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Additional Information

1 **Physical and structural properties and thermal behaviour of starch-**
2 **poly(ϵ -caprolactone) blend films for food packaging**

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26 **ABSTRACT**

27 Structural and physical properties (barrier, mechanical, and optical properties) and
28 thermal behaviour of corn starch-PCL blend films, containing glycerol as plasticizer,
29 obtained by compression molding, at 160°C and 130 bars, were studied. The stability on
30 the films' properties was also evaluated. Blend films showed phase separation of the
31 polymers in a heterogeneous matrix with starch rich regions and PCL rich regions.
32 Nevertheless, a small miscibility of PCL in the starch phase was detected through the
33 shift in the glass transition temperature of the starch phase, which leads to a partial
34 inhibition of amylose crystallization during film formation and storage. The lack of
35 interfacial adhesion of PCL and starch phases promoted films' fragility and reduced
36 stretchability, although elastic modulus of the films with small PCL ratios increased.
37 Water barrier properties of starch films were improved as the PCL increased in the
38 blend, but oxygen permeability increased. Due to the food compatibility of this polymer
39 blends (without any toxic compound) these could be an interesting alternative for food
40 packaging, where some drawbacks of starch films has been overcome.

41

42 Keywords: thermoplastic starch, poly(ϵ -caprolactone), films, stability.

43

44 Chemical compounds studied in this article

45 Glycerol (PubChem CID: 753); water (PubChem CID: 952); caprolactone? (PubChem
46 CID: 10401); Diphosphorus pentoxide (PubChem CID: 14812); Magnesium nitrate
47 (PubChem CID: 25212)

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51 **1. INTRODUCTION**

52 In the last decade, there has been growing interest in the development of biodegradable
53 materials for applications in packaging technology, medicine or agriculture in order to
54 mitigate the problems caused by non-biodegradable petroleum-derived plastics
55 (Hubackova *et al.*, 2013). In this sense, starch is a promising polymer because it is
56 abundant, cheap and renewable (Lourdin, Valle, & Colonna, 1995). Although starch
57 shows a high capacity to form homogeneous films with excellent oxygen barrier
58 properties, they exhibit some drawbacks, such as poor mechanical properties, high water
59 vapor sensitivity which leads to high water vapor permeability (Averous & Boquillon,
60 2004; Ghanbarzadeh, Almasi, & Entezami, 2011), and retrogradation. This consists of a
61 slow recoiling of gelatinized amylose and amylopectin molecules which back into their
62 native helical arrangements or into a new single helix conformation. The retrogradation
63 is undesirable as it increases crystallinity and reduces film elongation over time. In
64 order to improve the starch film properties, blends with other components, such as
65 plasticizers, cross-linking agents or other polymers have been studied. Glycerol can be
66 added as a plasticizer to enhance the mechanical properties of the film, increasing the
67 flexibility (Vieira, Altenhofen, Oliveira, & Masumi, 2011)

68 The addition of other thermoplastic polymers to form blend starch films can modulate
69 the films' properties in order to improve their functionality. Of the commercially
70 available biodegradable polymeric materials, blends based on thermoplastic starch
71 (TPS) and hydrophobic synthetic polymers, such as aliphatic polyesters, could offer
72 adequate solutions (Di Franco, Cyras, Busalmen, Ruseckaite, & Vázquez, 2004).

73 PCL is aliphatic polyester obtained by chemical synthesis from crude oil or from
74 renewable resources, such as polysaccharides. PCL-based films have good water
75 resistance. It is a thermoplastic, biodegradable, biocompatible and semi-crystalline

76 polymer that has a very low glass transition temperature ($\sim 60^{\circ}\text{C}$) (Cao, Chang, &
77 Huneault, 2008). It also has a low melting point ($58\text{--}60^{\circ}\text{C}$), low viscosity, and is easily
78 processable (Flieger, Kantorová, Prell, Řezanka, & Votruba, 2003). PCL can be blended
79 with other polymers to improve stress crack resistance, dyeability and adhesion and has
80 been used in combination with polymers such as cellulose propionate, cellulose acetate
81 butyrate, polylactic acid and polylactic acid-co-glycolic acid (Woodruff & Hutmacher,
82 2010; Takala *et al.*, 2013).

83 Properties of PCL-starch blends have been analysed by several authors for different
84 applications. Averous, Moro, Dole, & Fringant (2000), studied the mechanical
85 properties, the thermal and thermomechanical behaviour and the hydrophobicity of
86 wheat TPS-PCL materials blended by extrusion and injection moulded, containing
87 different ratios of TPS and PCL (up to 40 wt.%). They found a phase separation of
88 polymers due to their incompatibility, although thermal transitions of each polymer
89 suffered minor shifts in the characteristic temperatures. The hydrophobicity of the
90 blends considerably increased as compared with TPS. Rosa, Guedes, Pedroso, & Calil
91 (2004), also analysed the properties of PCL blends with different ratios of gelatinized
92 and non-gelatinized corn starch. They observed that the melt flow index increased when
93 the PCL ratio increased in the blend, while PCL reduced the water sorption capacity of
94 the materials. A decrease in the crystallinity of PCL in the blends was also observed.

95 On the basis of previous studies, and despite the polymer incompatibility, PCL-starch
96 blends could offer properties that are of interest for the development of biodegradable
97 packaging materials for food products where some drawbacks of starch films, such as
98 their highly hydrophilic nature, poor water barrier properties and retrogradation
99 phenomena could be overcome, while no potentially toxic compounds are present in the
100 film formulation, which is crucial for food packaging applications (Duquesne, Rutot,

101 Degee, & Dubois, 2001). Likewise, biodegradability of starch-PCL blends has been
102 reported by [REDACTED]. These authors found a reduction of the PCL degradation time when it is
103 blended with starch.

104 The aim of this work was to characterize the structural and physical properties (barrier,
105 mechanical, and optical properties) and thermal behaviour of corn starch-PCL blend
106 films, with a wide range of polymers' ratios, obtained by compression moulding. The
107 stability during storage time on the films' properties was also evaluated.

108

109 **2. MATERIALS AND METHODS**

110 **2.1. Materials**

111 Corn starch was purchased from Roquette (Roquette Laisa España, Benifaió, Spain).
112 Glycerol was obtained from Panreac Química, S.A. (Castellar del Vallès, Barcelona,
113 Spain). Polycaprolactone (pellets ~3 mm, average M_n 80.000, impurities <1.0% water)
114 was provided by Fluka (Sigma-Aldrich Chemie, Steinheim, Germany). P_2O_5 and
115 $Mg(NO_3)_2$ were obtained from Panreac Química, S.A. (Castellar Vallés, Barcelona).

116

117 **2.2. Film processing**

118 Native starch and glycerol were dispersed in water. The starch:glycerol ratio (w/w) was
119 1:0.3, which was established on the basis of previous studies (Ortega-Toro, Jiménez,
120 Talens & Chiralt, 2014) PCL was dispersed in the aqueous slurry of starch and glycerol
121 containing 0.5 g water/g starch at different ratios to obtain four blends with 80:20,
122 60:40, 40:60, 20:80 starch:PCL ratios (w/w). The blends were named S80, S60, S40 and
123 S20, respectively. Starch-glycerol (S) and pure PCL films were used as controls.

124 The formulations were gradually mixed on a two-roll mill (Model LRM-M-100,
125 Labtech Engineering, Thailand) at 160 °C and 8 rpm for 30 minutes until a

126 homogeneous paste sheet was obtained. The obtained paste sheets were conditioned at
127 25 °C and 53% relative humidity (RH) for 48 hours before compression molding.
128 The films were obtained by compression molding (Model LP20, Labtech Engineering,
129 Thailand). Four grams of the paste were put onto steel sheets and preheated on the
130 heating unit for 5 min. Films were obtained by compressing at 160 °C for 2 minutes at
131 30 bars, followed by 6 minutes at 130 bars; thereafter a cooling cycle was applied for 3
132 minutes. The obtained films were conditioned at 25 °C and 53% RH for 1 and 5 weeks
133 for their characterization.

134

135 **2.3. Film characterization**

136 2.3.1. Film thickness

137 The film thickness was measured with a Palmer digital micrometer at six random
138 positions around the film.

139

140 2.3.2. Moisture content

141 The films were conditioned at 53% RH and dried for 24 h at 60 °C using a convection
142 oven (J.P. Selecta, S.A. Barcelona, Spain) and placed in a desiccator at 25 °C with P₂O₅
143 for 2 weeks. This assay was performed in triplicate.

144

145 2.3.3. Solubility in water

146 The solubility in water was determined holding the sample in bi-distilled water for 48 h,
147 considering a film:water ratio of 1:10. Afterwards, the samples were transferred to a
148 convection oven (J.P. Selecta, S.A., Barcelona, Spain) for 24 h at 60 °C to remove free
149 water and then were transferred to a desiccator with P₂O₅ at 25 °C for 2 weeks till

150 constant weight. Solubility in water was obtained from the initial and final weights of
151 the films. Three samples were used for each formulation.

152

153 2.3.4. Water Vapour Permeability (WVP)

154 The ASTM E96-95 (ASTM, 1995) gravimetric method was used for determining the
155 WVP of the films. The modification proposed by McHugh, Avena-Bustillos, & Krochta
156 (1993) was considered. Distilled water was placed in Payne permeability cups (3.5 cm
157 diameter, Elcometer SPRL, Hermelle/s Argenteau, Belgium) to expose the film to 100%
158 RH on one side. Each cup was placed in a cabinet equilibrated at 25 °C and 53% RH,
159 with a fan placed on the top of the cup in order to reduce the resistance to water vapor
160 transport, thus avoiding the stagnant layer effect in this exposed side of the film. The
161 relative humidity of the cabinet (53%) was held constant using Mg(NO₃)₂ oversaturated
162 solutions. The cups were weighed periodically (0.0001 g) and the water vapour
163 transmission (WVTR) was determined from the slope obtained from the regression
164 analysis of weight loss data versus time. From this data, WVP was obtained according
165 to Jiménez, Fabra, Talens, & Chiralt (2012).

166

167 2.3.5. Oxygen Permeability (OP)

168 The oxygen permeation rate of the films was determined using an OX-TRAN Model
169 2/21 ML (Mocon Lippke, Neuwied, Germany) in samples conditioned at 53% RH and
170 25 °C. The transmission values were determined every 20 min until to reach the
171 equilibrium. The exposure area during the tests was 50 cm². Three samples were studied
172 for each formulation.

173

174 2.3.6. Tensile properties

175 A universal test machine (TA.XTplus model, Stable Micro Systems, Haslemere,
176 England) was used to determine the tensile properties of films. The tensile strength
177 (TS), the elastic modulus (EM), and the elongation (E) of the films were determined
178 from the stress-strain curves, estimated from force-distance data obtained for different
179 films (2.5 cm wide and 5 cm long), according to the ASTM standard method D882
180 (ASTM, 2001). Equilibrated samples were mounted in the film-extension grips of the
181 testing machine and stretched at 50 mm min⁻¹ until breaking. Tests were carried out at
182 25 °C and 53% RH. Ten replicates were considered for each formulation.

183

184 2.3.7. Optical properties

185 The Kubelka-Munk theory for multiple scattering was applied to the reflection spectra
186 to determinate the film's transparency (Hutchings, 1999). The surface reflectance
187 spectrum was determined from 400 to 700 nm with a spectro-colorimeter CM- 3600d
188 (Minolta Co., Tokyo, Japan) on both a white and a black background. Internal
189 transmittance (Ti) was obtained according to Jiménez *et al.* (2012).

190

191 The gloss was determined at an incidence angle of 85°, according to the ASTM standard
192 D523 method (ASTM, 1999) using a flat surface gloss meter (Multi.Gloss 268, Minolta,
193 Germany). Three films of each formulation were considered, taking three measurements
194 in each sample. All results are expressed as gloss units (GU), relative to a highly
195 polished surface of black glass standard with a value near to 100 GU.

196

197 2.3.8. Thermal properties

198 A Differential Scanning Calorimeter DSC 1 Star^e System (Mettler-Toledo Inc.,
199 Switzerland) was used to analyse the phase transitions in the polymer matrices. 10-15

200 mg of film samples were placed into aluminium pans, sealed and perforated to favour
201 possible moisture loss during the heating run. Three scans were performed for the
202 sample analyses. First, sample was heated from -80 °C to 160 °C at a heating rate of 20
203 °C /min, from which PCL melting properties ($\Delta H_m, T_m$) were obtained and in which the
204 bonded water in the film was eliminated. In the second scan, the temperature was
205 lowered to -80 °C at the same rate and the PCL crystallization properties ($\Delta H_c, T_c$) were
206 obtained. Finally, samples were heated to 160 °C at a 20 °C/min to obtain the starch
207 glass transition temperature and melting properties of PCL. The initial and final weights
208 of the pans were registered to assess water loss during the first heating step.

209

210 2.3.9. X-ray diffraction

211 A diffractometer (XRD, Bruker AXS/D8 Advance) was used to obtain X-ray diffraction
212 patterns. All samples (equilibrated for 1 and 5 weeks) were analyzed at 25 °C and 53%
213 RH, between 2θ : 5° and 30° using $K\alpha$ Cu radiation (λ : 1.542 Å), 40 kV and 40 mA with
214 a step size of 0.05°. For this analysis, 4 cm² samples were used.

215

216 2.3.10. Scanning Electron Microscopy (SEM)

217 The microstructural analysis of cross-sections of films was carried out by using a
218 Scanning Electron Microscope (JEOL JSM-5410, Japan). Film samples were
219 maintained in desiccators with P₂O₅ for two weeks at 25 °C and observations were
220 carried out in at least two samples per formulation. Pieces of about 0.5 cm² were
221 immersed in liquid nitrogen and then cryo-fractured to observe the revealed surface.
222 They were mounted on copper stubs and gold-coated for observation, using an
223 accelerating voltage of 10 kV.

224

225 2.3.11. Atomic Force Microscopy (AFM)

226 Samples conditioned for 5 weeks at 25 °C and 53% RH using P₂O₅ were observed by
227 AFM to analyze their surface morphology using an Atomic Force Microscope
228 (Multimode 8, Bruker AXS, Santa Barbara, USA) with a NanoScope[®] V controller
229 electronics. Measurements were taken from several areas of film surface (20 μm²) using
230 PeakForce QNM[®] mode (Quantitative Nanomechanical Mapping). The DMT Modulus
231 mode derived from PeakForce QNM was plotted in the 2-D plane of the sample. Three
232 samples were analyzed for each formulation.

233

234 2.3.12. Statistical analysis

235 Statgraphics Plus for Windows 5.1 (Manugistics Corp., Rockville, MD) was used to
236 carry out statistical analyses of data through analysis of variance (ANOVA). Fisher's
237 least significant difference (LSD) was used at the 95% confidence level. Homogenous
238 group samples were indicated in tables with the same letter or number superscripts.
239 Letters when film formulation was compared and numbers when the same sample at
240 different storage time was compared.

241

242

243 **3. RESULTS**

244 **3.1. Physical properties of films**

245 **3.1.1. Thickness, extensibility, water solubility and moisture content.**

246 Table 1 shows the thickness and the extensibility (film surface per mass unit during the
247 compression molding) of the starch-PCL based films equilibrated at 25 °C and 53% RH
248 for 1 week. A significant decrease in thickness and an increase in extensibility (p <
249 0.05) were observed when the content of PCL rose in the films, indicating greater

250 flowability. Films without PCL were the thickest as a result of the greater resistance to
251 flow of the material during compression. These results show the promotion of the
252 flowability of polymer blends by the addition of PCL, as observed by Rosa *et al.*
253 (2004), thus favouring their thermo-processing.

254 Table 1 also shows the solubility in water and the moisture content of the films. The
255 moisture content showed significant changes ($p < 0.05$) with the storage time for
256 formulations S, S80 and S60. As expected, the higher the starch content in the films, the
257 greater the water sorption capacity (Averous *et al.*, 2000; López, Zaritzky, Grossmann,
258 & García, 2013). The hydrophobic character of PCL reduces the water adsorption
259 capacity of the blend films and their equilibrium moisture content. Likewise, when the
260 ratio of PCL in the films increased, their water solubility decreased, as shown in table 1,
261 without significant ($p < 0.05$) changes during storage. The results confirm the expected
262 changes in the water affinity of the films when the ratio of PCL increased, which
263 supposes an advantage with respect to starch materials.

264

265 **3.1.2. Barrier properties**

266 Table 2 shows the values of Water Vapour Permeability (WVP) at a RH gradient of 53-
267 100 % and at 25 °C, after 1 and 5 storage weeks. The WVP values fell significantly ($p <$
268 0.05) when the PCL ratio increased in the films, without significant changes during
269 storage. Nevertheless, the obtained values for starch-PCL blends were not in the
270 established range of WVTR for food systems' requirements (Schmid *et al.* 2012) and
271 additional reduction would be necessary. In this sense the bilayer films composed by an
272 PCL layer and starch-PCL blend layer could be an alternative since perpendicular
273 resistance of both layers to water vapour transfer would be much more effective. The

274 WVP values of the PCL layer are in the range of the WVTR requirements for meat and
275 MAP products (Schmid et al. 2012).

276 Table 2 also shows the Oxygen Permeability (OP) values of the films. The control film
277 (S) had such low oxygen permeability that this value could not be measured with the
278 equipment used. The very low OP of starch films has been reported by other authors
279 (López *et al.*, 2013). However, PCL films and those containing a high ratio of this
280 component (S40, S20) exhibited such high OP values that they were beyond the
281 measurement range of the equipment. Samples S80 and S60 showed a significant
282 increase ($p < 0.05$) in the OP values with respect to the pure starch films as a result of
283 the PCL addition. No significant changes in the OP of the films occurred during the
284 storage. The hydrophobic character of PCL promoted the increase in the oxygen
285 permeability due to their chemical affinity which favours the gas solubility in the
286 polymer matrix (Park, Testin, Vergano, Park, & Weller, 1996). So, the incorporation of
287 PCL into starch matrices modifies their barrier properties, improving the water vapour
288 barrier properties, but reducing the barrier to oxygen.

289 Oxygen barrier properties of net starch films cover the whole range of food packaging
290 requirements, but when the PCL ratio increased in the blend films, different food
291 products fall outside of their OTR range (Schmid et al. 2012). As commented on above,
292 and according with the barrier properties of each film, the formation of PCL-starch
293 bilayer films would be an adequate option to obtain materials appropriate for food
294 packaging, particularly meat and MAP products or nuts and snacks.

295

296 **3.1.3. Tensile properties**

297 Figure 1 shows the typical stress-strain curves of the starch:PCL films stored at 53%
298 RH for 1 week. The pure PCL films showed a high plastic deformation after the yield

299 point as shown in Figure 1a. Values of the strength and deformation in the yield point
300 were 18.17 ± 1.06 MPa and $13 \pm 4\%$, respectively. PCL is a ductile polymer which can
301 be deformed until 1100% in agreement with Ishiaku, Pang, Lee, & Mohd Ishak (2002).
302 Films containing low ratio of starch (S20 and S40 samples) exhibited an initial rupture
303 followed by subsequent partial breaks (Figure 1b), while blends with less PCL content
304 exhibited only one clear break point (Figure 1b). This indicates that PCL tend to be the
305 continuous phase as its ratio increase in the matrix, but the interruptions provoked by
306 the starch phase promote the film failure, thus losing the ductile properties of PCL, as
307 reported by Averous *et al.* (2000).

308

309 Table 3 shows the tensile properties of the films conditioned at 53% RH and 25 °C for 1
310 and 5 weeks of storage. Significant changes ($p < 0.05$) were observed in all tensile
311 parameters when PCL was added to starch films. Despite the fact that the elastic
312 modulus of pure PCL and pure S films did not show significant differences, their blends
313 exhibited higher values. Nevertheless, the resistance to break (TS) and extensibility (E)
314 of the films significantly ($p < 0.05$) decreased when PCL was incorporated. No
315 significant differences in any tensile parameter were observed for the different blends.
316 The obtained results were similar to those reported by Corradini, Mattoso, Guedes, &
317 Rosa (2004) for blends of PCL and zein, and by Ishiaku *et al.* (2002) for PCL and sago
318 starch blends. In both cases, the incompatibility of polymers was observed.

319 The effect of storage time on the mechanical properties of the blend films reveals
320 different behaviour depending on the PCL ratio. Films with higher ratios of starch (up to
321 60 %) exhibit a marked increase (nearly two times) in the elastic modulus over the
322 storage time, whereas no significant changes were observed for films whose starch
323 content was under 40 % . This suggests that retrogradation phenomena occurred in the

324 continuous starch matrix, giving rise to recrystallization and chain aggregation which
325 makes the cohesion forces in the polymer network more intense (Mali, Grossmann,
326 Garcia, Martino, & Zaritzky, 2006). This effect was not observed for films with the
327 greatest proportions of PCL, where EM did not change during storage time. Blend films
328 did not show changes in the resistance at break (TS values), although this increased in
329 pure starch films in line with the retrogradation effects. Deformation at break decreased
330 in all the films over storage time, except for the one that contained the greatest ratio of
331 PCL. This reduction is especially marked in pure starch films.

332 The incorporation of PCL into starch matrices seems to reduce the changes in the
333 mechanical properties of starch films throughout time, but the polymer incompatibility
334 makes its efficiency limited due to the phase separation of polymers and the increase in
335 the interface area where adhesion forces are not intense enough.

336

337 **3.1.4. Thermal properties**

338 Table 4 shows the thermal properties of the studied films obtained from DSC analysis.
339 The T_g value of starch (obtained from the second heating scan) was about 126 °C,
340 similar to that reported by other authors (Ortega-Toro *et al.*, 2014). In S20 formulation,
341 the T_g value of starch was not observed because of the very weak signal associated with
342 the low starch ratio in the sample. The T_g value of PCL was not detected due to the
343 operation temperature range of the equipment, although its value (-60 °C) was reported
344 by other authors (Averous *et al.*, 2000).

345 When PCL was incorporated, the T_g of starch decreased significantly ($\Delta T_g \sim 12^\circ\text{C}$),
346 regardless of the ratio of PCL. This suggests a partial miscibility of PCL in the starch
347 phase. The decrease in T_g , as well as the higher values of ΔC_p , is coherent with the
348 lower molecular weight of PCL, which reduced the mean molecular weight of the

349 starch-rich phase. This favours the plasticization of the starch phase, thus increasing its
350 flowability during thermo-processing, as previously commented on, while favouring its
351 thermo-processing.

352 The melting behaviour of PCL, characterized in the first heating scan, was similar for
353 every film, regardless of the PCL ratio, even for 100 % PCL films. The T_m value for
354 films stored for 1 week was 63°C and the ΔH_m was 72 J/g of PCL, similar to those
355 reported by other authors (Averous *et al.*, 2000; Matzinos, Tserki, Kontoyiannis, &
356 Panayiotou, 2002; Kweon, Kawasaki, Nakayama, & Aiba, 2003). For samples stored
357 for 5 weeks, although the same T_m values were obtained, ΔH_m slightly increased (about
358 82 J/g of PCL) which indicates that the degree of crystallinity of PCL in the films
359 increased throughout storage in both pure and blend films. No effect of starch on the
360 PCL crystallinity was observed in the films.

361 The crystallization behaviour of PCL during the cooling step was also constant for all
362 the samples, regardless of the film composition. The T_c value (peak) was about 12 °C
363 and the ΔH_c was close to 52 J/g of PCL. As compared with melting constants, the
364 values of T_c and ΔH_c were lower, revealing the supercoiling effect during the cooling
365 step after the previous melting. As expected, the ΔH_m values of the second heating step
366 reproduced those obtained for ΔH_c , since all crystallized PCL melts during heating.

367 The results reveal that, for the obtained films, starch did not affect the melting
368 behaviour of PCL, which, in turn, suggests a very low, or null, miscibility of starch in
369 the PCL-rich phase. Likewise, the crystallization of the PCL progress during storage
370 time and supercoiling occurred in fast cooling processes, as given by the DSC analysis.
371 This is in contrast to that described by other authors (Averous *et al.*, 2000; Matzinos *et*
372 *al.*, 2002; Wang, Rodriguez-Perez, Reis & Mano, 2005) who report a small inhibition of
373 PCL crystallization in PCL-starch blend films obtained by different techniques.

374

375 **3.1.5. Optical properties**

376 Table 5 shows the gloss at an 85° incidence angle and the internal transmittance at 650
377 nm of the films conditioned for 1 and 5 weeks. Films of pure components (PCL and S)
378 presented the highest gloss values, while blend films were less glossy with no marked
379 differences. The decrease in the gloss of blends can be attributed to changes in the
380 surface roughness caused by the immiscibility of the polymers, which gives rise to the
381 formation of a heterogeneous matrix with greater surface roughness (Jiménez *et al.*,
382 2012). No formulation exhibited significant changes in the film gloss over storage time.
383 The internal transmittance values decreased when the ratio of PCL in the matrix rose, in
384 line with the greater opacity of this polymer. The PCL formulation had the lowest
385 transmittance and in no case did any significant changes in internal transmittance occur
386 during the storage time.

387

388 **3.2. Nano and microstructure of the films**

389 Figure 2 shows the micrographs of the cross sections of films obtained by SEM. The
390 heterogeneity of the blends was observed, evidencing the lack of miscibility of both
391 polymers while the S and PCL films presented a homogeneous structure. No granules of
392 native starch were observed in any case, which indicates that starch was effectively
393 melted in the process used, giving rise to thermoplastic starch. Random- order
394 conglomerates of starch and PCL were observed in the blend films. Likewise, blends
395 exhibited poor interfacial adhesion, due to the different polymer polarities (Rosa,
396 Rodrigues, Guedes, & Calil, 2003; Corradini *et al.*, 2004). The PCL phase can be
397 clearly distinguished due to its ductile behaviour, which defines a particular cryofracture
398 pattern, promoting stretched filamentous formations.

399 The spontaneous detachment of both phases caused a loss in cohesion of the blend
400 matrix and the lack of stretchability of the blend films (Ishiaku *et al.*, 2002; Corradini *et*
401 *al.*, 2004).

402 Figure 3 shows the DMT modulus maps of the films obtained from the PeakForce QNM
403 AFM analyses. The polymer matrices with pure components (S or PCL) show quite a
404 homogeneous structure in terms of the surface mechanical response in line with the
405 homogeneity of the material. The S surface was harder than the PCL, in agreement with
406 the higher value of the elastic modulus of starch films after 5 storage weeks. Blend
407 films had a more heterogeneous surface modulus, exhibiting light and dark areas,
408 according to the distribution of harder (starch phase) and softer (PCL) regions at surface
409 level. The film with formulation S20 shows the structure which bears the most
410 similarity to pure PCL films, due to the small ratio of starch which interrupts the
411 continuity of the PCL matrix.

412 The X-ray diffraction patterns of the films stored for 1 and 5 weeks are shown in Figure
413 4. The diffraction spectra of S films showed peaks at 13.5° , 20° and 24° 2θ angle,
414 characteristic of the helical amylose-lipid complexes in the V-type crystallization form
415 (Matzinos *et al.*, 2002; Gelders, Vanderstukken, Goesaert, & Delcour, 2004). The
416 intensity of the peaks increased in films stored for 5 weeks, which indicates the progress
417 of amylose crystallization during storage.

418 PCL films show the characteristics peaks of the crystalline polymer at 21° , 22° and 24°
419 2θ angle. No notable changes in diffraction pattern were observed for these films during
420 storage. For the blend films with the highest ratio of PCL, S20 and S40, the diffraction
421 spectra were similar to those of the PCL film, which indicates that starch crystalline
422 forms were not present after 1 or 5 storage weeks. Nevertheless, samples with higher
423 ratios of starch, S60 and, especially S80, showed the starch typical peak at 13.5° and an

424 overlapping of the characteristic peaks of PCL and some of the starch in the 2θ angle
425 range of 20-24°. In these films, the relative intensity of the starch peaks is lower than in
426 pure starch films. This suggests that starch crystallization is partially inhibited by
427 blending with PCL, mainly when the PCL ratio increased in the blend.

428

429 **4. CONCLUSIONS**

430 Corn starch and PCL blend films, containing 30 % glycerol with respect to starch, could
431 be obtained by compression molding at 160°C and 130 bars. The films showed phase
432 separation of the polymers, exhibiting a heterogeneous blend matrix where starch- rich
433 regions and PCL- rich regions could be observed. Nevertheless, a small degree of PCL
434 miscibility in the starch phase was detected through the shift in the glass transition
435 temperature of the starch phase, which leads to the partial inhibition of amylose
436 retrogradation during film formation and storage. The lack of interfacial adhesion of the
437 PCL and starch phases promoted the films' fragility and reduced their elongation,
438 although small PCL ratios increased the elastic modulus of the films, indicating its
439 adequate properties as reinforcing filler in starch matrices. Water barrier properties of
440 starch films were improved as the PCL increased in the blend but worsening of the
441 oxygen barrier properties was obtained. Bilayer films with both PCL and starch blend
442 layers could meet the requirements for packaging of some foods such as meat and MAP
443 products. Nevertheless, the overall migration in different food simulants must be
444 assessed, according to migration limits established by regulation for plastic materials in
445 contact with food.

446

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