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Additional Information

1 **|Improvement of properties of glycerol plasticized starch films by blending with a low**
2 **ratio of polycaprolactone and/or polyethylene glycol**

3

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13

14 **ABSTRACT**

15 The effect of the melt blending of polycaprolactone (PCL) (5 and 10 wt. %) and
16 polyethylene glycol (PEG 4000 D) (2 wt. %) with corn thermoplastic starch (with 30 %
17 glycerol) on film properties was studied through the characterization of the structural,
18 thermal and physical properties of the films obtained by compression moulding, after 1 and
19 5 storage weeks. PCL and PEG decreased the glass transition temperature of starch,
20 whereas no changes in PCL melting properties were observed. Starch films could
21 incorporate 5% PCL without a notable phase separation, leading to more stretchable and
22 stable films. Blend films with 10% PCL showed clear phase separation, without any
23 improved tensile properties, but with lower water vapour permeability. In ternary systems,
24 PEG reduced the PCL-starch affinity, enhancing phase separation, whereas it did not
25 improve the film properties with respect to starch films.

26

27 **Keywords:** corn starch, polycaprolactone, polyethylene glycol, compression moulding.

28

29 Chemical compounds studied in this article

30 Cornstarch (PubChem CID: 24836924); Polycaprolactone (PubChem SID: 85240250);

31 Polyethylene Glycol (PubChem CID: 174 ethylene glycol); Glycerol (PubChem CID: 753);

32 water (PubChem CID: 952); Diphosphorus pentoxide (PubChem CID: 14812); Magnesium

33 nitrate (PubChem CID: 25212).

34

35

36 **1. INTRODUCTION**

37 Synthetic polymers have been widely used for food packaging because of their accessible
38 cost and suitable properties. However, the growth of environmental problems caused by
39 petrochemical-based plastics has aroused interest in the use of biodegradable alternatives
40 coming from renewable sources (Petersen *et al.*, 1999; Weber, Haugaard, Festersen, &
41 Bertelsen, 2002).

42 Among the natural polymers, such as polysaccharides and proteins, starch is a promising
43 candidate from which to develop biodegradable films. Starch has high film-forming
44 capability, low cost, wide availability from renewable sources and is relatively easy to
45 handle (Bertuzzi, Armada, & Gottifredi 2007; Romero-Bastida *et al.*, 2005; Talja, Helén,
46 Roos, & Jouppila, 2007). Many studies have reported the development of starch-based
47 films as a means of reducing the environmental impact of synthetic plastics (Averous &
48 Boquillon, 2004; Park, Yang, Kim, & Lee, 2004).

49 Starch based-films exhibit good barrier properties to oxygen (Dole, Joly, Espuche, Alric, &
50 Gontard, 2004), carbon dioxide and lipids, biodegradability (Iovino, Zullo, Rao, Cassar, &
51 Gianfreda, 2008) and compostability (Lörcks, 1998). However, starch itself has poor
52 thermoprocessability and exhibits some drawbacks such as a strong hydrophilic character
53 (Teixeira *et al.*, 2009), and poor mechanical properties compared to conventional synthetic
54 polymers (Averous & Boquillon, 2004; Teixeira *et al.*, 2009), which limit its use as
55 packaging material.

56 Chemical modification (López, Zaritzky, & García, 2010), plasticization and blending with
57 other polymers and additives (Jiménez, Fabra, Talens, & Chiralt, 2012) are common
58 methods used to overcome the starch limitations. The most common plasticizers used on
59 starch-based materials are polyols, principally glycerol and sorbitol (Mali, Grossmann,

60 García, Martino, & Zaritzky, 2002; McHugh, Avena-Bustillos, & Krochta, 1993;
61 Sothornvit & Krochta, 2005).

62 Different polymers used in starch blends are poly (β -hydroxyalkanoates) (PHA), Poly(lactic
63 acid) (PLA) and poly (ϵ -caprolactone) (PCL). PCL is a linear, partially crystalline,
64 hydrophobic polyester (Li, Espartero, Foch, & Vert, 1997) with good mechanical properties
65 and high extensibility. Its elongation and tensile strength at break point is higher than
66 1100% and 33 MPa, respectively (Matzinos, Tserki, Gianikouris, Pavlidou, & Panayiotou,
67 2002; Ortega-Toro, Collazo, Talens, & Chiralt, 2015)

68 Starch and PCL blends have been extensively studied by several authors (Avella *et al.*,
69 2000; Averous, Moro, Dole, & Fringant, 2000; Li & Favis, 2010, Matzinos *et al.*, 2002;
70 Ortega-Toro *et al.*, 2015; Singh, Pandey, Rutot, Degée, & Dubois, 2003; Wu, 2003).

71 Several disadvantages of pure starch-based films, such as their low resilience, high degree
72 of moisture sensitivity and high shrinkage have been overcome by adding PCL to the starch
73 matrix (Averous *et al.*, 2000). However, the main problem of the starch/PCL blend is the
74 phase separation of both incompatible polymers and the weak interfacial adhesion due to
75 the lack of chemical affinity between polymers. To overcome this problem, compatibilizers
76 have been used or the polymers have been modified (Avella *et al.*, 2000). Nevertheless, the
77 incorporation of small amounts (10%) of PCL into starch films led to a very fine dispersion
78 of PCL in the starch matrix, decreasing the starch glass transition temperature and
79 improving the water vapour barrier properties of starch films (Ortega-Toro *et al.*, 2015).

80 Polymer compatibilizers, such as amphiphilic, low molecular weight compounds
81 (Yolesahachart & Yoksan, 2011), ionomers (Landreau, Tighzert, Bliard, Berzin, & Lacoste,
82 2009) or partially miscible polymers in both blend components (Parulekar & Mohanty,
83 2007) generally improve the blend film properties. Kim, Choi, & Park (2000) reported that

84 the mechanical and structural properties of 40/60 (wt. %) starch-PCL blend films were
85 greatly improved when 10% (wt.) polyethylene glycol (PEG) of intermediate molecular
86 weight (MW: 3.400 D) was added. PEG of intermediate molecular weight could be used as
87 a possible compatibilizer in starch-PCL blend films, while acting as a starch plasticizer.
88 The aim of this work was to analyse the influence of adding PEG of intermediate molecular
89 weight on the structural, thermal and physicochemical properties of compression moulded
90 starch films containing a low ratio (less than 10%) of PCL in order to obtain low cost starch
91 films with improved properties.

92

93 **2. MATERIALS AND METHODS**

94 **2.1. Materials**

95 Corn starch was obtained from Roquette (Roquette Laisa España, Benifaió, Spain). Its
96 moisture content was 10% w/w and amylose percentage was 14%. Glycerol was purchased
97 from Panreac Química, S.A. (Castellar del Vallès, Barcelona, Spain). Polyethylene Glycol
98 (PEG) and the polycaprolactone (PCL) were provided by Aldrich Chemistry (Sigma-
99 Aldrich Co. LLC Madrid, Spain); their molecular weights were 4000 dalton and 80000
100 dalton, respectively. Magnesium nitrate 6-hydrate and phosphorus pentoxide were
101 purchased from Panreac Química, S.A. (Castellar del Vallés, Barcelona, Spain).

102

103 **2.2. Film preparation**

104 PEG and glycerol were dissolved in water, and then native starch was dispersed in the
105 aqueous solution. Afterwards, the respective amount of PCL was added to the mixture. The
106 starch:glycerol ratio was 10:3 and the starch:water ratio was 2:1 in every case. The other
107 components were added in different proportions depending on the blend. The starch:PEG

108 ratio was 100:2 and the starch:PCL ratios were 100:5 and 100:10. Two control films (S:
109 glycerol plasticized starch and PCL: pure PCL) and 5 blend films were prepared: S-PEG
110 (starch, glycerol and PEG), S-PCL5 (starch, glycerol and PCL at 5%), S-PCL5-PEG
111 (starch, glycerol, PCL at 5%, and PEG), S-PCL10 (starch, glycerol and PCL at 10%) and S-
112 PCL10-PEG (starch, glycerol, PCL at 10%, and PEG).

113 The formulations were hot-mixed on a two-roll mill (Model LRM-M-100, Labtech
114 Engineering, Thailand) at 160 °C and 8 rpm for 30 min. A visually good miscibility among
115 the components was observed. When the mixing was finished, the paste sheets formed were
116 removed from the mill and conditioned at 25 °C and 53% Relative Humidity (RH), using a
117 $Mg(NO_3)_2$ oversaturated solution for 48 hours, to increase the blend moisture content, thus
118 improving processability. Afterwards, films were made in a compression moulding press
119 (Model LP20, Labtech Engineering, Thailand). Four g of the pre-conditioned paste were
120 put onto steel sheets and pre-heated on the heating unit for 5 min. Compression moulding
121 was performed at 160 °C and 50 bars for 2 min, followed by 6 min at 150 bars; thereafter,
122 the cooling cycle was applied for 3 min. Starch-based films were conditioned at 25 °C and
123 53% RH for 1 week for the initial time characterization and for 5 weeks for the final time
124 characterization.

125

126 **2.3. Film characterization**

127 2.3.1. Structural properties

128 The surface morphology of the films was analysed using an atomic force microscope
129 (AFM) (Multimode 8, Bruker AXS, Santa Barbara, USA) with NanoScope[®] V controller
130 electronics. Measurements were taken from 20 μm^2 areas using the PeakForce QNM mode.
131 Samples conditioned for 1 week at 25 °C and 53% RH were analysed. The maps of

132 Derjaguin-Muller-Toropov (DMT) modulus derived from the model of elastic contact
133 (Derjaguin, Muller & Toropov, 1975) were obtained from the PeakForce QNM Mode
134 analysis, showing the surface mechanical properties of the materials. Three replicates were
135 considered for every case.

136 Scanning Electron Microscopy (SEM) of the cross-sections of the films was performed by
137 means of a microscope JEOL JSM-5410, Japan. The film samples were maintained in
138 desiccators with P₂O₅ for 1 week to guarantee that water was not present and 2 samples per
139 formulation were analysed. Film pieces, 0.5 cm² in size, were cryofractured (by immersion
140 in liquid nitrogen and subsequent break) and fixed on copper stubs, gold coated, and
141 observed using an accelerating voltage of 10 kV.

142 A diffractometer (XRD, Bruker AXS/D8 Advance) was used to obtain the X-ray diffraction
143 patterns of the films. The samples (conditioned for 1 and 5 weeks at 25 °C and 53% RH)
144 were analyzed between 2 θ : 5° and 2 θ : 30° using K α Cu radiation (λ : 1.542 Å), 40 kV and
145 40 mA with a step size of 0.05°, using a sample holder of quartz. For this analysis, samples
146 were cut into 4 cm squares. Pure PEG film was also analysed, so as to identify its
147 characteristic peaks.

148 Fourier Transform Infrared spectroscopy in Total Attenuated Reflection mode (ATR-FTIR)
149 was used to study the films at initial time. Measurements were carried out using a Tensor
150 27 mid-FTIR Bruker spectrometer (Bruker, Karlsruhe, Germany) equipped with a Platinum
151 ATR optical cell and an RT-D1a TGS detector (Bruker, Karlsruhe, Germany). During
152 analysis, the diaphragm was set at 4 mm whereas the scanning rate was 10 kHz. For the
153 reference (air) and each formulation, 100 scans were considered from 4000 to 800 cm⁻¹,
154 with a resolution of 4 cm⁻¹. The obtained data were treated by using the OPUS software
155 (Bruker, Karlsruhe, Germany): initial absorbance spectra were smoothed using a nine-

156 points Savitskye Golay algorithm, an elastic baseline correction (200 points) was applied
157 and then centred and normalized.

158

159 2.3.2. Thermal properties

160 A Differential Scanning Calorimeter (DSC 1 Star^e System, Mettler-Toledo Inc.,
161 Switzerland) was used to analyse the thermal properties. Films conditioned at initial and
162 final time were analysed. Weighed amounts of samples were placed into aluminium pans
163 and sealed and drilled to promote the bonded moisture loss during heating. The
164 thermograms were obtained by heating from 25 °C to 160 °C at 20 °C/min, afterwards
165 samples were cooled till 25 °C, and heated in a second step to 160 °C at the same rate. In
166 the first scan, the bonded water in the film was eliminated and the PCL fusion parameters
167 were determined. In the second heating scan, the glass transition of starch was analysed.

168

169 2.3.3. Physicochemical properties

170 A Palmer digital micrometer was used to measure film thickness to the nearest 0.0025 mm
171 at six random positions around the film. Every film obtained was measured.

172 A universal test Machine (TA.XTplus model, Stable Micro Systems, Haslemere, England)
173 was used to determine the tensile strength (TS), elastic modulus (EM), and elongation (E)
174 of the films, following ASTM standard method D882 (ASTM, 2001). Films conditioned at
175 25 °C and 53% RH for 1 and 5 weeks were evaluated. EM, TS, and E were determined
176 from the stress-strain curves, estimated from force-distance data obtained for the different
177 films (2.5 cm wide and 5 cm long). Samples were mounted in the film-extension grips of
178 the testing machine and stretched at 50 mm min⁻¹ until breaking. At least ten replicates
179 were obtained from each sample.

180 The Water Vapour Permeability (WVP) of films was determined according to the ASTM
181 E96-95 (ASTM, 1995) gravimetric method, taking into account the modification proposed
182 by McHugh *et al.* (1993). Distilled water was placed in Payne permeability cups (3.5 cm
183 diameter, Elcometer SPRL, Hermelle/s Argenteau, Belgium) to expose the film to 100%
184 RH on one side. Once the films were secured, each cup was placed in a relative humidity
185 equilibrated cabinet at 25 °C, with a fan placed on the top of the cup in order to reduce
186 resistance to water vapour transport, thus avoiding the stagnant layer effect in this exposed
187 side of the film. The RH of the cabinets (53%) was held constant using oversaturated
188 solutions of magnesium nitrate-6-hydrate. The cups were weighed periodically (0.0001 g)
189 and water vapour transmission (WVTR) was calculated from the slope obtained from the
190 regression analysis of weight loss data versus time (once the steady state had been reached),
191 divided by the film area. From WVTR data, the vapour pressure on the film's inner surface
192 (p_2) was obtained using eq. (1), proposed by McHugh *et al.* (1993), to correct the effect of
193 concentration gradients.

194

$$195 \quad WVTR = \frac{P \cdot D \cdot L_n [P - p_2 \setminus P - p_1]}{R \cdot T \cdot \Delta z} \quad (1)$$

196

197 where P, total pressure (atm); D, diffusivity of water through air at 25 °C (m^2/s); R, gas
198 law constant ($82.057 \times 10^{-3} \text{ m}^3 \text{ atm kmol}^{-1} \text{ K}^{-1}$); T, absolute temperature (K); Δz , mean
199 stagnant air gap height (m), considering the initial and final z value; p_1 , water vapour
200 pressure on the solution surface (atm); and p_2 , corrected water vapour pressure on the film's
201 inner surface (atm). Water vapour permeance was calculated using eq. (2) as a function of
202 p_2 and p_3 (pressure on the film's outer surface in the cabinet).

203

$$204 \quad \text{permeance} = \frac{WVTR}{p_2 - p_3} \quad (2)$$

205

206 Permeability was calculated by multiplying the permeance by film thickness.

207 The Oxygen permeability (OP) of the films was determined at 53% RH and 25 °C using an
208 OX-TRAN (Model 2/21 ML Mocon Lippke, Neuwied, Germany) following the ASTM
209 standard D3985-95 method (ASTM, 2002). The samples were conditioned at the relative
210 humidity level of the test in a desiccator using a magnesium nitrate-6-hydrate oversaturated
211 solution for 1 and 5 weeks. Samples were placed in the equipment for analysis, and the
212 transmission values were determined every 20 min until equilibrium was reached. The
213 exposure area during the tests was 50 cm² for each sample. To obtain the oxygen
214 permeability, the film thickness was considered. Analyses were carried out in triplicate for
215 each sample.

216 The film water content (X_w) was determined in conditioned films at 53% RH by drying at
217 60 °C for 24h (J.P. Selecta, S.A. Barcelona, Spain) and afterwards, placing them in a
218 desiccator with P₂O₅ (Panreac Quimica, S.A. Castellar Vallés, Barcelona) to adjust them to
219 0% RH and 25 °C for 2 weeks. Analyses were carried out in triplicate for each sample.

220 Film solubility in water was determined by keeping the samples in bidistilled water at a
221 film: water ratio of 1:10, for 48 h. Afterwards, the film samples were transferred to a
222 convection oven (J.P. Selecta, S.A., Barcelona, Spain) for 24 h at 60 °C to remove the free
223 water and then transferred to a desiccator with P₂O₅ at 25 °C for 2 weeks to complete film
224 drying. Sample solubility was estimated from the film initial and final weights. Analysis
225 was carried out in triplicate for each formulation.

226 The Kubelka-Munk theory for multiple scattering was applied to the reflection spectra to
227 determine the film's transparency (Hutchings, 1999). The surface reflectance spectra were
228 determined from 400 to 700 nm using a spectro-colorimeter CM- 3600d (Minolta Co.,
229 Tokyo, Japan) on both a white and a black background. As the light passes through the
230 film, it is partially absorbed and scattered, which is quantified by the absorption (K) and the
231 scattering (S) coefficients. The internal transmittance (Ti) of the films was determined
232 using eq. (3). In this equation, R₀ is the reflectance of the film on an ideal black
233 background. Parameters *a* and *b* were calculated by means of eqs. (4) and (5), where R is
234 the reflectance of the sample layer backed by a known reflectance, R_g. Three replicates
235 were used for each sample on the free film surface. For this analysis, a wavelength of 650
236 nm was considered.

237

$$238 \quad T_i = \sqrt{(a - R_0)^2 - b^2} \quad (3)$$

239

$$240 \quad a = \frac{1}{2} \left(R + \frac{R_0 - R + R_g}{R_0 R_g} \right) \quad (4)$$

241

$$242 \quad b = \sqrt{a^2 - 1} \quad (5)$$

243

244 The gloss was determined on the free film surface, at an 85° incidence angle by means of a
245 flat surface gloss meter (Multi Gloss 268, Minolta, Germany), following the ASTM
246 standard D523 method (ASTM, 1999). The measurements were carried out in triplicate in
247 each film and three films were considered for each formulation. The results were expressed

248 as gloss units (GU) relative to a highly polished surface of black glass standard with a value
249 near to 100 GU.

250

251 2.3.4. Statistical analysis

252 Statgraphics Plus for Windows 5.1 (Manugistics Corp., Rockville, MD) was used to carry
253 out statistical analyses of data through an analysis of variance (ANOVA). Fisher's least
254 significant difference (LSD) was used at the 95% confidence level.

255

256 **3. RESULTS**

257 **3.1. Structural properties**

258 Film microstructure, determined by the structural arrangement of film components, has a
259 great impact on the physical properties. Figure 1 shows the maps of the DMT modulus of
260 the films' surface obtained from AFM in Peak Force QNM mode. The control formulations
261 (S and PCL) showed more homogenous values of the surface modulus than the blend films,
262 although net starch films had a much harder surface than net PCL films. The starch matrix
263 containing PEG was less homogeneous, exhibiting softer zones (lower values of DMT
264 Modulus), which suggests that PEG was not completely integrated in the glycerol
265 plasticized starch matrix, while PEG reduced the overall rigidity of the material. When the
266 PCL was added to the starch matrix, the heterogeneity of the material greatly increased,
267 showing zones with values of the modulus near to those obtained for starch films and very
268 soft zones corresponding to the PCL domains. In the case of S-PCL5 formulations, PCL
269 (softer zones) showed finer distribution in the starch matrix than in S-PCL10 samples. The
270 polymer phase separation on the film surface was more evident in S-PCL10 formulations,
271 where large, soft PCL domains could be observed. The addition of PEG to the S-PCL

272 blends promoted the heterogeneity of the film surface; a greater differentiation of soft and
273 hard phases could be appreciated, thus suggesting a clearer polymer phase separation at
274 surface level.

275 Figure 2 shows the SEM micrographs of the cross section of the studied films where the
276 greater heterogeneity of the blend films can also be observed. Incorporating PEG into the
277 starch matrix hardly affected the film microstructure, although qualitative differences could
278 be appreciated in the film matrix. The incorporation of the lowest ratio of PCL into the
279 starch matrix led to a good dispersion in the starch continuous matrix, with very fine PCL
280 particles. The increase in the PCL content enhanced the size of the PCL domains,
281 coherently with the greater difficulty of dispersing a greater amount of the immiscible
282 polymer in the starch matrix. These results indicate that the partial miscibility of PCL in the
283 glycerol plasticized starch phase is lower than 10%, actually nearer to 5%.

284 The addition of PEG to blends clearly promoted the phase separation of polymers, since
285 greater PCL separated domains appeared. This occurred at both ratios of PCL, but
286 especially at that of 10%. The lack of adhesion of both polymer phases could also be
287 observed. So, the starch-PCL interactions were modified when PEG was present in the
288 films. This could be due to the fact that PEG has a higher chemical affinity with starch than
289 with PCL because of its predominantly hydrophilic character (HLB: 18.5, Cao & Aita,
290 2013) and the active points of starch able to interact with PCL could be more hindered
291 when PEG was present in the blend.

292 Figure 3 showed the X-ray diffraction patterns obtained for the films conditioned at 25 °C
293 and 53% RH for 1 and 5 weeks. The applied thermo-process disrupted of the typical
294 crystallinity of native starch (type A or B) (Blanshard, 1987; Wu & Sarko, 1978) and
295 provoked the formation of new structures attributed to the complex formation between the

296 helical conformation of amylose and endogenous starch lipids (Guilbort & Mercier, 1985).
297 These typical forms of amylose V-type crystals were observed in all films, with peaks at
298 2θ : 13.5 and 20° in the diffraction spectra, as previously reported by Lesmes, Cohen,
299 Shener, & Shimoni, 2009 and Ortega-Toro, Jiménez, Talens, & Chiralt, 2014.

300 The net PCL diffractograms (Figure 3) showed thinner and more intense peaks than starch
301 at 2θ : 21-22 and 24° , in agreement with the bigger crystalline zones of PCL, with lower
302 contribution of the amorphous region to the diffraction pattern. The addition of PEG to the
303 starch films slightly modified the diffraction patterns of the starch films, enhancing the
304 crystalline response (sharper peaks), especially after 5 storage weeks. This could be due to
305 the promotion of starch crystallization or PEG crystallization, whose peaks overlap with
306 those of starch. Characteristic diffraction spectra of PEG can be observed in Figure 3,
307 showing the main peaks at 2θ : 18 and 22.6° . At final time, marked shoulders appeared at 18
308 and 22.6° in starch films containing PEG, while the characteristic peak at 20° splits, thus
309 indicating changes in the starch crystallization and possible PEG crystallization, despite its
310 low ratio in the blend.

311 The characteristic peaks of PCL, at 2θ 22° and 24° , appeared in the PCL-starch blends, both
312 with and without PEG, while the amorphous response in the film diffractograms was much
313 less pronounced when the PCL ratio increased in the film. The addition of PEG also
314 affected the diffraction patterns of blend films in a similar way to the net starch films.

315 Figure 4 shows the FTIR spectra of studied films conditioned at 25°C and 53% RH for 1
316 week, as well as that of pure PEG. The wavenumber of the typical vibration mode of the
317 characteristic groups was indicated for each sample in the figure. The PCL spectrum
318 showed the C=O stretching vibrations of the carbonyl at 1722 cm^{-1} and the C-O-C
319 stretching of the ether group at 1170 cm^{-1} and 1240 cm^{-1} , according to Elzein, Nasser-

320 Eddine, Delaite, Bistac, & Dumas (2004). The PEG spectrum showed the C-O-C-
321 stretching at 847 cm^{-1} and the -C-H stretching of the methylene groups at 2887 cm^{-1} ,
322 according to Jagadish, Raj, Parameswara, & Somashekar, 2012. The -OH stretching of the
323 hydroxyl group in the region of $3000\text{-}3700\text{ cm}^{-1}$ was observed in the starch spectrum (Yu,
324 Prashantha, Soulestin, Lacrampea, & Krawczak, 2013).

325 The IR spectra of blends did not show new peaks, which indicates that no new chemical
326 bonds were formed during the film processing. However, a shift in the wavenumber of
327 some peaks was registered in blends as compared with control formulations (S, PCL and
328 PEG), which could indicate that molecular interactions among the components were
329 established.

330 The FTIR spectra of S and S-PEG samples were very similar, with a small difference in the
331 methylene band. The -C-H stretching of methylene in PEG was observed at 2887 cm^{-1} and
332 in net starch films at 2926 cm^{-1} . Likewise, the IR band at 1149 cm^{-1} assigned to the C-O-C
333 stretching in starch shift to 1145 cm^{-1} in samples containing PEG. So, interactions between
334 starch and PEG chains could be deduced, as reported by other authors (Kim *et al.*, 2009).
335 Nevertheless, the simultaneous use of glycerol and PEG as plasticizers could inhibit the
336 establishment of strong interactions between starch and PEG groups (Yu *et al.*, 2013).

337 The stretching of the PCL carbonyl group shifted to $1726\text{-}1728\text{ cm}^{-1}$ in films containing 5%
338 PCL and to 1724 cm^{-1} when films contained 10%, against 1722 cm^{-1} in pure PCL films.
339 This suggests that carbonyl groups interact more effectively with the starch groups when
340 low proportions of PCL (5%) were blended. With a higher proportion of PCL, the prevalent
341 amount of non-interacting PCL molecules gave rise to a less altered spectral response of the
342 carbonyl groups. When PEG is present in the S-PCL5 blend, the carbonyl group vibration
343 mode was more affected (1728 cm^{-1}), which suggests that carbonyls could more effectively

344 interact with the terminal -OH groups of PEG when higher ratio PEG:PCL were present in
345 the blend.

346 These results indicate that a complex balance of molecular interactions takes place in the
347 ternary blends affecting the final arrangement of the polymer chains in matrix. As a result
348 of the balance a clearer polymer phase separation was observed in the microstructural
349 analyses when PEG was present in the blend.

350

351 **3.2. Thermal properties**

352 Table 1 shows the glass transition (T_g) of starch, the melting temperature (T_m) and the
353 enthalpy (ΔH_m) of PCL in the studied films conditioned at 25 °C and 0% RH for 1 and 5
354 weeks. No significant differences ($p < 0.05$) between the respective T_g values of the
355 different samples were observed for samples stored for 1 and 5 weeks, so only one value
356 was included. The incorporation of 5% PCL in the films promoted a decrease in the T_g of
357 starch of about 18 °C, whereas when 10% PCL was added this was only of 12 °C. For PCL
358 amounts higher than 10%, a constant decrease in the starch T_g of 12 °C was previously
359 observed (Ortega Toro *et al.*, 2015). This suggests that a greater amount of PCL was
360 effectively miscible in the starch phase when a total of 5% is blended.

361 The addition of PEG also promoted a decrease in the T_g of starch ($\Delta T = 22$ °C), in
362 agreement with the contribution of PEG to the polymer plasticization. Incorporating PEG
363 was more effective than PCL because of its lower molecular weight (4,000 D, against
364 80,000 D of PCL). In the PCL-starch blends, PEG promoted an additional decrease in the
365 T_g , but only of 4 °C, which indicates that PEG interactions with the starch phase are
366 modified in the presence of PCL and *vice versa*, as previously observed from the FTIR

367 data. The T_g values of the two blend formulations containing PEG did not exhibit
368 significant differences. This agrees with new balance of molecular interactions when PEG
369 was added to the starch-PCL blends. This new balance reduces the starch chain's capacity
370 to positively interact with PCL molecules leading to lower polymer compatibility, as
371 observed in SEM and AFM images.

372 The melting properties of PCL are also shown in Table 1 for films stored for 1 and 5 weeks.
373 Likewise, a melting endotherm, attributable to PEG, appeared in S-PEG films stored for 5
374 weeks at similar temperature range as PCL. The melting temperature of PEG (4000 D) was
375 reported by Boscá, Bellver, & Ramos (2002) at 61.5 °C, with an enthalpy value of 238 J/g.
376 Taking into account this enthalpy value, 22% of the PEG present in the S-PEG films
377 crystallized after 5 storage weeks. This probably corresponded to the amount of free PEG
378 molecules, separated from the polymer matrix, as deduced from the AFM analysis. This
379 crystallization could also occur in ternary blend films, but the endotherm would overlap
380 with the PCL melting endotherm.

381 After 1 storage week, no PEG melting was observed in starch films and the PCL melting
382 behaviour revealed very small differences among S-PCL and SPCL-PEG samples. Taking
383 into account the melting enthalpy for totally crystallized PCL (136 J/g, Avella *et al.*, 2000),
384 the degree of crystallinity of PCL in the samples was 53%, with no significant differences
385 between the different blend films. Nevertheless, the PCL melting enthalpy increased after 5
386 storage weeks for both pure PCL and blend films, in line with the crystallization progress
387 of this polymer. Pure PCL films reached a crystallinity degree of 60%, similar to that
388 attained in blend films with 10% PCL without PEG. In the other blend films, crystallinity
389 only reached 56%, which indicates that PCL chains were more bonded to starch or PEG
390 molecules, thus limiting their ability to crystallize.

391

392 **3.3. Physicochemical properties**

393 Figure 5 shows the tensile behaviour of the films stored for 1 and 5 weeks and Table 2
394 shows the corresponding values of the film thickness and tensile parameters (EM: Elastic
395 Modulus; TS: Tensile Strength and E: Elongation at break point). A reduction in film
396 thickness was obtained when PEG or PCL was added, in agreement with the increase in the
397 blend flowability during compression moulding; this is due to the plasticizing effect of both
398 components, as deduced from T_g values. The addition of PEG to the starch films led to a
399 decrease in both the elastic modulus and tensile stress at break but increased the films'
400 extensibility, according to the plasticizing effect of PEG. Likewise, PEG also reduced how
401 much the starch films harden during storage while the films maintained their stretchability
402 better. Adding 5% PCL had a similar effect on the tensile behaviour of starch films to PEG,
403 but with a greater increase in the film extensibility. The incorporation of PEG to this blend
404 greatly reduced the films' extensibility coinciding with the above mentioned changes in
405 molecular interactions. PCL at 10% provoked smaller changes in the tensile behaviour of
406 starch films after both 1 and 5 storage weeks. The hardening of the S-PCL10 films during
407 storage was similar to what occurred in net starch films, which agrees with the fact that
408 PCL-starch interactions were less effective in this formulation. The incorporation of PEG to
409 S-PCL10 films led to behaviour which was similar to that of S-PCL5-PEG films, but with
410 slightly lower extensibility.

411 Mechanical behaviour showed that the addition of a low ratio of PCL to thermoplastic
412 starch had a positive effect on its tensile properties, giving rise to more stretchable films
413 with lower degree of hardening during storage, but the simultaneous incorporation of PEG
414 inhibited this effect, although films maintained the stability of the tensile response. This

415 suggests that the progressive chain aggregation of starch chains during storage (Mali,
416 Grossmann, García, Martino, & Zaritzky, 2006) was inhibited with small amounts of PCL
417 and/or PEG, but it progressed with a greater ratio of PCL (S-PCL10 samples).

418 Table 3 shows the water vapour permeability (WVP) and oxygen permeability (OP) of the
419 studied films after 1 and 5 storage weeks. The OP values for S and PCL were beyond the
420 detection limit (D. L.) ($0.1-200 \text{ cc m}^{-2}\text{día}^{-1}$); lower and higher, respectively. The addition of
421 PEG to the starch films promoted their WVP and OP, according to the greater plasticization
422 of the starch matrix, with the corresponding enhancement of all diffusion dependent
423 processes. The addition of 5% PCL did not affect the WVP of the starch films, although
424 WVP was reduced when PCL was incorporated at 10%. On the other hand, OP increased in
425 both blend films with respect to the net starch film. The balance of two effects can explain
426 this behaviour: 1) the plasticizing effect of PCL which enhance mass transport processes
427 and 2) the increase in the tortuosity factor for mass transfer by the presence of different
428 amounts of hydrophobic dispersed phase. The latter limits water transport rate (Fabra,
429 Pérez-Masiá, Talens, & Chiralt, 2011), but favours oxygen transfer due to the higher
430 oxygen solubility in the hydrophobic phase. At 5 % PCL, higher plasticizing effect was
431 observed, whereas a greater amount of dispersed phase was present with 10% PCL. The
432 incorporation of PEG to the binary blends led to a reduction in the WVP and an increase in
433 the OP, but this was only significant in S-PCL5 and S-PCL10 samples, respectively. This
434 can be explained by the promotion of PCL phase separation, commented on above, which
435 gave rise to the notable increase of PCL dispersed domains in the samples. This notably
436 affected the balance of the two above mentioned factors, modifying the barrier properties of
437 the films. In no formulation did any significant changes in the films' barrier properties
438 occur during storage.

439 Table 4 shows the water content (X_w) and film solubility in water of the studied films.
440 After 5 weeks, when equilibrium was reached, the moisture content of films containing
441 PEG and 5% PCL was higher than that of the net starch films, which suggests that starch
442 interactions with these molecules led to an increase in the active points for water sorption.
443 This behaviour has also been observed in corn starch-carboxymethylcellulose
444 /methylcellulose films (Arik Kibar & Ferhunde, 2013). Nevertheless, samples with 10%
445 PCL showed values closer to those of the starch films. Likewise, the water solubility of the
446 films was only significantly reduced when they contained 10% PCL, without PEG.
447 Table 5 showed the optical properties of the films: gloss and internal transmittance, related
448 to the film transparency. No marked changes in gloss or transparency were provoked by the
449 addition of PEG or PCL to starch films. The least glossy and transparent sample was S-
450 PCL10, due to the greater amount of dispersed PCL domains with the subsequent increase
451 in discontinuities in the refractive index through the film and irregularities at surface level.
452 Throughout storage, a gloss reduction occurred in every formulation, whereas transparency
453 slightly increased in almost all cases.

454

455 **4. CONCLUSIONS**

456 Glycerol plasticized starch films could incorporate 5% PCL without a notable phase
457 separation, leading to the improved stretchability and storage stability of the films. Blend
458 films with 10% PCL exhibited clear phase separation and poor starch-PCL interactions
459 which did not improve the starch tensile properties, although the film water vapour
460 permeability was reduced. In ternary systems with PEG, the total balance of molecular
461 interactions reduced the PCL-starch affinity, enhancing phase separation. Ternary blends

462 did not exhibit improved film properties with respect to starch films. PEG partly separates
463 from the glycerol plasticized starch matrix, crystallising after long storage times.

464

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471

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