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Additional Information

1           **Influence of plasticizers on thermal properties and**  
2 **crystallization behaviour of poly(lactic acid) films obtained**  
3 **by compression molding**

4  
5           **Justine Muller, Alberto Jiménez, Chelo González-Martínez, Amparo Chiralt**

6  
7           **Key words:** Poly(lactic acid), plasticizer, compression molded films, crystallization,  
8 glass transition temperature, stretchability.

9  
10           **Abstract**

11 Neat and plasticized poly(lactic acid) (PLA) films were obtained by compression molding.  
12 Three different plasticizers, at concentrations of 5% and 10%, were used: poly(ethylene  
13 glycol) (PEG) 1000 and 4000 g/mol molecular weights and a commercial plasticizer,  
14 Palamoll®638. Crystallization behaviour and glass transition of PLA in the films were  
15 analysed using differential scanning calorimetry (DSC) and X-Ray diffraction. Films were  
16 also characterised in terms of structural, tensile, barrier and optical properties. The addition of  
17 the three plasticizers reduced the glass transition temperature ( $T_g$ ) while promoting the  
18 crystallization of PLA in the compression molded films, depending on their type and  
19 concentration. PEG 4000 enhanced crystallization more than PEG 1000 and Palamoll®638,  
20 the latter being the one which induced the lowest degree of crystallization. The  $T_g$  values of  
21 the PLA amorphous phase was reduced by the addition of plasticizers, proportionally to their  
22 concentration. Nevertheless, all of the plasticized films exhibited similar elastic modulus and  
23 were less resistant to break and less extensible due to the greater induced crystallinity. PEG

24 4000 drastically reduced the film's stretchability whereas this effect was less marked when  
25 Palamoll®638 was used.

26

## 27 **1. Introduction**

28 PLA is a linear aliphatic thermoplastic polyester derived from lactic acid and obtained from  
29 100% renewable plant sources, such as corn starch or sugar. Best known for its  
30 biodegradability, PLA is a good alternative to replace petroleum-based polymers, such as  
31 polystyrene or polyethylene. Since the field of packaging is one of the major consumers of  
32 plastics, it is becoming more and more necessary to use biodegradable polymers to limit  
33 pollution associated with plastic wastes. PLA is biocompatible and has been approved by the  
34 Food and Drug Administration (FDA) for direct contact with biological fluids<sup>1</sup>. It can be  
35 processed either by extrusion, injection molding, film casting or fibre spinning<sup>2-5</sup>. It also has  
36 good transparency, higher than that of polyethylene terephthalate (PET) or polystyrene (PS),  
37 and a high comparable mechanical strength. However, it is very brittle, with an elongation at  
38 break (%  $\epsilon$ ) of less than 10%<sup>6,7</sup>, which restricts its application as films for the packaging  
39 industry. Plasticizers are widely used to improve the processability, flexibility and ductility of  
40 polymers. In the case of amorphous or semi-crystalline polymers, such as PLA, an efficient  
41 plasticizer not only has to reduce the glass transition temperature, but also to depress the  
42 melting point and the crystallinity. Considerable efforts have been made to improve the  
43 mechanical flexibility of PLA by blending it with compatible plasticizers or other soft  
44 polymers.

45 The use of various low molecular weight plasticizers, such as citrates or adipates<sup>8</sup>, leads to the  
46 migration of plasticizers within the PLA matrix, due to their high molecular mobility. To  
47 avoid this migration problem, many high molecular weight plasticizers including  
48 poly(ethylene glycol) (PEG), poly(propylene glycol), polyester diol or poly(diethylene

49 adipate) have been used<sup>2,9</sup>. The plasticizing properties of PEG, with different molecular  
50 weights, in PLA matrices have been extensively studied. A large amount of these compounds  
51 is usually needed in order to be effective at promoting film plasticity, which can overcome the  
52 miscibility limit<sup>10</sup>, leading to phase separation, and negatively affecting the properties of the  
53 material. The aging of plasticized PLA also provoked the migration and phase separation of  
54 PEG<sup>11</sup>. Hu et al.<sup>12</sup> observed crystallization of PEG 8000 when it was added as plasticizer in  
55 PLA at 30 % wt. in PLA matrices. This compound accelerated the PLA crystallization,  
56 depending on the cooling rate, and PEG crystallinity was proportional to PLA crystallinity.  
57 Sungsanit et al.<sup>13</sup> also reported phase separation and crystallization of PEG 1000 above 15 %  
58 in the PLA blends. The impact resistance and crystallinity of PLA films rose in line with the  
59 increase in plasticizer content, whereas both a drop in glass transition temperature and less  
60 stiff films were observed. Similar results were obtained by Chieng et al.<sup>14</sup> using PEG 200 at  
61 different ratios in the PLA blends. The plasticization of the PLA with PEG 200 effectively  
62 lowers  $T_g$  as well as the cold-crystallization temperature, in line with the increase in the  
63 plasticizer content. Baiardo et al.<sup>15</sup> reported a very good correlation between mechanical  
64 properties of plasticized PLA and the  $T_g$  of the blend using PEGs with different molecular  
65 weights. The lower the  $T_g$  depression by the plasticizer, the more extensible the PLA material,  
66 although some deviations from the established tendencies were observed, which could be  
67 explained by the contribution of the degree of crystallinity of the samples. In this sense, it is  
68 remarkable that, whereas the thermal history of the samples was erased to obtain thermal  
69 parameters, tensile properties were analyzed in the samples with their own thermal history of  
70 unknown crystallinity. The contribution of the crystalline fraction to the mechanical  
71 properties of PLA has not been reported.

72 Other compounds, such as hazelnut and cocoa extract, can also act as plasticizers for PLA<sup>16</sup>,  
73 as well as keratins and brown alpaca fibres<sup>17</sup>. Likewise, PLA was toughened by blending

74 with a PEG-based polyester, poly (polyethylene glycol-co-citric acid)<sup>18</sup>, which greatly  
75 improved elongation at break and the impact resistance as compared with the same amount of  
76 the corresponding PEG.

77 The presence of compatible plasticizers enhances the free volume of the chains which induces  
78 molecular mobility. This reduces the glass transition temperature but it can also favour the  
79 crystallization process in semi-crystalline polymers. These two phenomena have opposing  
80 effects on the ductility of the polymer and can be dependent on the molecular structure of  
81 plasticizer, and the associated intrinsic viscosity, and the molecular interactions with the  
82 polymer chains. Likewise, the processing conditions, with different heating and cooling rates,  
83 determine the crystallinity degree of the polymer, which in turn affects the mechanical  
84 performance of the material.

85 In this study, two extensively studied plasticizers (PEG 1000, PEG 4000) and one new one  
86 (Palamoll<sup>®</sup>638), in two different ratios (5 and 10 %), were melt blended with PLA to obtain  
87 films by compression molding and their effect on the crystallization and thermal behaviour of  
88 the PLA during film processing was analysed, as well as their impact on the tensile and  
89 barrier properties of the obtained films. The relatively low amount of plasticizers was  
90 considered in order to avoid phase separation of these compounds in the films, as described in  
91 previous studies. The overall migration values of both un-plasticized and plasticized films in  
92 aqueous food simulants were also analysed for the purposes of determining the influence of  
93 plasticizers on the potential film compound release into food systems.

94

## 95 **2. Materials and methods**

96

### 97 **2. 1. Materials**

98 PLA resin (LL700, density of 1.25 g/cm<sup>3</sup>) was purchased from Ercros (Spain). Poly(ethylene  
99 glycol) 1000 and 4000 g/mol molecular weights (PEG 1000 and PEG 4000) were obtained  
100 from Sigma–Aldrich (Germany). Palamoll<sup>®</sup>638 was purchased from BASF (Germany). This  
101 commercial polymeric plasticizer is derived from adipic acid, 1,2 propane diol and 1 octanol,  
102 with a high viscosity of 7000-9500 mPa.s (at 20°C), listed for food contact applications and it  
103 is practically insoluble in water and oils.

104

## 105 **2. 2. *Film preparation***

106 PLA was first dried at 60°C for 24 h to remove residual water. PLA and plasticizers (10%  
107 w/w) were then hot-mixed in a two-roll mill (ModelLRM-M-100, Labtech Engineering,  
108 Thailand) at 200°C and 10 rpm for 20 min to ensure a good homogenization of plasticizers  
109 with the polymer. Nevertheless, this relatively long time could provoke chain scission in the  
110 polymer. The resulting paste was then compression molded in a hydraulic press (Model LP20,  
111 Labtech Engineering, Thailand). 3 g of sample were placed onto steel sheets and pre-heated at  
112 200°C for 4 min. Then, compression was performed at 200°C and 100 bars for 4 min,  
113 followed by a cooling cycle of 3 min until the temperature reached about 70°C. The obtained  
114 films were maintained in desiccators with silica-gel at room temperature until analyses were  
115 carried out.

116

## 117 **2. 3. *Film characterization***

118

### 119 **2. 3. 1. *Film thickness***

120 A hand-held digital micrometer (Electronic Digital Micrometer, Comecta S.A., Barcelona,  
121 Spain) was used to measure film thickness to the closest 0.001mm, at 6 random positions  
122 around the film prior to mechanical test analyses.

123

### 124 *2. 3. 2. Thermal properties*

125 Differential scanning calorimetry analyses were carried out using a DSC (1 StareSystem,  
126 Mettler-Toledo, Inc., Switzerland). Small amounts (5–10 mg approx.) of samples were placed  
127 into aluminium pans (Seiko Instruments, P/N SSC000C008) and sealed. Samples were heated  
128 from room temperature to 200°C at 10K/min in order to analyse phase transitions in the PLA  
129 film. Samples were kept a 200°C for 5min, cooled to -10°C at -50K/min, kept at -10°C for  
130 5min and heated again to 200°C at 10K/min; finally they were cooled to 25°C at -100K/min.  
131 An empty aluminium pan was used as reference. The same method was used to analyse  
132 melting properties of PEG 1000 and PEG 4000. Each sample was analysed in duplicate.

133 A thermo-gravimetric analyser (TGA/SDTA 851e, Mettler Toledo, Schwarzenbach,  
134 Switzerland) was used to characterize thermal degradation. The analysis was performed from  
135 room temperature to 600°C at 10°C/min under a nitrogen flow (50 mL/min). Each sample was  
136 analysed in duplicate. The initial degradation temperature ( $T_{\text{onset}}$ ), i.e. the temperature at  
137 which 5% mass loss is registered, was recorded. The temperature at which the maximum  
138 degradation rate was observed ( $T_{\text{max}}$ ) was also determined. Each sample was analysed in  
139 duplicate.

140

### 141 *2. 3. 3. Microstructure*

142 The microstructural analysis of the cross-sections of the films was carried out by means of a  
143 scanning electron microscope (JEOL JSM-5410, Japan). Film pieces, 0.5 x 0.5 cm<sup>2</sup> in size,  
144 were cryofractured from films and fixed on copper stubs, gold coated, and observed using an  
145 accelerating voltage of 10 kV. Observations were taken in duplicate for each formulation.

146

### 147 *2. 3. 4. X-ray diffraction*

148 A diffractometer (XRD, Bruker AXS/D8 Advance) was used to record the X-ray diffraction  
149 patterns. All the samples were analysed at room temperature, between  $2\theta = 5^\circ$  and  $2\theta = 30^\circ$   
150 using  $K\alpha$  Cu radiation ( $\lambda$ : 1.542 Å), 40 kV and 40 mA with a step size of  $0.05^\circ$ . For this  
151 analysis, samples were cut into 4 x 4 cm<sup>2</sup>. Each sample was analysed in duplicate.

152

### 153 2.3.5. Tensile properties

154 A texture analyser (TA-XT plus, Stable Micro Systems, Surrey, United Kingdom) was used to  
155 measure the mechanical properties of films. Strips of films (25 mm wide and 100 mm long)  
156 were mounted in the tensile grips (A/TG model) and stretched at a rate of 50 mm/min until  
157 breaking. The elastic modulus (EM), tensile strength at break (TS) and percentage of  
158 elongation at break (%  $\epsilon$ ) were determined from stress-strain curves, obtained from force-  
159 deformation data. The experiments were carried out at 25°C and eight replicates were made  
160 for each film.

161

### 162 2. 3. 6. Water Vapour Permeability (WVP) and Oxygen Permeability (OP)

163 The WVP of films was measured using a modification of the ASTM E96-95 gravimetric  
164 method<sup>19</sup>, using Payne permeability cups (Elcometer SPRL, Hermelle/s Argenteau, Belgium)  
165 of 3.5 cm diameter. For each formulation, the measurements were replicated four times and  
166 the WVP was calculated following the methodology described by Gennadios et al.<sup>20</sup>, at 25°C  
167 and a 53-100% relative humidity (RH) gradient, which was generated using an oversaturated  
168  $Mg(NO_3)_2$  solution and pure distilled water. To determine the WVP, the cups were weighed  
169 periodically for 4 days after the steady state was reached using an analytical balance  
170 ( $\pm 0.00001$  g). The slope obtained from the weight loss vs. time was used to calculate WVP,  
171 according to ASTM (1995).



172 The OP of the films was determined by using the ASTM F1927 method<sup>21</sup>, using OXTRAN  
173 SL 2/21 MOCON equipment (U.S.A.). Measurements were carried in duplicate at 23°C and  
174 50% RH. Film thickness was considered in all samples to obtain the oxygen permeability  
175 values.

176

### 177 *2. 3. 7. Optical properties*

178 The optical properties of the films were determined in film samples by means of a  
179 spectrophotometer (CM-3600d, MinoltaCo., Tokyo, Japan) with a 10 mm diameter window.

180 The internal transmittance ( $T_i$ ) of the films was determined, as an indicator of the  
181 transparency of the films, by applying the Kubelka-Munk theory<sup>22</sup> for multiple scattering to  
182 the reflection spectra, following the methodology described by Pastor et al.<sup>23</sup>.

183

### 184 *2. 3. 8. Ultraviolet–visible spectrophotometry (UV–VIS)*

185 UV–VIS absorption spectra of the samples ( $4.5 \times 1.2 \text{ cm}^2$ ) were recorded in the wavelength  
186 range of 250–700 nm using a Thermo Scientific (Evolution 201) UV–VIS spectrophotometer.

187

### 188 *2.3.9. Overall migration (OM) in aqueous food simulants*

189 Overall migration tests were carried out for plasticized and unplasticized films, following the  
190 current legislation<sup>24</sup>. Film samples with a total area of  $15 \text{ cm}^2$  were immersed in 25 mL of  
191 different simulants: simulant A (ethanol 10% in water, simulating foods which are hydrophilic  
192 in nature) and simulant B (acetic acid 3% in water, simulating hydrophilic foods with pH  
193 below 4.5). All the samples were kept in contact with the simulants for 10 days at 20°C, to  
194 simulate any food contact under frozen or refrigerated conditions. After incubation, the film  
195 samples were removed from the simulants, which were evaporated to dryness. The migration

196 value in each case was taken as the residue weight. The results were expressed as mg per dm<sup>2</sup>  
197 of film. All the tests were run in duplicate.

198

### 199 *2. 3. 10. Statistical analysis*

200 StaTgraphics Plus for Windows 5.1 (Manugistics Corp., Rockville, MD, U.S.A.) was used to  
201 carry out statistical analyses of data through an analysis of variance (ANOVA). Fisher's least  
202 significant difference (LSD) was used at the 95% level.

203

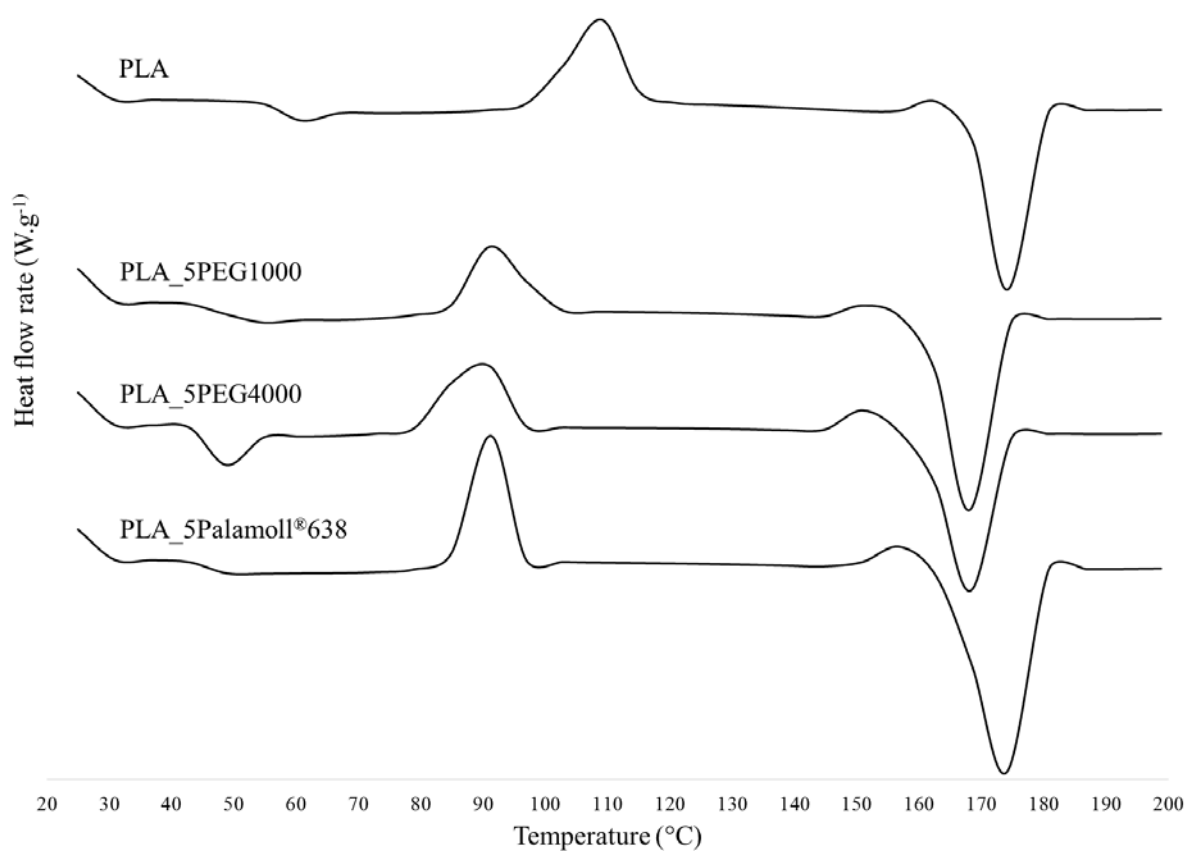
## 204 **3. Results and discussion**

205

### 206 *3. 1. Characterization of amorphous and crystalline phases of the films.*

207 The degree of crystallization of compression molded films with and without plasticizers was  
208 analysed from the first heating scan of DSC, taking the X-Ray diffraction pattern of the films  
209 into account. Figure 1 shows the thermograms obtained for both neat PLA films and those  
210 containing 5% of plasticizers. Glass transition was observed in all cases, followed by a  
211 crystallization exotherm and the subsequent melting endotherm of the polymer. An excess  
212 enthalpy of relaxation ( $\Delta H_{ex}$ ) was observed as an endotherm at the glass transition. As  
213 observed by other authors for PLA<sup>3</sup>, this has been associated with the physical aging of the  
214 material, since  $\Delta H_{ex}$  increases as the material ages. Likewise, a small exotherm prior to the  
215 melting endotherm was observed in all the samples, which is characteristic of a solid-solid  
216 transition<sup>25</sup>. This corresponds to the disorder-to-order ( $\alpha'$ -to- $\alpha$ ) phase transition, in which the  
217 chain packing of the crystal lattice becomes more ordered. This thermal behaviour of the films  
218 indicates that a large part of the polymer is in an amorphous state after compression molding  
219 under the conditions applied (fast cooling rate after thermocompression). Then, after glass  
220 transition, crystallization occurs when the temperature rises to nearly 100°C. Afterwards, the

221 polymer melts at about 175°C, but prior to that, the  $\alpha'$  crystal fraction crystallizes into the  $\alpha$   
222 form (small exotherm before melting).



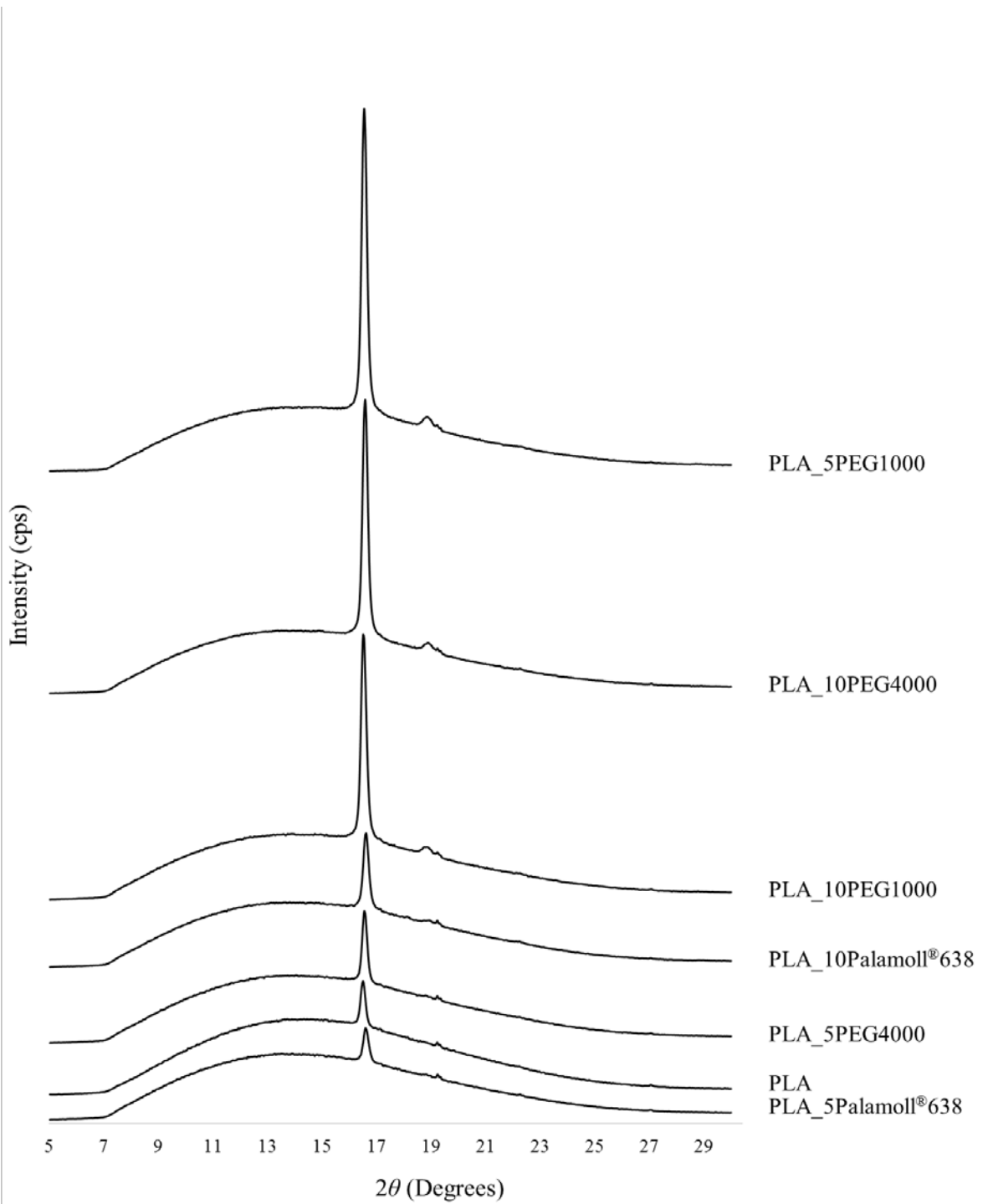
223  
224 **Figure 1. DSC thermograms of neat PLA and PLA with 5% of plasticizers at the first**  
225 **heating.**

226  
227 As shown in Table 1, the onset glass transition temperature ( $T_{g0}$ ) of PLA significantly  
228 decreased after the addition of plasticizers, regardless of their type; the higher the  
229 concentration of plasticizer, the greater the decrease in  $T_{g0}$ . This indicates that the compounds  
230 used effectively plasticize the amorphous phase of the polymer, depending on their  
231 concentration, reducing the interchain forces of the polymer and increasing its free volume,  
232 thus enhancing the rubbery character. No notable differences in the plasticizing effect of the  
233 different compounds used were observed despite their different molecular weight, since a  
234 similar  $T_g$  decrease was obtained at a determined concentration of each compound. It is

235 remarkable that, in no case did PEG crystallization occur in the films, as deduced from the  
236 DSC curves where no melting of PEG was observed. Melting properties of pure PEG 1000  
237 and PEG 4000, determined by DSC, gave melting temperature values of 38°C and 56°C  
238 (within the range of the film analyses) with melting enthalpies of 181 and 210 J/g,  
239 respectively. Therefore, a good miscibility of the plasticizers and polymer, at the used ratios,  
240 was observed in all cases, exhibiting no phase separation.

241 Table 1 also gives the crystallization temperature ( $T_c$ ), crystallization enthalpy ( $\Delta H_c$ ), melting  
242 temperature ( $T_m$ ) and melting enthalpy ( $\Delta H_m$ ), determined from the respective exothermic and  
243 endothermic peaks of the registered first heating scan. Taking into account the temperature at  
244 which crystallization occurs in the heating step,  $\alpha$  and  $\alpha'$  crystals could be formed, according  
245 to previous studies about the influence of the temperature on PLA crystallization<sup>26</sup>. Yasuniwa  
246 et al.<sup>27</sup> carried out the isothermal crystallization of PLA at various crystallization temperatures  
247 and elucidated that the crystallization behaviour discretely changes at crystallization  
248 temperatures below and above 113 and 135°C, respectively and a double melting behaviour  
249 was observed when crystallization occurred between 113 and 135°C. The observed  $\alpha'$ -to- $\alpha$   
250 transition could be partly attributed to the crystalline forms present in the thermocompressed  
251 films, in line with the fast cooling applied. In fact, the X-ray diffraction patterns of all the  
252 samples (Figure 2) presented the main peak at  $2\theta = 16.5$ , which is characteristic of the  $\alpha'$   
253 crystals of the PLA, slightly displaced at low angle with respect to the  $\alpha$  form ( $2\theta = 16.8$ )<sup>28</sup>.

254 A broad amorphous band can also be observed in every sample, in line with the presence of  
255 amorphous polymer regions in the films.



256

257 **Figure 2. X-Ray diffraction patterns of neat and plasticized PLA films.**

258

259 The degree of crystallinity of PLA ( $X_c$  film (%)) was estimated from the difference between  
 260 the melting and crystallization enthalpies, by assuming that  $\alpha$  crystals were formed, and  
 261 considering the melting enthalpy of the fully  $\alpha$  crystalline PLA phase ( $\Delta H_m^0(\alpha) = 96 \text{ J}\cdot\text{g}^{-1}$ ),

262 reported by Kalish et al.<sup>29</sup>. From this estimation (Table 1), a very low crystallinity degree  
263 (5%) was obtained in the PLA compression molded films, which notably increased when  
264 plasticizers were incorporated. In general, the greater the amount of plasticizer, the higher the  
265 degree of crystallinity obtained in the film. Likewise, it is remarkable that PEG 4000 was  
266 significantly more effective than PEG 1000 and Palamoll®638 to promote PLA  
267 crystallization. The values obtained are coherent with the X-Ray diffraction patterns, which  
268 exhibited different relative intensities for the peak at  $2\theta = 16.5$ .

269 As concerns the melting temperature, films containing Palamoll®638 show a peak value that  
270 is very similar to that of the neat PLA film (175°C) whereas significantly lower values were  
271 obtained for films with PEG 1000 and PEG 4000, which indicates that the latter plasticizers  
272 also interact with the PLA lattice, reducing the melting point of about 5°C.

273 The previous thermal history of the films was erased in the second heating scan in the DSC  
274 analysis, but the thermal behaviour was similar to that obtained in the first scan, with the same  
275 events appearing on the thermograms, except for the relaxation endotherm at  $T_g$  which does  
276 not appear because of the newly crystallized polymer. The fast cooling rate applied during the  
277 cooling scan (50°C/min) in DSC allowed for reproducing thermal behaviour of the thermo-  
278 compressed films with their thermal history. The obtained values of  $T_g$ ,  $T_c$  and  $T_m$  were  
279 similar to those obtained in the first heating scan, as well as the crystallization and melting  
280 enthalpy values (Table 2). The crystallization degree which occurred in the fast cooling scan  
281 was also estimated by the difference between exo and endo transitions and very small  
282 crystallization was determined for the neat PLA films. Nevertheless, crystallinity increased to  
283 a greater extent in this step when films contained plasticizers, in line with the promotion of  
284 molecular mobility. The higher the plasticizer concentration, the higher the crystallization  
285 rate. As observed in the first heating scan, PEG 4000 greatly enhanced PLA crystallization  
286 despite the scarce differences induced in the  $T_g$  compared to the other used plasticizers. The

287 fact that plasticizers promote the crystalline form of thermocompressed PLA can be explained  
288 by the  $T_g$  reduction, which allows for enhanced molecular mobility at lower temperatures  
289 during the cooling step of the film, favouring the polymer chain rearrangement in crystalline  
290 forms. In fact, the crystallization temperature for all the plasticized films (Tables 1-2) was  
291 lower than for the neat PLA film and the reduction was in line with the  $T_g$  decrease, since  
292 crystallization occurred at 45-50 °C above  $T_g$  in every case.

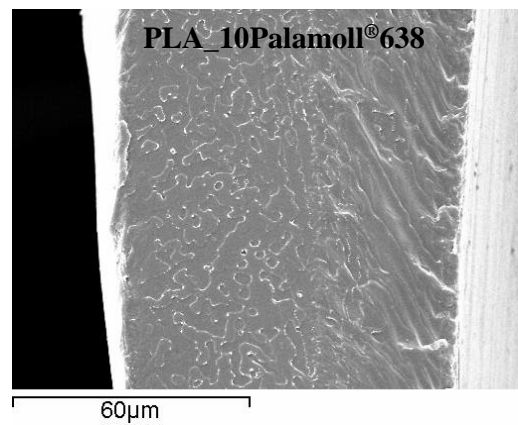
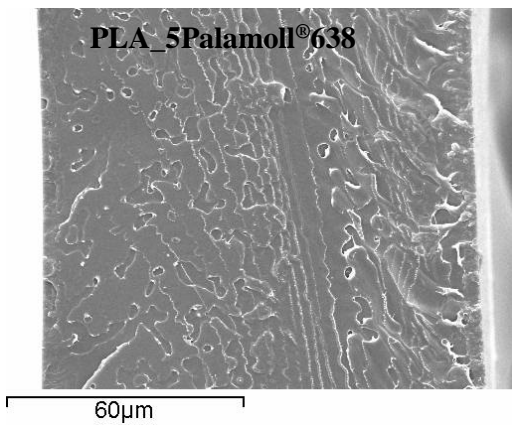
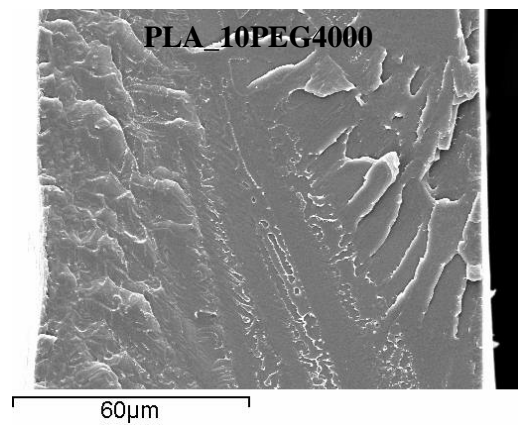
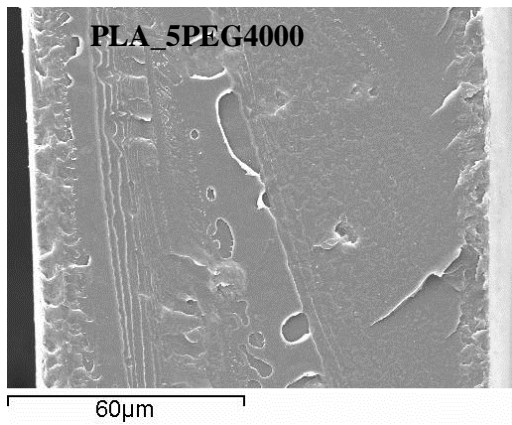
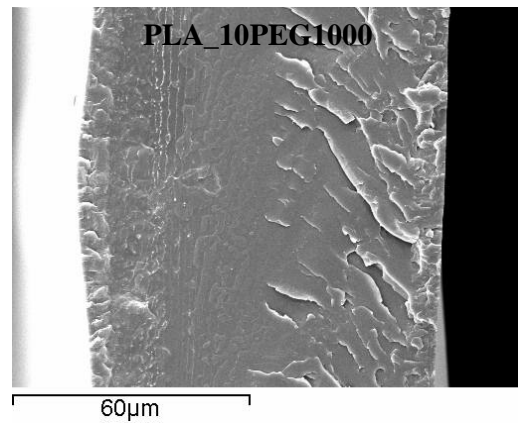
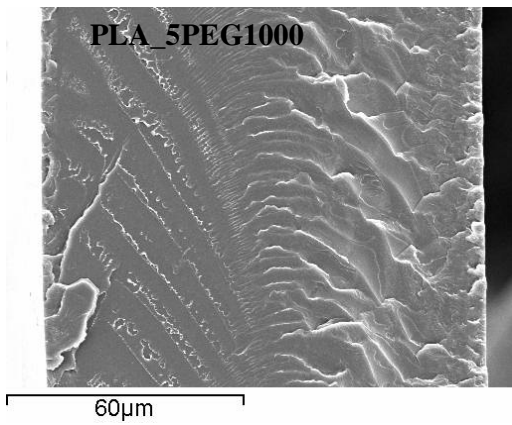
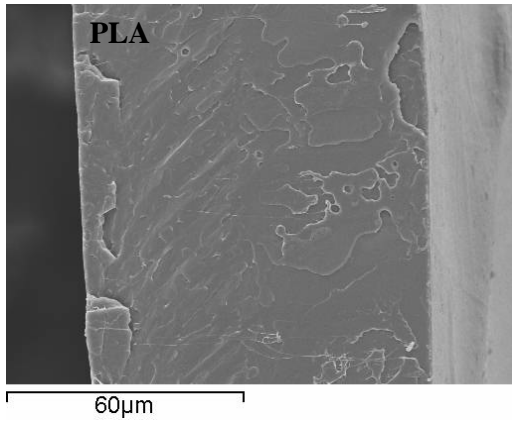
293 These results, valuable for lab scale production of films, could be far from those obtained at  
294 industrial level, mainly due to very different times of processing. In industry, the times of  
295 processing are considerably shorter and this will have an effect on film crystallinity.  
296 Nevertheless, a faster cooling of the polymer melt will lead to more amorphous material,  
297 since it is only above  $T_g$  that crystallization occurs extensively. The incorporation of  
298 plasticizers reduces the  $T_g$  and so, extends the time range for polymer crystallization during  
299 the cooling step, which suggests that a fast-cooling, quenching process must be implemented  
300 to optimize the plasticizer role.

301 Film microstructure (Figure 3) revealed a rather brittle fracture in both plasticized and  
302 unplasticized PLA films, exhibiting no plastic deformation, as correspond to the sample  
303 fracture conditions, below the  $T_g$  values. No phase separation of plasticizers was observed in  
304 any case, which confirms the good integration of the compounds into the polymer matrix.  
305 Nevertheless, some qualitative differences, reflected in a higher frequency of stripes and  
306 white dots, can be observed in the fractured surface of samples with the different plasticizers,  
307 which could be attributed to certain local plasticization effect, affecting the fracture  
308 behaviour.

309 The thermal stability of the PLA-based films is also coherent with the observed effect of  
310 plasticizers. The incorporation of plasticizers should reduce the thermal degradation  
311 temperature depending on how much they weaken the polymer network<sup>10</sup>, but the increase in

312 the degree of crystallization should promote the opposite effect due to the higher energy of the  
313 matrix. Table 3 shows the obtained degradation temperatures (onset:  $T_{\text{onset}}$  and at the  
314 maximum rate:  $T_{\text{max}}$ ) for the different films, where very small differences can be observed for  
315 the different samples. These range from 317°C to 324°C (onset) and from 337°C to 339°C  
316 (max) for all the samples. The opposite effect produced by the plasticizing of the amorphous  
317 region and the increase in crystallization only led to scarce changes in the thermo-stability of  
318 the films.





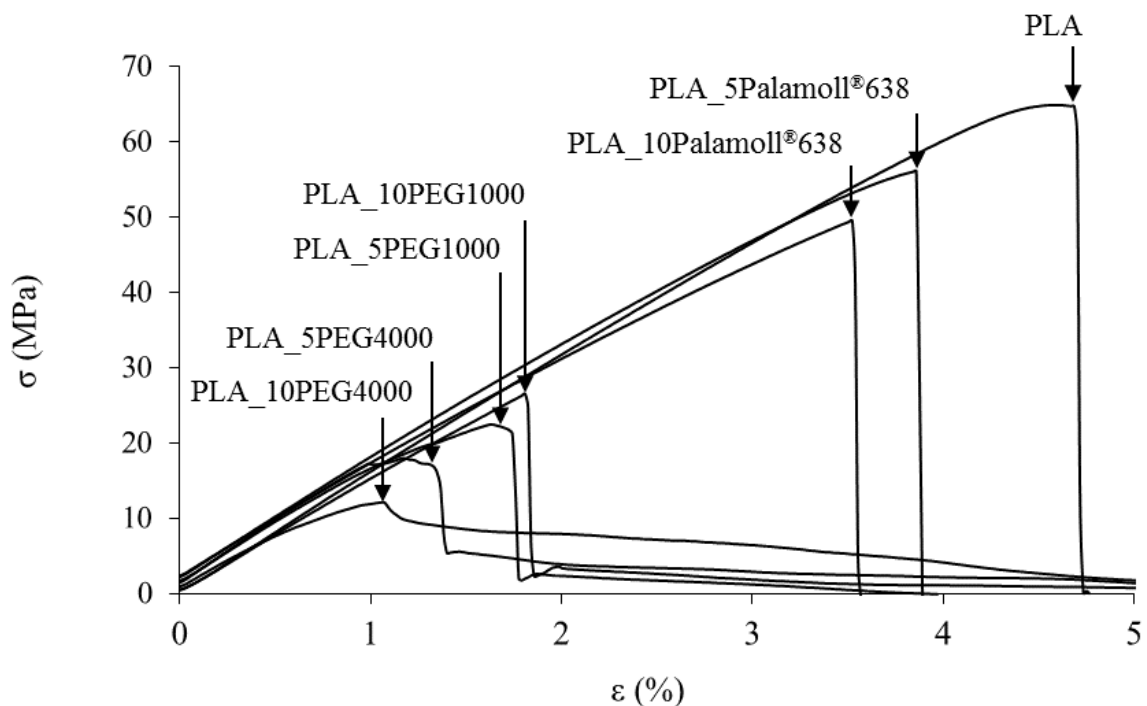
319

320 **Figure 3. SEM images of the cross-sections of neat and plasticized PLA films.**

321

322 *3. 2. Influence of the changes induced by plasticizers on the film's physical properties*

323 The tensile behaviour of the different PLA films can be observed in Figure 4. All of the  
324 plasticizers significantly reduced the film's stretchability, contrary to what was expected from  
325 the plasticization effect. The most marked reduction occurred for PEG 4000, whereas  
326 Palamoll®638 was the least effective.



327

328 **Figure 4. Tensile behaviour of neat and plasticized PLA films.**

329

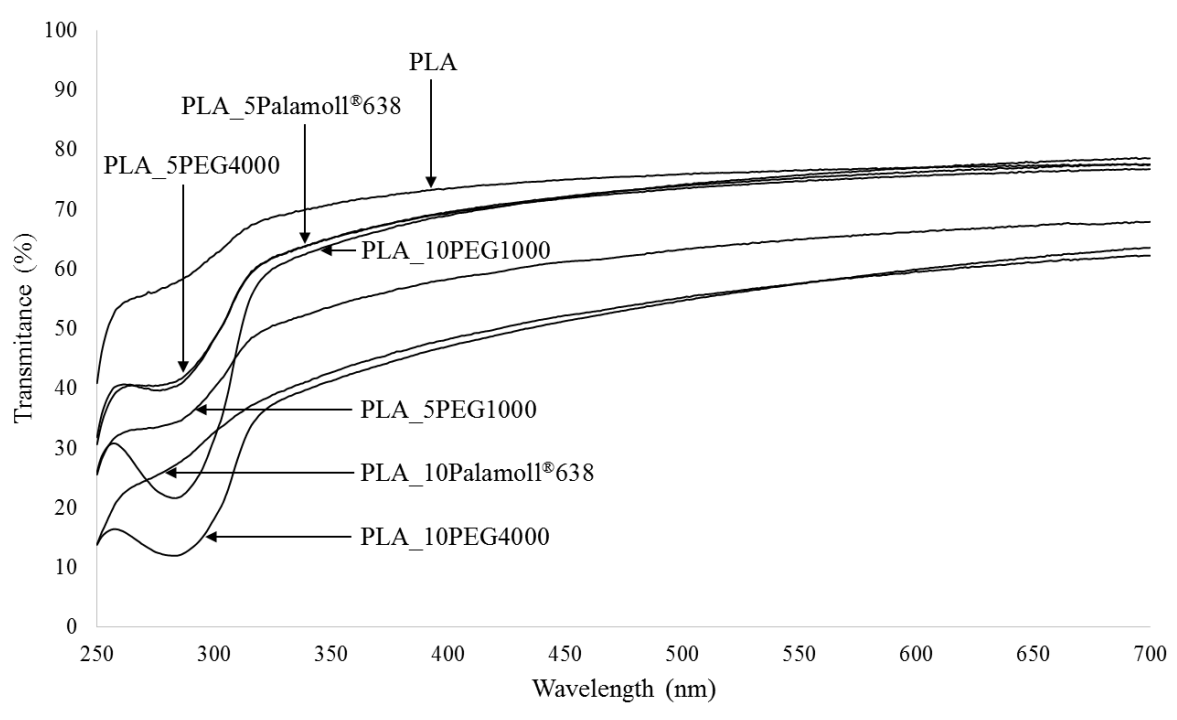
330 Table 4 shows the tensile parameters obtained for the different films, where similar values to  
331 those obtained by Wang et al.<sup>30</sup> can be observed for un-plasticized PLA (about 5%). All the  
332 formulations exhibited values of the elastic modulus in the same range, but tensile and  
333 deformation at break were notably reduced by the addition of plasticizer. Of the plasticized  
334 films, that containing Palamoll®638 showed the greatest resistance to break while that  
335 containing PEG 4000 exhibited the lowest value. The plasticizer concentration hardly affected

336 the tensile behaviour for a given compound, although a tendency to reduce the resistance to  
337 break when the concentration increased could be appreciated. This effect of the incorporated  
338 plasticizers can be explained by the reduction of the interchain attraction forces in the  
339 amorphous matrix, while a higher ratio of crystalline domains appeared when the plasticizer  
340 concentration increased. A different effect of each plasticizer suggests different molecular  
341 interactions between polymer chains and compound molecules.

342 The water vapour permeability of the PLA films slightly increased when plasticizers were  
343 added, which can be explained by the decrease in the glass transition temperature of the  
344 amorphous phase, which facilitates all of the diffusion controlled processes. However, the  
345 reduction in the film barrier capacity will be limited by the increase in the crystalline fraction  
346 in the films. On the contrary, OP decreased in plasticized films with 5% of PEG 1000, but  
347 increased in the other cases, even overcoming the upper sensitivity limit of the used  
348 equipment. This behaviour can be explained by the overall enhancement of the hydrophilic  
349 character of the film amorphous phase when PEG 1000 molecules are present at low  
350 concentration, although plasticization effect predominates at the highest concentration level.  
351 The promotion of hydrophilic character decreases the oxygen solubility in the amorphous  
352 phase, thus limiting their permeation capacity. In the case of PEG 4000 and Palamoll®638,  
353 more non-polar in nature, the OP was enhanced at the two used concentration levels.

354 On the other hand, all the films were highly transparent when exposed to wavelengths  
355 between 400 and 700 nm, as deduced from the high values of the internal transmittance  
356 shown in Table 4, and a very slight decrease in transparency with respect to the control film  
357 was provoked by the addition of plasticizers. Nevertheless, packaged food products are also  
358 submitted to UV irradiation, which may affect both the material and the foodstuff. Different  
359 published works have studied the behaviour of PLA films when exposed to UV-vis  
360 irradiation. Arrieta et al.<sup>31</sup> found that cellulose nanoparticles were able to block the UV-light

361 when added to PLA-PHB films whereas Cele et al.<sup>32</sup> observed that clay nanoparticles reduced  
362 the transparency of films but no further discussion was considered in the UV range. For the  
363 obtained PLA films, a marked reduction in the UV light transmission was observed when they  
364 contained plasticizers as shown in Figure 5.



365

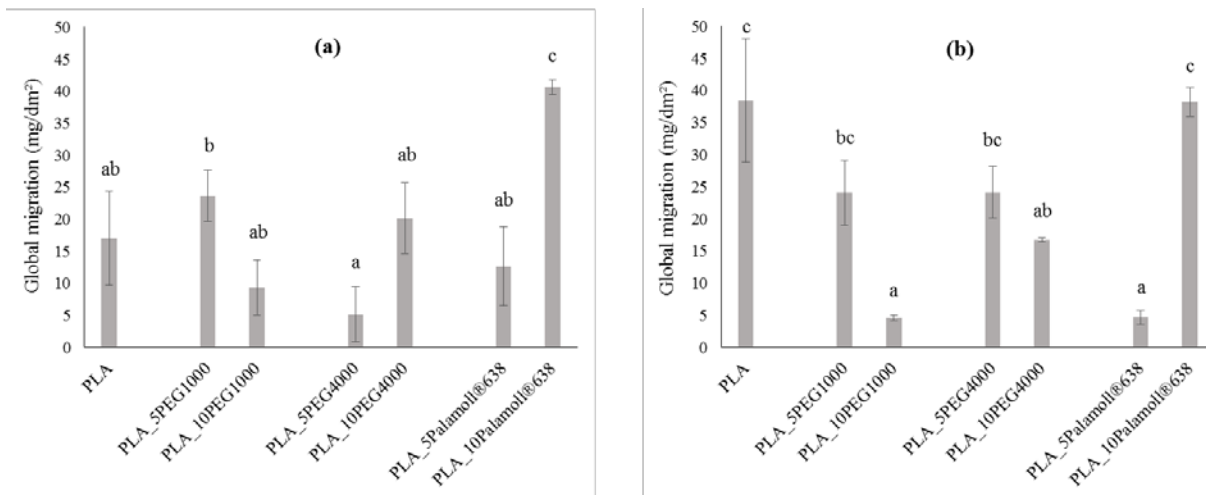
366 **Figure 5. Transmittance of neat and plasticized PLA films in the UV-vis range.**

367

368 The most significant differences in the film transmittance were found in the UV region, where  
369 Palamoll®638 and PEG containing films highly blocked the UV light. The main reduction of  
370 the transmittance started approximately at wavelengths below 340 nm, regardless of the  
371 formulation, in accordance with the observations of Cele et al.<sup>32</sup>. The highest blocking effect  
372 was found when the plasticizer content was 10%, thus indicating that this effect is directly  
373 related to the plasticizer content. Furthermore, both PEG were more effective at reducing the  
374 transmission of UV irradiation than Palamoll®638. The UV blocking effect of PEG also  
375 observed by Guha et al.<sup>33</sup>.

376 As concerns overall migration of the PLA films in aqueous food simulants, the values of the  
377 different samples showed great variability in both A (10% ethanol in water) and B (3%  
378 aqueous acetic acid) simulants. This suggests that different factors such as the sample  
379 crystallinity degree could affect the total migration, since crystalline zones are usually less  
380 soluble than amorphous ones. The relative chemical affinity of plasticizers with the polymer  
381 and solvent determines the migration of these compounds to the simulant. In this sense,  
382 different migration levels are expected depending on the crystallinity degree of the samples,  
383 the type of plasticizer, its amount in the film and the type of simulant.

384 In simulant A, the incorporation of PEG 4000 at 5% significantly decreased the OM levels of  
385 the films, whereas 10% Palamoll®638 greatly promoted it. In simulant B, unplasticized PLA  
386 exhibited higher migration, which can be attributed to the partial hydrolyses of the polyester  
387 and the release of more soluble monomers. However, the incorporation of 5% Palamoll®638  
388 and 10 % PEG (1000 and 4000) reduced the migration of the films. In general, the  
389 incorporation of the studied plasticizers in PLA matrices, obtained by compression molding,  
390 did not enhance the migration of PLA in aqueous food simulants, except when Palamoll®638  
391 was used at 10%, where total migration increased in simulant A. In contrast, in the other  
392 cases, the plasticizers did not significantly affect the migration capacity of the polymer or  
393 decrease it. It is remarkable that only some plasticized PLA films meet the requirements for  
394 total migration (10 mg/dm<sup>2</sup>) established by the EU Commission Regulation 2015/174<sup>24</sup> in  
395 simulants A and B.



396  
 397 **Figure 6. Overall migration values for different films in aqueous food simulants (A: 10%**  
 398 **Ethanol (a) and B: 3% acetic acid (b)). Different letters within the same figure indicate**  
 399 **significant differences among formulations ( $p < 0.05$ ).**

400  
 401 **Conclusion**

402 Although a low degree of crystallinity was obtained (5%) in the PLA films obtained by  
 403 compression molding, crystallization was promoted by the addition of plasticizers (PEG 1000,  
 404 PEG 4000 and Palamoll®638); the greater their ratio, the higher the degree of crystallinity. All  
 405 of the plasticizers reduced the glass transition temperature of the film's amorphous phase to a  
 406 similar extent, proportionally to their concentration. Nevertheless, in no case did this imply an  
 407 improved film ductility, since all of the plasticized films were less resistant to break and less  
 408 extensible. The extent of the reduction in these parameters depended on the plasticizer used,  
 409 Palamoll®638 being the one which promoted the smallest reduction in line with the lower  
 410 degree of crystallization induced by this compound. So, the studied plasticizers, at 5-10 wt%,  
 411 were not effective at reducing the film's brittleness, mainly due to the fact that they enhanced  
 412 the polymer's crystallization at the same time as they reduced the glass transition temperature  
 413 of the amorphous PLA. Further studies with other potential plasticizing substances would be  
 414 required, taking into account the potential antagonistic effect of plasticizers, increasing the

415 molecular mobility of the polymer chains which, at the same time, can promote polymer  
416 crystallization, all of which affects the mechanical performance of materials based on PLA.

417

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535 **Table 1. Thermal data obtained by DSC measurements (first heating scan) for PLA**  
 536 **films with different contents of plasticizers. Mean values  $\pm$ standard deviation.**

	$T_{g1}^1$ (°C)	$T_c^1$ (°C)	$\Delta H_c^1$ (J/g PLA)	$\Delta H_{ex}^1$ (J/g PLA)	$T_m^1$ (°C)	$\Delta H_m^1$ (J/g PLA)	$X_{c1}^1$ (%)	$X_{c2}^1$ (%)	$X_c$ film (%)
PLA	55.6 $\pm$ 0.4 <sup>e</sup>	108.0 $\pm$ 0.1 <sup>d</sup>	47.0 $\pm$ 2.0 <sup>d</sup>	1.4 $\pm$ 0.1 <sup>ab</sup>	175.7 $\pm$ 0.1 <sup>d</sup>	52.3 $\pm$ 0.3 <sup>a</sup>	49.0 $\pm$ 3.0 <sup>d</sup>	54.5 $\pm$ 0.1 <sup>a</sup>	5 $\pm$ 3 <sup>a</sup>
PLA_5PEG1000	48.5 $\pm$ 0.4 <sup>d</sup>	93.7 $\pm$ 0.1 <sup>c</sup>	37.8 $\pm$ 0.2 <sup>c</sup>	3.8 $\pm$ 0.3 <sup>bc</sup>	169.9 $\pm$ 0.4 <sup>b</sup>	60.0 $\pm$ 0.4 <sup>c</sup>	39.4 $\pm$ 0.2 <sup>c</sup>	62.5 $\pm$ 0.6 <sup>c</sup>	23 $\pm$ 1 <sup>b</sup>
PLA_10PEG1000	38.0 $\pm$ 5.0 <sup>a</sup>	87.0 $\pm$ 3.0 <sup>bc</sup>	30.8 $\pm$ 1.1 <sup>bc</sup>	3.0 $\pm$ 2.0 <sup>abc</sup>	170.2 $\pm$ 0.6 <sup>b</sup>	62.8 $\pm$ 0.3 <sup>c</sup>	32.0 $\pm$ 2.0 <sup>bc</sup>	65.4 $\pm$ 0.5 <sup>c</sup>	33 $\pm$ 2 <sup>cd</sup>
PLA_5PEG4000	45.4 $\pm$ 0.2 <sup>bcd</sup>	87.5 $\pm$ 0.4 <sup>bc</sup>	32.0 $\pm$ 3.0 <sup>bc</sup>	4.3 $\pm$ 0.5 <sup>bc</sup>	170.8 $\pm$ 0.0 <sup>b</sup>	60.5 $\pm$ 0.3 <sup>c</sup>	33.0 $\pm$ 4.0 <sup>bc</sup>	63.0 $\pm$ 0.5 <sup>c</sup>	30 $\pm$ 3 <sup>c</sup>
PLA_10PEG4000	38.4 $\pm$ 1.4 <sup>ab</sup>	75.0 $\pm$ 3.0 <sup>a</sup>	17.0 $\pm$ 4.0 <sup>a</sup>	5.0 $\pm$ 1.2 <sup>c</sup>	168.1 $\pm$ 0.3 <sup>a</sup>	61.0 $\pm$ 2.0 <sup>c</sup>	17.0 $\pm$ 6.0 <sup>a</sup>	63.0 $\pm$ 3.0 <sup>c</sup>	46 $\pm$ 2 <sup>c</sup>
PLA_5Palamoll®638	46.2 $\pm$ 1.2 <sup>cd</sup>	91.8 $\pm$ 1.4 <sup>c</sup>	37.0 $\pm$ 2.0 <sup>c</sup>	0.3 $\pm$ 0.1 <sup>a</sup>	174.1 $\pm$ 0.3 <sup>c</sup>	56.7 $\pm$ 0.5 <sup>b</sup>	38.0 $\pm$ 3.0 <sup>c</sup>	59.0 $\pm$ 0.8 <sup>b</sup>	21 $\pm$ 2 <sup>b</sup>
PLA_10Palamoll®638	39.0 $\pm$ 2.0 <sup>abc</sup>	81.0 $\pm$ 4.0 <sup>ab</sup>	26.0 $\pm$ 2.0 <sup>b</sup>	2.4 $\pm$ 1.0 <sup>abc</sup>	173.4 $\pm$ 0.2 <sup>c</sup>	62.9 $\pm$ 0.5 <sup>c</sup>	27.0 $\pm$ 3.0 <sup>b</sup>	65.5 $\pm$ 0.7 <sup>c</sup>	38 $\pm$ 2 <sup>d</sup>

537  
 538  $X_{c1}$ : degree of crystallization estimated from crystallization exotherm =  $\Delta H_c / \Delta H_m^0$

539  $X_{c2}$ : degree of crystallization estimated from the melting endotherm =  $\Delta H_m / \Delta H_m^0$

540  $X_c$  film: deduced from the difference between  $X_{c2}$  and  $X_{c1}$

541 Different superscript letters within the same column indicate significant differences among formulations  
 542 ( $p < 0.05$ ).

543

544 **Table 2. Thermal data obtained by DSC measurements (second heating scan) for PLA**  
 545 **films with different contents of plasticizers. Mean values  $\pm$ standard deviation.**

	$T_{g2}^2$ (°C)	$T_c^2$ (°C)	$\Delta H_c^2$ (J/g PLA)	$\Delta H_{ex}^2$ (J/g PLA)	$T_m^2$ (°C)	$\Delta H_m^2$ (J/g PLA)	$X_{c1}^2$ (%)	$X_{c2}^2$ (%)	$X_c$ cool (%)
PLA	57.1 $\pm$ 0.1 <sup>d</sup>	108.0 $\pm$ 0.2 <sup>d</sup>	46.0 $\pm$ 1.4 <sup>d</sup>	0.38 $\pm$ 0.01 <sup>c</sup>	175.3 $\pm$ 0.1 <sup>d</sup>	53.1 $\pm$ 0.3 <sup>a</sup>	48.0 $\pm$ 2.0 <sup>d</sup>	55.3 $\pm$ 0.4 <sup>a</sup>	7 $\pm$ 2 <sup>a</sup>
PLA_5PEG1000	45.8 $\pm$ 0.2 <sup>bc</sup>	95.3 $\pm$ 0.4 <sup>bc</sup>	39.4 $\pm$ 0.7 <sup>cd</sup>	0.18 $\pm$ 0.02 <sup>b</sup>	169.4 $\pm$ 0.2 <sup>b</sup>	61.4 $\pm$ 0.4 <sup>cd</sup>	41.0 $\pm$ 0.8 <sup>cd</sup>	63.9 $\pm$ 0.6 <sup>c</sup>	23 $\pm$ 1 <sup>b</sup>
PLA_10PEG1000	36.0 $\pm$ 5.0 <sup>ab</sup>	86.0 $\pm$ 3.0 <sup>a</sup>	24.0 $\pm$ 8.0 <sup>b</sup>	n.d.	169.1 $\pm$ 0.8 <sup>b</sup>	64.4 $\pm$ 0.9 <sup>e</sup>	25.0 $\pm$ 8.0 <sup>b</sup>	67.1 $\pm$ 0.9 <sup>d</sup>	42 $\pm$ 9 <sup>d</sup>
PLA_5PEG4000	42.0 $\pm$ 0.9 <sup>abc</sup>	90.7 $\pm$ 0.4 <sup>abc</sup>	34.0 $\pm$ 3.0 <sup>bc</sup>	0.09 $\pm$ 0.02 <sup>a</sup>	170.2 $\pm$ 0.1 <sup>b</sup>	60.1 $\pm$ 0.7 <sup>bc</sup>	36.0 $\pm$ 5.0 <sup>bc</sup>	62.6 $\pm$ 0.7 <sup>bc</sup>	27 $\pm$ 4 <sup>bc</sup>
PLA_10PEG4000	34.0 $\pm$ 5.0 <sup>a</sup>	86.0 $\pm$ 6.0 <sup>ab</sup>	7.0 $\pm$ 3.0 <sup>a</sup>	n.d.	167.5 $\pm$ 0.5 <sup>a</sup>	63.0 $\pm$ 2.0 <sup>cde</sup>	7.0 $\pm$ 4.0 <sup>a</sup>	65.4 $\pm$ 3.0 <sup>cd</sup>	58 $\pm$ 7 <sup>c</sup>
PLA_5Palamoll®638	48.3 $\pm$ 1.1 <sup>cd</sup>	98.7 $\pm$ 0.9 <sup>cd</sup>	41.4 $\pm$ 0.5 <sup>cd</sup>	0.18 $\pm$ 0.01 <sup>b</sup>	173.7 $\pm$ 0.4 <sup>c</sup>	57.9 $\pm$ 0.2 <sup>b</sup>	43.1 $\pm$ 0.7 <sup>cd</sup>	60.3 $\pm$ 0.3 <sup>b</sup>	17 $\pm$ 1 <sup>ab</sup>
PLA_10Palamoll®638	40.0 $\pm$ 4.0 <sup>abc</sup>	87.0 $\pm$ 5.0 <sup>ab</sup>	26.6 $\pm$ 0.7 <sup>b</sup>	n.d.	173.0 $\pm$ 0.2 <sup>c</sup>	63.2 $\pm$ 0.5 <sup>de</sup>	27.7 $\pm$ 0.7 <sup>b</sup>	65.8 $\pm$ 0.7 <sup>cd</sup>	38 $\pm$ 1 <sup>cd</sup>

546  
 547 n.d.: non detected

548  $X_{c1}$ : degree of crystallization estimated from crystallization exotherm =  $\Delta H_c / \Delta H_m^0$

549  $X_{c2}$ : degree of crystallization estimated from the melting endotherm =  $\Delta H_m / \Delta H_m^0$

550  $X_c$  cool: occurred during the cooling step and deduced from the difference between  $X_{c2}$  and  $X_{c1}$

551 Different superscript letters within the same column indicate significant differences among formulations  
 552 ( $p < 0.05$ ).

553 **Table 3. Thermal degradation temperatures (onset value and value at maximum**  
 554 **degradation rate) of the different films obtained by TGA. Mean values  $\pm$ standard**  
 555 **deviation.**

	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)
PLA	324.0 $\pm$ 0.5 <sup>e</sup>	339.6 $\pm$ 0.6 <sup>c</sup>
PLA_5PEG1000	320.4 $\pm$ 0.2 <sup>cd</sup>	338.9 $\pm$ 0.4 <sup>bc</sup>
PLA_10PEG1000	319.7 $\pm$ 0.5 <sup>bc</sup>	337.3 $\pm$ 0.2 <sup>ab</sup>
PLA_5PEG4000	318.8 $\pm$ 0.3 <sup>ab</sup>	337.3 $\pm$ 0.2 <sup>ab</sup>
PLA_10PEG4000	317.9 $\pm$ 0.6 <sup>a</sup>	337.0 $\pm$ 0.3 <sup>a</sup>
PLA_5Palamoll®638	321.5 $\pm$ 0.1 <sup>d</sup>	338.8 $\pm$ 0.3 <sup>bc</sup>
PLA_10Palamoll®638	321.3 $\pm$ 0.6 <sup>d</sup>	338.8 $\pm$ 1.0 <sup>bc</sup>

556  
 557 Different superscript letters within the same column indicate significant differences among formulations  
 558 (p<0.05).

559  
 560 **Table 4. Thickness, tensile parameters (TS, EM, %  $\epsilon$ ), water vapour permeability**  
 561 **(WVP: m.g.h<sup>-1</sup>.Pa<sup>-1</sup>.m<sup>-2</sup>), oxygen permeability (OP: cm<sup>3</sup>.m<sup>-1</sup>.s<sup>-1</sup>.Pa<sup>-1</sup>) and internal**  
 562 **transmittance (T<sub>i</sub> at 600 nm) of films. Mean values  $\pm$ standard deviation.**

	Thickness (mm)	TS (MPa)	EM (MPa)	$\epsilon$ (%)	WVP	OP x10 <sup>12</sup>	T <sub>i</sub> (%)
PLA	0.136 $\pm$ 0.008 <sup>d</sup>	62 $\pm$ 2 <sup>f</sup>	1583 $\pm$ 17 <sup>cde</sup>	4.4 $\pm$ 0.2 <sup>d</sup>	0.093 $\pm$ 0.003 <sup>a</sup>	2.44 $\pm$ 0.14 <sup>a</sup>	88.96 $\pm$ 0.02 <sup>e</sup>
PLA_5PEG1000	0.126 $\pm$ 0.011 <sup>b</sup>	25 $\pm$ 4 <sup>c</sup>	1530 $\pm$ 50 <sup>bc</sup>	1.9 $\pm$ 0.4 <sup>b</sup>	0.113 $\pm$ 0.007 <sup>ab</sup>	1.90 $\pm$ 0.01 <sup>b</sup>	88.79 $\pm$ 0.03 <sup>d</sup>
PLA_10PEG1000	0.129 $\pm$ 0.008 <sup>bc</sup>	27 $\pm$ 3 <sup>c</sup>	1500 $\pm$ 40 <sup>ab</sup>	1.9 $\pm$ 0.1 <sup>b</sup>	0.127 $\pm$ 0.011 <sup>b</sup>	> D.L.	88.54 $\pm$ 0.06 <sup>b</sup>
PLA_5PEG4000	0.119 $\pm$ 0.009 <sup>a</sup>	18 $\pm$ 7 <sup>b</sup>	1620 $\pm$ 30 <sup>e</sup>	1.2 $\pm$ 0.5 <sup>a</sup>	0.115 $\pm$ 0.010 <sup>ab</sup>	> D.L.	88.67 $\pm$ 0.02 <sup>c</sup>
PLA_10PEG4000	0.117 $\pm$ 0.010 <sup>a</sup>	10 $\pm$ 3 <sup>a</sup>	1400 $\pm$ 100 <sup>a</sup>	1.0 $\pm$ 0.7 <sup>a</sup>	0.147 $\pm$ 0.002 <sup>c</sup>	> D.L.	88.46 $\pm$ 0.02 <sup>a</sup>
PLA_5Palamoll®638	0.132 $\pm$ 0.007 <sup>cd</sup>	56 $\pm$ 2 <sup>e</sup>	1600 $\pm$ 70 <sup>de</sup>	3.9 $\pm$ 0.1 <sup>c</sup>	0.103 $\pm$ 0.009 <sup>a</sup>	2.90 $\pm$ 0.60 <sup>a</sup>	88.85 $\pm$ 0.04 <sup>d</sup>
PLA_10Palamoll®638	0.129 $\pm$ 0.009 <sup>bc</sup>	51 $\pm$ 3 <sup>d</sup>	1550 $\pm$ 60 <sup>bcd</sup>	3.7 $\pm$ 0.3 <sup>c</sup>	0.108 $\pm$ 0.008 <sup>a</sup>	> D.L.	88.80 $\pm$ 0.05 <sup>d</sup>

563  
 564 D.L.: 200 cm<sup>3</sup>/m<sup>2</sup>.day

565 Different superscript letters within the same column indicate significant differences among formulations  
 566 (p<0.05).