535 (0.0008) ^{e1} | 0.061 (0.002) ^{d2} | 0.132 (0.003) ^{bc1} | 0.137 (0.013) ^{b1} | --- |
| S80-CA | 0.056 (0.003) ^{ef1} | 0.06161 (0.00015) ^{d2} | 0.362 (0.013) ^{f1} | 0.32 (0.02) ^{e2} | 0.86(0.03) ^a |
| S70 | 0.057 (0.003) ^{fg1} | 0.063 (0.004) ^{d1} | 0.099 (0.003) ^{b1} | 0.106 (0.006) ^{b1} | --- |
| S70-CA | 0.047 (0.003) ^{d1} | 0.0578 (0.005) ^{c2} | 0.24 (0.02) ^{e1} | 0.30 (0.02) ^{e2} | 0.81(0.04) ^a |
| S60 | 0.0409 (0.0006) ^{c1} | 0.046 (0.002) ^{b2} | 0.13 (0.03) ^{bc1} | 0.13 (0.02) ^{b1} | --- |
| S60-CA | 0.03331 (0.00014) ^{b1} | 0.0458 (0.0014) ^{b2} | 0.16 (0.02) ^{cd1} | 0.19 (0.02) ^{c1} | 0.83(0.04) ^a |
| PCL | 0.003 (0.002) ^{a1} | 0.0021 (0.0005) ^{a1} | 0.00022 (0.00011) ^{a1} | 0.0004 (0.0002) ^{a1} | --- |

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 727 Different superscript letters within the same column indicate significant differences among formulations (p < 0.05).
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729 Different superscript numbers within the same row indicate significant differences due to storage time (p < 0.05).
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740 Table 4. Mean values and standard deviation of water vapour permeability (WVP) and oxygen permeability (OP) of the different films at 1
 741 (Initial time) and 5 (Final time) weeks of storage at 53% relative humidity and 25 °C.
 742

| Films | WVP (g·mm·kPa ⁻¹ ·h ⁻¹ ·m ⁻²) | | OP · 10 ¹⁴ (cm ³ ·m ⁻¹ ·s ⁻¹ ·Pa ⁻¹) | |
|--------|---|-----------------------------|--|-----------------------------|
| | Initial | Final | Initial | Final |
| S | 18.1 (1.4) ^{h1} | 16 (2) ^{e1} | < D.L. | < D.L. |
| S-CA | 12 (2) ^{de1} | 15.6 (1.2) ^{e1} | 0.26 (0.05) ^{a1} | 0.281 (0.004) ^{a1} |
| S90 | 14.5 (0.7) ^{f1} | 15.8 (1.2) ^{e1} | 0.22 (0.09) ^{a1} | 0.23 (0.15) ^{a1} |
| S90-CA | 13.0 (1.4) ^{ef1} | 15 (2) ^{e1} | 0.4 (0.2) ^{a1} | 0.54 (0.06) ^{a1} |
| S80 | 11 (2) ^{de1} | 9.3 (0.6) ^{cd1} | 6.5 (0.3) ^{ab1} | 6 (3) ^{b1} |
| S80-CA | 10.0 (0.6) ^{d1} | 10.8 (1.0) ^{d1} | 2.4 (0.3) ^{a1} | 3.9 (0.2) ^{ab2} |
| S70 | 7.5 (0.7) ^{c1} | 10.4 (0.7) ^{cd2} | 17.1 (0.9) ^{cd1} | 14.6 (1.1) ^{c1} |
| S70-CA | 6.3 (0.7) ^{c1} | 8.5 (0.3) ^{c1} | 11.6 (1.2) ^{bc1} | 12 (2) ^{c1} |
| S60 | 8 (2) ^{c1} | 5.4 (0.4) ^{b1} | 33 (12) ^{e1} | 26 (3) ^{d1} |
| S60-CA | 2.9 (0.8) ^{b1} | 3.55 (0.11) ^{b1} | 24 (2) ^{d1} | 27.1 (0.8) ^{d1} |
| PCL | 0.120 (0.04) ^{a1} | 0.117 (0.011) ^{a1} | > D.L. | > D.L. |

743
 744 D.L.: 0.1-200 cc/(m².day)
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746 Different superscript letters within the same column indicate significant differences among formulations (p < 0.05).
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748 Different superscript numbers within the same row indicate significant differences due to storage time (p < 0.05).
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757 Table 5. Mean values and standard deviation of surface roughness parameters and optical properties of the different films at 1 (Initial time) and 5
 758 (Final time) weeks of storage at 53% relative humidity and 25 °C.
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| Films | Roughness parameters | | | Gloss (85°) | | Ti (650nm) | |
|--------|--------------------------|------------------------|-----------------------|------------------------|----------------------------|-----------------------------|---------------------------|
| | r (%) | Ra (nm) | Rq (nm) | Initial | Final | Initial | Final |
| S | 6.1 (0.9) ^{abc} | 215 (61) ^a | 263 (63) ^a | 40 (5) ^{c1} | 37.2 (1.5) ^{bcd1} | 85.1 (0.3) ^{h1} | 84.2 (0.2) ^{fg2} |
| S-CA | 2.5 (0.2) ^a | 165 (59) ^a | 206 (72) ^a | 39 (5) ^{c1} | 32 (2) ^{b1} | 85.5 (0.6) ^{h1} | 85.9 (0.8) ^{g1} |
| S90 | 13 (5) ^d | 198 (60) ^a | 247 (65) ^a | 37 (9) ^{bc1} | 35 (6) ^{bc1} | 77.3 (0.6) ^{bc1} | 79.8 (0.6) ^{cd2} |
| S90-CA | 3.2 (1.2) ^a | 148 (30) ^a | 200 (38) ^a | 52 (3) ^{d1} | 43 (17) ^{de2} | 79.4 (0.3) ^{def1} | 81 (0.4) ^{de2} |
| S80 | 8 (3) ^{bc} | 202 (26) ^a | 255 (26) ^a | 29 (9) ^{c1} | 31 (9) ^{b1} | 82.4 (0.6) ^{g1} | 82.5 (1.1) ^{ef1} |
| S80-CA | 14 (4) ^d | 390 (216) ^b | 497 (35) ^b | 20 (13) ^{a1} | 14 (2) ^{a1} | 73.6 (0.6) ^{a1} | 76 (0.7) ^{a1} |
| S70 | 8 (3) ^{bc} | 220 (57) ^a | 271 (68) ^a | 34 (10) ^{bc1} | 46 (4) ^{e2} | 80.9 (0.14) ^{efg1} | 80.9 (0.4) ^{de1} |
| S70-CA | 11 (3) ^{cd} | 199 (58) ^a | 265 (72) ^a | 31(9) ^{bc1} | 35 (10) ^{bcd1} | 76.2 (0.7) ^{b1} | 77.1 (0.6) ^{ab1} |
| S60 | 5.6 (1.4) ^{ab} | 163 (60) ^a | 210 (79) ^a | 38 (6) ^{c1} | 37 (4) ^{bcd1} | 81.2 (1.3) ^{fg1} | 81.6 (0.7) ^{de1} |
| S60-CA | 9.2 (1.3) ^{bcd} | 163 (26) ^a | 214 (26) ^a | 50 (7) ^{d1} | 41 (10) ^{cde2} | 78.8 (0.8) ^{cde1} | 79.4 (0.8) ^{cd1} |
| PCL | 6.0 (0.9) ^{ab} | 154 (16) ^a | 195 (25) ^a | 59 (16) ^{e1} | 57 (9) ^{f1} | 78 (2) ^{cd1} | 78 (2) ^{bc1} |

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763 Different superscript numbers within the same row indicate significant differences due to storage time (p < 0.05).
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