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Additional Information

1 **Enhancement of interfacial adhesion between starch and poly(ε-caprolactone) by**

2 **using PCL-grafted compounds**

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ABSTRACT

In the present paper, films based on thermoplastic starch (S) and modified poly(ε-caprolactone) (gPCL) were employed to prepare films with enhanced polymer miscibility. PCL was functionalized by grafting with maleic anyhdride (MA) and/or glycidyl methacrylate (GMA) by reactive blending in a batch mixer. gPCL based films were analysed in terms of their grafting degree, structural and thermal properties. Binary blends based on starch and neat PCL or gPCL were obtained by extrusion and compression moulding. Ternary blends, where 2.5-5% by weight of grafted PCL were used as compatibilizers in S-PCL based system, were also prepared. Structural, thermal, mechanical and barrier properties of all obtained blends were investigated. Ternary blends evidenced better interfacial adhesion between starch and PCL, as deduced both by structural (XRD, FTIR, SEM) and bulk properties (DSC, TGA) of films. Moreover, grafted PCL-based compatibilizers improved functional properties of S-PCL based films, as pointed out from mechanical performance and higher barrier properties, valuable to meet the food packaging requirements.

Keywords: starch, polycaprolactone, polymer compatibilization, food packaging

1. INTRODUCTION

The growing environmental awareness due to the fast landfill accumulation of post-used petroleum-based plastics and the currently reduction of fossil fuel sources, induced scientists to focus their attention on biodegradable polymer based materials as valid eco-sustainable alternative. However, high costs still limit their application. Starch is produced by plants as their energy reserve (Zhang *et al*., 2013), and represents a

promising material for biodegradable plastics due to availability, renewability and low

cost (BeMiller & Whistler, 2009; Xie *et al.,* 2013; Pérez*et al.,* 2013). Starch-based

materials, such as thermoplastic starch (S), obtained from native starch and plasticizers

as polyhydric alcohols and/or water, can be processed by means of conventional

equipment used for traditional thermoplastics materials and transformed into injection

or blow moulded final products (Li & Favis, 2010; Averous *et al.,* 2000). For this

reason thermoplastic starch films can be considered as appealing eco-sustainable and

cost-effective bio-based materials, potentially exploitable for packaging applications.

Anyway, some important drawbacks, including poor mechanical properties and high

water absorption, responsible of both short-term stability and poor barrier properties,

and retrogradation process occurring during starch storage time (Wu, 2003; Arık Kibar

& Us, 2013; Ortega-Toro *et al.,* 2014), restrict the exploitation window of starch-based

products. In order to overcome these problems, several attempts have been performed,

from blending S with biopolymers (Leroy *et al.,* 2012; Ortega-Toro *et al*., 2014),

polyesters and low molecular weight compounds (Averous *et al*., 2000; Li & Fabis,

2010; Teixeira *et al.,* 2012; De Camargo *et al.,* 2013), to reinforcing S with organic and

inorganic fillers (Woehl *et al.,* 2010), to modifying it by means of blending or grafting

with biodegradable sinthetic polyesters (Rutot *et al*., 2000).

In this paper, polycaprolactone (PCL) was chosen due to its biodegradability, good

mechanical properties and hydrophobicity. Hence, S-PCL blends could represent a valid

alternative for improving starch functionality while preserving full biodegradability

(Ortega-Toro *et al*., 2015). Nevertheless, due to differences in polarity, these polymers

exhibit phase separation, responsible for undesirable poor mechanical performance,

which limits the application range (Avella *et al*., 2000; Averous *et al*., 2000). To

74 improve interfacial association between starch and hydrophobic polymers,

75 compatibilizers or cross-linking agents (Avella *et al.,* 2000; Wu, 2003; Sugih *et al.,*

76 2009) have been commonly used.

77 In this regard, PCL can be functionalized with reactive polar groups, such as epoxide

78 (Kim *et al.,* 2001; Sugih *et al.,* 2009), or anhydride (Wu, 2003; Arbelaiz *et al.,* 2006)

79 able to react with the –OH groups of starch backbone.

80 Laurienzo *et al.,* (2006) adopted a rather innovative method to functionalize PCL, with

81 simultaneous melt grafting of maleic anhydride (MA) and glycidyl methacrylate (GMA)

82 in a batch mixer and in presence of peroxide as initiator. They found that the addition of

83 GMA improved the grafting efficiency (Laurienzo *et al*., 2006 and Mangiacapra *et al.,*

84 2007). Nevertheless, the use of such grafted PCL as compatibilizer for starch-PCL

85 systems has not yet been investigated.

86 The aim of this work was to carry out two different strategies to overcome the

87 incompatibility between starch and PCL. The first one consisted of direct melt blending

88 of PCL grafted with GMA (PCL_G) or both MA and GMA (PCL_{MG}) to starch

89 macromolecular backbone. The second approach consisted of adding PCL_G or PCL_{MG}

90 as third component to compatibilize starch-PCL based blends. The structure of

91 functionalized PCL and the yield of the grafting reactions were analysed, as well as the

92 structural, thermal, mechanical and barrier properties of binary and ternary blend films.

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94 **2. MATERIALS AND METHODS**

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96 **2.1. Materials**

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97 Corn starch was purchased from Roquette (Roquette Laisa, Benifaió, Spain). Glycerol

98 was obtained from Panreac Química, S.A. (Castellar del Vallès, Barcelona, Spain).

99 Polycaprolactone (PCL) (pellets~3 mm, average M_n 80.000 Da, impurities <1.0%

100 water) was provided by Fluka (Sigma–Aldrich Chemie, Steinheim, Germany). Glycidyl

101 methacrylate (GMA) (purity 97%), maleic anhydride (MA) (purity 99.8%) and benzoyl

102 peroxide (BPO) were supplied by Aldrich Chemicals and used as received. All other

103 chemicals used in this work were reagent grade and used without further purification.

104

105 **2.2. Chemical modification of PCL**

106 PCL was modified using the methodology reported by Laurienzo *et al*. (2006). The

107 grafting reaction was carried out in the melt using a Brabender Plastograph EC GmbH

108 & Co. KG batch mixer, (Duisburg, Germany) equipped with two counter rotating roller

109 blades. The modification of PCL with MA and GMA to obtain PCL_{MG} was performed

110 as follows: a mixture of 45 g of PCL, 2.5 g (0.025 mol) of MA, 0.5 g (2.1 mmol) of

111 BPO and 2.5 g (0.018 mol) of GMA, the last one added dropwise, was fed into the

112 mixer at 100 °C. The reaction was carried out at 100 °C for 20 min at a screw rate of 32

113 rpm. In order to remove any excess of ungrafted reagents (residual monomers and

114 oligomers), the functionalized PCL was dissolved in 500 mL of chloroform ($CHCl_3$)

115 and then re-precipitated in a large excess of hexane. The purification procedure was

116 repeated twice. The obtained samples were kept in a desiccator under vacuum at 25 ºC

117 for 12 h and then stored at -20°C for 24 h before using. The synthesis of PCL modified

118 only with glycidyl methacrylate, PCL_G, was performed as follows: a mixture of 45 g of

119 PCL, 0.5 g (2.1 mmol) of BPO and 5 g (0.036 mol) of GMA was fed into the mixer at

5

120   100 °C. The reaction was carried out following the same procedure reported as in the

121   case of PCL_{MG} synthesis.

122

123   **2.3. Characterization of grafted PCL**

124   The content of GMA grafted onto PCL was determined through ^{1}H NMR spectra

125   recorded with a Bruker Avance DPX300 apparatus operating at 300 MHz. The sample

126   (about 12 mg) was dissolved in chloroform-deuterated ($CDCl_3$) and one dimensional ^{1}H

127   NMR spectra were obtained. The relative peak area of the methylene proton of PCL α-

128   carbon (2.30 ppm) and the methine proton of GMA (3.20 ppm) were considered to

129   estimate the molar grafting ratio.

130   The grafting degree of PCL_{MG} was evaluated by measuring the content of grafted

131   maleic anhydride by FTIR spectroscopy (Perkin Elmer Paragon 500), performed in

132   chloroform solutions. The bands at 1777 and 1850 cm^{-1}, which correspond to the

133   symmetric and asymmetric stretching vibration of anhydride group, were taken as the

134   analytical reference bands for quantitative determination. Before determination, a

135   calibration curve was built up with different amounts of succinic anhydride in

136   chloroform Laurienzo *et al.* (2006).

137   PCL and grafted PCL materials were characterized as to their structural properties

138   through FTIR analysis, crystallization pattern by means of X-Ray diffraction spectra,

139   and thermal behaviour by DSC, as described below. To this aim, films of PCL and

140   grafted PCL were prepared by compression moulding, using the procedure following

141   described for S-PCL and S-gPCL films.

142

143   **2.4. Preparation of formulations**

144   Thermo-plasticization of starch was performed as follows: native corn starch,

145   previously dried overnight in an oven at 60°C under vacuum, was hand-blend with

146   glycerol and water in a starch:glycerol:water weight ratio of 1:0.3:0.5 w/w. This

147   formulation (S) was the control. Starch was the polymeric matrix in all investigated

148   blends. In S-PCL binary blends, neat or functionalized PCL (PCL_{MG} or PCL_G) were

149   added in a weight ratio of 0.2 g/g of starch.

150   In ternary blends, where PCL weight ratio was fixed at 0.2 g/g of starch, 2.5 g and 5 g

151   of PCL_G or PCL_{MG} were added per 100 g of plain polymeric blend S-PCL. Hence, four

152   ternary blends were obtained and coded as follows: $S_{PCLG2.5}PCL$, $S_{PCLG5}PCL$,

153     $S_{PCLMG2.5}PCL$, $S_{PCLMG5}PCL$.

154   Binary and ternary blends were obtained by melt processing, using a co-rotating twin-

155   screw extruder (Teach-Line® ZK 25T, Collin, Germany). The temperature profile was

156   as follows (from hopper to die): 60, 90, 110, 120 and 110 °C and the residence time was

157   5 min. The final blend strands were pelletized, and compression moulded by means of a

158   compression moulding press (Model C, Carver Laboratory Press, USA), in order to

159   prepare films. 3 g of pellets were placed between two steel plates, pre-heated at 130 °C

160   for 2 min and compression moulded for 2 minutes by increasing the pressure up to 90

161   bars and for further 2 minutes by rising pressure up to 220 bars; lastly, a cooling cycle,

162   applied for about 8 minutes, allowed films of about 230 µm to be obtained.

163   Before each test, all the films were conditioned in a climatic chamber, set at 25°C and

164   50% Relative Humidity (RH) for one week.

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166   **2.5. Film characterization**

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168   2.5.1. <u>Fourier Transform Infrared (FTIR) spectroscopy</u>

169   Attenuated Total Reflection Fourier Transform Infrared (FTIR-ATR) spectroscopy was

170   carried out on the surface of compression moulded samples by means of a Perkin Elmer

171   Spectrum 100 spectrometer, equipped with a Universal ATR diamond crystal sampling

172   accessory. All the samples were analysed at room temperature. Spectra were recorded as

173   an average of 64 scans in the range 4000–480 cm^{-1}, with a resolution of 4 cm^{-1}.

174

175   2.5.2. <u>X-ray diffraction</u>

176   A diffractometer (XRD, Bruker AXS/D8 Advance) was used to obtain X-ray diffraction

177   patterns. All the samples were analysed at 25 °C and 50% RH, in a 2θ range between 5°

178   and 30°, using Kα Cu radiation (λ: 1.542 Ǻ), 40 kV and 40 mA with a step size of 0.05°.

179   For this analysis, 4 cm^2 samples were used. The degree of crystallinity of the samples

180   was calculated from the integrated area of X-ray diffraction data, using OriginPro 8.5

181   software, for which Gaussian profiles for crystalline and amorphous peaks were

182   assumed. The areas under the crystalline (Ac) and amorphous (Aa) phases were

183   determined in arbitrary units and the degree of crystallinity (X_c) was obtained as

184   reported by Monteiro *et al*. (2013).

185

186   2.5.3. <u>Scanning Electron Microscopy (SEM)</u>

187   Morphological analysis of films was performed by means of a FEI Quanta 200 FEG

188   Scanning Electron Microscope (SEM) on cryogenically fractured cross-sections. SEM

189   observations were performed in low vacuum mode (P_{H2O}: 0.7 torr), using a large field

190   detector (LFD) and an acceleration voltage of 5–20 kV. Prior to the observation, the

191   sample surfaces were coated with a homogeneous layer (18 ± 0.2 nm) of Au–Pd alloy

192   by means of a sputtering device (MED 020, Bal-Tec AG).

193

194   2.5.4. Differential Scanning Calorimetry and Thermogravimetric Analysis

195   Differential Scanning Calorimetry (DSC) measurements were performed by a TA DSC-

196   Q2000 instrument equipped with a TA Instruments DSC cooling system. The analyses

197   were performed under 30 mL min^{-1} nitrogen purge gas flow. Indium was used to

198   calibrate the calorimeter. Approximately 6 mg of the samples were placed into

199   aluminium pans, sealed and analysed according to the following procedures. All the

200   specimens were equilibrated at 25 ºC and heated up to 110 ºC at 20 ºC/min. Then an

201   isotherm step was performed at 110°C for 60 min in order to remove the free and bound

202   water that masked starch T_g (Russo *et al*., 2010). Afterwards, the samples were cooled

203   to -80 ºC at 10 ºC/min, thermally stabilized for 2 min at that temperature and re-heated

204   up to 200 ºC at 20 ºC/min,. For each sample, data analysis was averaged on a set of

205   three measurements.

206   Thermogravimetric analyses (TGA) were carried out with a Mettler Thermogravimetric

207   Analyzer Mod. TG 50. The measurements were performed on samples of about 8–10

208   mg, placed in ceramic crucibles and heated from 25 to 700 ºC at 10 ºC/min, in a

209   nitrogen atmosphere, with a nominal gas flow rate of 30 mL/min. For each composition,

210   the thermogravimetric tests were performed in triplicate.

211

212   2.5.5. Tensile properties

213   Tensile tests were performed using an Instron dynamometer, model 4505, equipped

214   with a 1 kN load cell, according to the ASTM D638 standard test method at 23 ± 2 °C

215 and 45 ± 5% RH. Dumbbell-shaped films (4 mm wide, 50 mm long, 0,23 mm thick)

216 were used. All the measurements were carried out at room temperature, at a crosshead

217 speed of 10 mm min^{-1}, and a gauge length of 25 mm. Tensile tests were also carried out

218 on films aged for 5 weeks in climatic chamber at 25ºC and 50% RH, in order to follow

219 mechanical properties changes associated to polymeric structural modifications. The

220 reported data are the average values of seven determinations.

221

222 2.5.6. Water vapour permeability, oxygen permeability and carbon dioxide permeability

223 Water vapour and carbon dioxide permeability tests were performed by means of Extra

224 Solution Multiperm equipment, whereas the oxygen permeability analyses were carried

225 out using an Extra Solution PermO$_2$ device. All the films were tested at 25°C and 50%

226 RH. The exposed area of the film was 50 cm^2. The collected data were converted into

227 water vapour, oxygen and carbon dioxide transmission rates (WVTR, O$_2$TR, CO$_2$TR),

228 corresponding to the gas flow between two parallel surfaces under steady conditions, at

229 a specific temperature and RH. The permeability coefficient, P, was calculated by

230 normalizing WVTR, O$_2$TR, and CO$_2$TR with respect to film thickness and dividing by

231 the gas partial pressure in the bottom chamber. At least three tests were conducted for

232 each sample in order to confirm the reproducibility of the data.

233

234 2.5.7. Statistical analysis

235 Statgraphics Plus 5.1 (Manugistics Corp. Rockville, MD) was used to carry out

236 statistical analyses of data through analysis of variance (ANOVA). Fisher's least

237 significant difference (LSD) was used at the 95% confidence level. Homogeneous

238 groups were reported as numbers or letter superscripts.

239

3. RESULTS

241

3.1.Synthesis of PCL$_{MG}$ and PCL$_{G}$ and structural characterization

In order to enhance the interfacial adhesion between starch and PCL, polar functional

groups were chemically grafted on hydrophobic PCL chains, by inserting both MA and

GMA reactive molecules (PCL$_{MG}$) or only GMA (PCL$_{G}$) on its macromolecular

backbone, thus obtaining two differently functionalized polymers. As concerns PCL$_{MG}$,

direct free radical grafting of MA on PCL was somewhat deterred due to the low

reactivity and steric hindrance of maleic anhydride, as shown by John *et al.* (1997).

Besides, MA is not keen to react with radicals arising from itself, showing a very low

tendency to homopolymerize. On the other hand, it is well known that MA is prone to

co-polymerize (Laurienzo *et al.*, 2006). To enhance the functionalization degree of MA,

the more reactive GMA co-monomer was added to the bulk. Being an electron donor

towards MA, GMA supports its insertion, thus increasing the grafting efficiency.

Figures 1 shows the reaction mechanisms involved in the synthesis of the two

functionalized PCL products.

Structural characterizations were performed on samples obtained by compression

moulding. Figure 2 shows FTIR-ATR spectra of PCL and grafted PCL. In particular,

PCL$_{MG}$ spectrum shows new peaks at 1780 and 1850 cm^{-1}, respectively attributed to the

symmetric and asymmetric stretching of the carbonyl groups of the grafted anhydride.

The quantitative determination of grafted maleic anhydride, performed by FTIR

analysis as reported in the experimental section, revealed a grafting weight percentage

of $4.5 \pm 0.9\%$. NMR analysis (spectrum not shown) confirmed the occurrence of MA

263   grafting through the presence of the typical anhydride signal at δ = 2.5 ppm (Laurienzo

264   *et al.*, 2006).

265   As concerns PCL$_G$, the FTIR-ATR spectrum displays the characteristic peak of the

266   asymmetric stretching vibration of epoxy ring C-O bonds at 910 cm^{-1}, thus suggesting

267   that PCL functionalization mostly involved the double bond of the methacrylate unit.

268   This hypothesis is furthermore confirmed by NMR analysis. Indeed, PCL$_G$ spectrum

269   shows characteristic signals relative to methine and methylene protons of epoxy rings of

270   GMA, at 3.2 ppm, 2.8 ppm and 2.6 ppm (Figure 3). GMA molar grafting degree was

271   evaluated from the relative peak area of the PCL proton in α–position with respect to

272   carbonyl (δ = 2.3 ppm) and the GMA methine proton of the epoxy ring (δ = 3.2 ppm),

273   and was found to be 4.3 ± 0.4%, which correspond to a weight percentage of 5%.

274   Figure 4 shows XRD patterns and crystallinity degree (X$_c$) of all analysed films. In

275   particular, Figure 4a evidences X-ray diffraction profiles of both neat and grafted PCL

276   samples. Three distinct crystalline peaks were observed at 2θ values of around 21.6°,

277   22.2° and 23.3° in the diffractograms of all three PCL-based samples, which are

278   indexed to be (110), (111) and (200) planes, respectively, of an orthorhombic crystalline

279   structure of PCL. The amorphous halo was fitted to a broad peak centered at 21.0°

280   (Haque *et al.*, 2012; Suzuki *et al.*, 2013). Nevertheless, small displacements of the peaks

281   could be observed for grafted PCL, thus indicating small changes in the interplanar

282   basal spacing associated with the different packing of grafted molecules.

283   Crystallinity of the samples was evaluated by the area underlying peaks, after

284   performing a curve fitting and a linear background correction, for which a Gaussian

285   profile was assumed. A crystallinity degree of 44% was calculated for PCL. Both

286   functionalized PCL samples displayed a clear enhancement of crystallinity up to 66%,

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287   although smaller crystalline formations were obtained, as deduced from the wider

288   peaks, especially in PCL_{MG}. Hence, the presence of maleic anhydride and glycidyl

289   methacrylate led to a more structured polymeric matrix. The effect was particularly

290   marked in the case of PCL_{MG}. Actually, MA reactivity is expected to be different from

291   that of GMA. Indeed, MA easily grafts onto a GMA reactive molecule, but the

292   following reactions of MA onto already grafted PCL_{MG} hardly occur due to MA

293   molecules steric hindrance, as previously discussed. Hence, in PCL_{MG} sample, short-

294   grafted chains, promoting PCL crystallization, could be obtained. On the contrary,

295   GMA molecules may either directly graft onto PCL radical chains, or homopolymerize

296   through a chain transfer process, leading to longer GMA grafted chains on PCL

297   backbone, responsible of a delay in PCL_G crystallization during cooling step of

298   compression moulding process (Sugih *et al*., 2009).

299   XRD results are supported by the higher crystallization temperature (T_c) of grafted PCL

300   samples with respect to PCL (less super-cooling effect), evaluated by DSC cooling

301   ramp from the melt (as shown in Table 2). The polar groups grafted on PCL backbone

302   acted as nucleating sites, inducing the formation of PCL crystalline nuclei in different

303   domains of the matrix; as a consequence, the crystals growth kinetics was hampered, as

304   indicated by ΔH_c values.

305   In order to compare the results of structural and bulk analyses of PCL based samples,

306   DSC data of first heating run were evaluated (Table 1), as better reproducing the

307   thermal history of samples analysed by NMR, FTIR and XRD. Hence, in Table 1,

308   melting temperature (T_m), relative enthalpy (ΔH_m) and crystallization degree (X_c) of

309   neat and functionalized PCL, are shown. From reported data, it is worthy to stress that

310   T_m, ΔH_m and X_c values of functionalized PCL were lower than the ones of neat PCL.

311   Actually, the introduction of grafted polar groups on PCL backbone induced some

312   structural modifications, hampering the regular packing of macromolecular chains in

313   crystalline domains. Similar observations were made by Kim *et al*. (2001) for PCL_G.

314   Nevertheless, in the second heating run of DSC analysis (Table 2), where thermal

315   history of the samples was erased, no differences were found between melting

316   behaviour (T_m and ΔH_m) of PCL and grafted PCL, which showed the same crystallinity

317   degree. So, it can be concluded that GMA and MA polar molecules could act as

318   nucleating agents in PCL matrix, but they were not able to promote the growth of

319   crystalline domains, in this way giving rise to more amorphous material, depending on

320   the cooling conditions.

321

322   **3.2. Properties of starch-based blends**

323

324   3.2.1.Structural properties of films

325   Infrared Spectroscopy represents a valid tool aimed to assess the physical or chemical

326   interactions between components in polymeric blend systems. In Figure 5 FTIR-ATR

327   spectra of carbonyl stretching adsorption, related to neat PCL, S-PCL and S-gPCL. in

328   binary and ternary blends are shown (inset region in Fig. 5). As usually evidenced by a

329   semicrystalline polyester, the carbonyl region is composed of two overlapping peaks; in

330   PCL spectrum there is a relatively broad band centered at 1738 cm^{-1}, occurring as a

331   shoulder of a sharper and more intense band at 1720 cm^{-1}. Previous studies showed that

332   the above mentioned peaks arise from the amorphous and crystalline phases of the

333   polymer, respectively (He *et al*., 2000). In S-PCL and S-gPCL samples, two interesting

334   changes in carbonyl stretching modes were observed: a variation of the relative intensity

3

335 of the above-mentioned amorphous and crystalline peaks and a shift of the PCL

336 crystalline band to 1724 cm^{-1}. In particular, the decrease in intensity of the crystalline

337 carbonyl band in favour of a widening of the amorphous region, observed both in binary

338 and ternary blends (close up region in Fig. 5), suggests that starch chains disturb the

339 regular packing of both PCL and functionalised PCL macromolecular structures,

340 increasing their amorphous phases. The amorphous (Ap) and the crystalline (Cp)

341 components of PCL carbonyl groups were quantified in the different samples by using

342 the GRAMS 8.0AI software package (Thermo Electron Corporation). The area of each

343 peak was calculated after performing a linear background correction and assuming

344 mixed Gaussian-Lorentzian functions. The percentage ratios of amorphous and

345 crystalline areas (Ap/Cp) are shown in Figure 5 (close up region in Fig 5). Analysis of

346 data evidences that in S-gPCL samples the percentage of PCL amorphous carbonyl

347 band increases, thus confirming the previous hypothesis.

348 Furthermore, the crystalline carbonyl band moves towards higher stretching vibration

349 frequencies, thus suggesting that a new PCL crystalline domain forms. As a matter of

350 fact, the interaction with starch provokes both the disruption of the previous inter and

351 intramolecular dipole interactions of carbonyl groups, responsible for hindering local

352 stretching vibration, and the development of a different structural organization

353 characterized by a slight increase in the intrinsic vibration energy of the carbonyl bond

354 (Murphy *et al*., 2012).

355 Another characteristic broad peak occurring about 1646 cm^{-1} is ascribed to the tightly

356 bound water of starch (Kizil *et al*., 2002). Santha *et al*. (1990) reported that this band

357 concerns the vibration modes of water molecules adsorbed in amorphous region of

358 starch, since it is barely visible when starch crystalline fraction increases. This peak is

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359 well discernible both in binary and ternary blends, thus suggesting that in all

360 investigated blends, starch amorphous phase plays a key role.

361 This hypothesis is confirmed by X ray diffraction data (see Figures 4a,b). Indeed, all the

362 starch-based films display lower crystallinity percentages if compared to those of PCL

363 and gPCL samples, since the blending of all the components is widely affected by the

364 amorphous phase of starch. Nevertheless, it is worth highlighting that in binary blends

365 crystallinity is higher if compared to that of neat S and SPCL, as found in the case of

366 gPCL films when compared to plain PCL. This supports the hypothesis that reactive

367 polar groups of maleic anhydride and glycidyl methacrylate, pendant on the

368 hydrophobic PCL backbone, can react with –OH groups of starch chains, by means of

369 hydrogen bond. In this way, both the interfacial association between the two polymer

370 phases and the fast crystallization of a more packed structure are triggered.

371 On the other hand, in ternary blends, the degree of crystallinity is comparable to that of

372 an SPCL binary one. Maybe the low concentration of compatibilizers (2.5-5% w/w)

373 inhibits polymer crystallization following to compression moulding process, hindering

374 the development of tight interactions between the two phases. This hypothesis,

375 strengthened by FTIR-ATR results, is furthermore supported by the analysis of XRD

376 patterns reported in Figure 4b, related to starch-based films. Spectrum of neat starch

377 film (S) evidences a low degree of crystallinity (3.8%), a large amorphous region with

378 peaks at 2θ of 12.7º and 19.5º corresponding to characteristic crystalline forms of

379 amylose V type. These peaks were observed in all starch based films. According to

380 Castillo *et al*. (2013), the crystalline V type can be divided into two subtypes, namely

381 V_a (anhydrous fraction) with peaks at 13.2º and 20.6º and V_h (hydrated fraction) with

382 peaks at 12.6º and 19.4º. The V_h subtype was present in neat starch film, and a tendency

383   of the peaks to shift towards higher values (typical of the V_a subtype) was observed for

384   blends with PCL, especially in the ternary blend of $S_{PCLMG2.5}PCL$ (2θ 13.1º and 20.0º),

385   with the subsequent decrease in the interplanar basal spacing with respect to the control

386   formulation.

387   In S-PCL or S-gPCL films, the characteristic peaks of PCL at about 21º and 23º 2θ

388   values clearly appeared, since overlapping with starch peaks only occurs at 2θ values

389   near 21º. Binary formulations showed a marked increase in crystallinity if compared to

390   S, especially in blends with PCL_{-g} (up to 31%), but this effect was attenuated in ternary

391   blends (up to 18%). As regards the interplanar spacing of PCL crystalline forms in

392   blends, very small differences could be observed with respect to neat PCL, the

393   exception being $S_{PCLMG5}PCL$ sample, which showed a slight increase, coherently with a

394   more crystalline structure of PCL. The above remarked behaviour of starch and PCL

395   crystallization revealed that the compatibilizers induce different effects on

396   crystallization pattern of the polymers.

397

398   3.2.2.<u>Morphological properties of films</u>

399   Figure 6 shows the micrographs of cryogenically fractured cross-section of binary (S-

400   PCL, $S-PCL_G$ and $S-PCL_{MG}$), and ternary ($S_{PCLG5}PCL$ and $S_{PCLMG5}PCL$) blends. From

401   the analysis of SEM picture of S-PCL sample, it is possible to observe some isolated but

402   fairly dispersed PCL particles within the polymeric matrix, and some voids formed as a

403   consequence of the debonding and pulling out of PCL domains, following the

404   mechanical stress applied during cryogenic fracture. This morphology suggests a poor

405   macromolecular interconnection between the two polymeric phases (Li & Favis, 2010;

406   Sugih *et al*., 2009; Cocca *et al.,* 2015).

6

However, SEM micrographs of functionalized binary and ternary blends generally evidenced an improved interfacial adhesion between the phases, with a diffuse halo surrounding the dispersed phase, indicating an interaction between the polymers. The chemical interactions between hydroxyl groups of starch and polar groups of PCL_G and PCL_{MG} seriously affected their microstructure. Indeed, binary blends exhibited a smoother and more homogeneous structure, resulting both in a partial coating of PCL_G domains with the polymeric matrix and in a complete embedding of PCL_{MG} within the starch network.

Actually, the structure of PCL_G, as previously discussed, is quite inhomogeneous at a microscopic level, probably because of the homopolymerization occurring during the grafting process on PCL backbone. This could restrain the reactive GMA groups in relatively concentrated spots, as evidenced by SEM micrographs (Haque *et al*., 2012). Moreover, morphological analysis of binary blends containing PCL_{MG} showed a massive embedding of grafted PCL within the starch network, resulting in large phase domains; this outcome could be due to the increasing of dispersed phase size with respect to polymeric matrix, able to provide larger segregated polymeric areas, in which physical interactions between starch polar groups and functionalized PCL are promoted. As far as ternary blends are concerned, only $S_{PCLG5}PCL$ and $S_{PCLMG5}PCL$ micrographs are reported for brevity. Generally, it is possible to observe a fairly rough cross-section surface with a pronounced coarsening of small size dispersed phase. Nevertheless, the absence of voids, the fine and homogeneous dispersion of PCL, PCL_G and PCL_{MG} particles within the polymeric matrix, suggests an effective improvement of interfacial adhesion. Specifically, in case of $S_{PCLMG5}PCL$ sample, the presence of smaller and very finely distributed PCL domains highlights that PCL_{MG} is a very good compatibilizer.

431 The enhancement of S-PCL compatibilization is probably due to the stronger interaction

432 between the –OH groups of starch and both functional polar groups of PCL_{MG}. Similar

433 observations were reported by Haque *et al*. (2012), who studied PCL-based composites

434 with cellulose micro-fibres containing PCL grafted with maleic anhydride and glycidyl

435 methacrylate as compatibilizers. Finally, as far as $S_{PCLG5}PCL$ is concerned,

436 morphological analysis evidences a quite homogeneous distribution of the dispersed

437 phase, even if some relatively concentrated spots of larger domains can be noticed; a

438 plausible explanation of this outshot could be found in the structural heterogeneity of

439 PCL_G moieties, due to homopolymerization occurring during the grafting process of

440 GMA groups along PCL backbone, as previously shown .

441

442 3.2.3.<u>Thermal properties</u>

443

444 3.2.3.1. Differential Scanning Calorimetry (DSC)

445 The values of phase transition temperatures (Tc: crystallization peak temperature, T_m:

446 melting peak temperature, T_g: glass transition temperature), enthalpies (ΔH_c:

447 crystallization enthalpy, ΔH_m: melting enthalpy) and degree of crystallinity (X_c),

448 calculated from DSC thermograms, are reported in Tables 1 and 2.

449 The content of crystallinity (X_c) was calculated as $\Delta H/\Delta H_\infty$ ratio where ΔH is the fusion

450 enthalpy of PCL in the samples, while ΔH_∞ refers to the hypothetically perfect crystal

451 of PCL ΔH_∞=136 J/g (Avella *et al*., 2000). From the analysis of Table 2, it is possible to

452 observe that SPCL sample exhibited lower values of ΔH_c and X_c, due to the mixing of

453 the components in the starch matrix amorphous phase, whereas SPCL$_{-g}$ samples of

454 binary blends evidenced higher crystallization enthalpy, ΔH_c, and crystallinity, X_c, a

8

455   noticeably improved crystallization temperature T_c (less supercooling effect) and an

456   enhanced melting enthalpy, ΔH_m. These experimental data could be attributed to the

457   marked interactions occurring between hydroxyl residues of starch and polar groups of

458   functionalized PCL based samples, both able to support the nucleation process and to

459   endorse the crystallization kinetics (Liu *et al*., 2009).

460   It is worth highlighting the peculiar behaviour of S-PCL$_G$ sample, exhibiting the highest

461   values of ΔH_c, X_{cc}, ΔH_{mc}, probably due to the formation of a very tight structure, able

462   to drastically reduce the mobility of amorphous regions of S, as evidenced by the

463   increase in starch T_g values. The proposed explanation for this behaviour may be found

464   in the high concentration of starch hydroxyl residues available for reaction with GMA

465   groups. As a matter of fact, this assumption could be in contrast with the previous

466   hypothesis that long GMA branches, pending from PCL backbone in secluded domains

467   could hinder its grafting efficiency. Anyway, when PCL$_G$ was melt blended with starch,

468   chemical reactions between hydroxyl groups of starch and GMA occurred at the

469   expense of both reactive double bond and epoxy ring groups. Actually, FTIR-ATR

470   analysis of the S-PCL$_G$ spectrum (Figure 5), compared to that of the PCL$_G$ one (Figure

471   2), points out that the band related to the asymmetric stretching vibration of epoxy ring

472   C-O bonds at 910 cm^{-1} disappears, thus indicating GMA epoxy ring opening as a

473   consequence of the reaction with available starch hydroxyl groups (Odusanya *et al*.,

474   2000). In this way, a strong crosslinked network formed with a consequent starch Tg

475   increase (Dean *et al.;* 2007), following a steric and structural stabilization mechanism,

476   as shown by Macosko *et al* (1996).

477   DSC cooling curves of all the blends are reported in Figure 7. Unlike binary blends,

478   PCL melt crystallization of ternary blends generally follows a complex pattern,

9

479 characterized by the presence of multiple and broad peaks, probably due to the existence

480 of two fairly distinct crystalline domains, one related to PCL in S-PCL system, and one

481 associated to PCL_G and PCL_{MG} compatibilizers. In $S_{PCLMG5}PCL$ and $S_{PCLG5}PCL$

482 samples, less peak separation was observed evidencing a better compatibilization

483 degree.

484 Actually, it could be hypothesized that the restrained amounts of compatibilizers used

485 with respect to the S-PCL polymeric batch, induce a spot grafting process along the

486 macromolecular backbone, with the subsequent isolated regions of interfacial

487 compatibilization; as a consequence, during fast cooling from melt, a homogeneous

488 nucleation is avoided. Nevertheless, it is worthwhile to underscore that both ΔH_c, and

489 X_{cc} values were higher than those of SPCL samples, particularly when PCL_G was used

490 as compatibilizer, thus reproducing the trend previously observed in $S-PCL_G$ binary

491 blend. As a final point, it is worthy to emphasize the increase of starch Tg in all

492 compatibilized blends, as a consequence of the chemical interactions between starch

493 hydroxyl groups and GMA epoxy ring that restrict the molecular motions responsible

494 for the glass transition. On the other hand, Table 2 evidences an overall dropping of

495 PCL Tg. Raquez *et al.* (2008) found that during melt reactive blending of polymer with

496 functional groups of MA and GMA, some PCL shorter macromolecular chains could be

497 developed; moreover thermal and mechanical stress undergone by starch based films

498 during extrusion process could promote PCL hydrolysis with following decreasing of

499 molecular weight.

500

501 3.2.3.2. Thermogravimetric analysis.

502 Table 3 reports the water loss percentage, the onset degradation temperatures (T_{onset}),

503 the maximum decomposition rate temperature (T_{peak}) of the investigated samples.

504 All thermograms (not reported) exhibited three separate weight loss steps; the first one

505 is related to the evaporation of free and freezing bound water between 25°C and 150 °C,

506 the second one is ascribed to starch degradation between 293 °C and 300 °C and the last

507 one is due to PCL degradation at about 393°C. The blends showed a slight decrease of

508 weight loss when compared to neat starch film, coherently with the introduction of

509 hydrophobic polymer. Moreover, a drop of T_{onset} of functionalized PCL based samples

510 could be evidenced in opposition to the slight increase of T_{peak} of the same samples.

511 These results are consistent with DSC data, showing that GMA and MA were not able

512 to promote PCL crystallization, thus encouraging its thermal degradation at lower

513 temperatures. On the other hand, the complex network of PCL_G and PCL_{MG} samples

514 influenced their degradation kinetics pattern, resulting in T_{peak} values slightly shifted to

515 higher temperatures.

516 PCL is markedly affected by starch amorphous phase, confirming the results previously

517 evidenced by DSC data (see Table 2). Indeed the onset of PCL degradation temperature

518 decreased of about 20°C with respect to the neat polymer, both in binary and in ternary

519 blends. Anyway, no significant differences were observed for compatibilized binary

520 blends. In ternary blends, a fair thermal stabilization of PCL may be observed,

521 particularly emphasized in S_{PCLMG5} PCL sample, where T_{peak} is shifted to higher

522 temperatures, as a consequence of a very strongly packed network (see Table 2). As

523 concerning starch, a slight increase of thermal stability may be pointed out, both in

524 binary and ternary blends, as evidenced by the shifting of T_{onset} towards higher

525 temperatures. This result is particularly marked in S-PCL_G and S_{PCLMG5}PCL samples,

11

526 due to the formation of a very tight crystalline structure as confirmed by DSC analysis

527 (see Table 2).

528

529 3.2.4. <u>Mechanical properties</u>

530 Table 4 shows the tensile properties of the studied formulations at initial time (1 week)

531 and after 4 weeks of storage time in climatic chamber. Compatibilized binary blends did

532 not show any significant improvements in mechanical response with respect to neat

533 starch and uncompatibilized S-PCL blend, concerning both stress (σ) and strain (ε) at

534 break; anyway S-PCL$_G$ and S-PCL$_{MG}$ films evidenced a slight increase of Young

535 Modulus (YM), meaning that the influence of compatibilizers at low deformations are

536 not negligible. The scarce tensile strength of S-PCL$_G$ and S-PCL$_{MG}$ films suggests that

537 the efficiency of compatibilization is somehow limited when gPCL molecules are

538 directly grafted on polymeric matrix. Moreover, after storage time, quite all samples

539 showed higher stiffness and tensile strength. These results suggest that both PCL and

540 gPCL did not inhibit starch chain re-aggregation during storage time. The amorphous

541 component in S fastly changes after film forming since retrogradation process occurs,

542 eliciting some short-range ordering of the amorphous components over time, (Frost *et*

543 *al*., 2009). Both retrogradation and crystallization phenomena may take place in S-PCL

544 or S-gPCL blends, supported by the strong interactions between the epoxy/anhydride

545 groups of compatibilizers and the hydroxyl groups of starch, as previously shown.

546 As for ternary blends, significant increases ($p < 0.05$) of tensile strength (up to 49% -

547 S$_{PCLMG5}$PCL) and YM (up to 58.4% -S$_{PCLMG5}$PCL), despite of drastic drop in elongation

548 at break (up to 84% -S$_{PCLG2.5}$PCL) can be observed, thus confirming the effectiveness of

549 compatibilizers in upgrading S-PCL interfacial adhesion. The higher concentration of

550   compatibilizers did not significantly affect the values of tensile properties, even if a

551   slight trend was observed, meaning that the greater the amount of compatibilizer, the

552   better the matrix reinforcement. It is well known that, in compatibilized blends, the fine

553   distribution of small size dispersed phase induces enhancement in mechanical response

554   (Xie *et al*., 2013). Effectively, morphological analysis evidenced a very fine distribution

555   of gPCL domains into SPCL macromolecular network, resulting in better mechanical

556   reinforcement. On the other hand, in binary blends, the existence of larger phase

557   domains, previously evidenced by morphological analysis, were responsible for poor

558   polymeric interfacial adhesion.

559   As a final remark, storage time severely modified tensile properties of ternary blends.

560   Specifically, an increase of tensile strength (up to 15.5% -$S_{PCLG2.5}$PCL) and a

561   substantial enhancement of polymeric ductility (up to 65.5% -$S_{PCLG2.5}$PCL) could be

562   observed despite of a YM decrease (up to 37.1% -S_{PCLG5}PCL), thus suggesting that

563   starch retrogradation process was somehow limited in ternary blends.

564

565   3.2.5.<u>Barrier properties</u>

566   Table 5 shows the barrier properties (oxygen, carbon dioxide and water vapour) of the

567   studied formulations stored at 25 ºC and 50% RH. As concerns binary blends, the

568   addition of PCL caused an increase in oxygen and carbon dioxide permeability, whereas

569   SPCL$_{MG}$ showed a significant reduction in both parameters and SPCL$_G$, on the

570   contrary, did not display any remarkable variation with respect to neat starch behaviour.

571   Ternary blends exhibited a significant decrease of O_2 and CO_2 permeability values with

572   respect to neat starch and binary blends.

573 Gas permeability in polymeric materials consists of two contributions: the dissolution

574 phenomenon and the interaction between the diffusing molecule and specific polymer

575 sites (Gain *et al*., 2005). The obtained results could be explained in terms of changes in

576 gas solubility in the continuous matrix and dispersed phase. Nevertheless, differences in

577 diffusion coefficients due to hindrance effects provoked by dispersed PCL particles

578 must be taken into account, as well as the respective gas molecule interactions with the

579 specific polar and non-polar polymeric sites. In this regard, the increase in gas

580 permeability when pure PCL was added to starch can be attributed to the better affinity

581 of molecules with dispersed PCL than with S. When grafted PCL was blended with

582 starch, both O_2 and CO_2 permeability values were reduced due to the overall increase in

583 PCL polarity caused by the grafting of polar groups (epoxy and anhydride). This

584 outcome resulted particularly enhanced in ternary blends, where grafted PCL

585 compounds were mainly confined at polymer interface, drastically hindering the gas

586 diffusion into PCL particles.

587 As WVP concerns, an overall progressive decreasing could be observed both in binary

588 and in ternary blends, probably associated to the increase in the tortuosity factor for

589 mass transfer when hydrophobic particles (PCL or PCL_{-g}) are dispersed within the

590 polymeric matrix or arranged in complex network with starch, as previously discussed.

591 It is worth to mention that ternary blends exhibited WVP values similar to those of

592 PCL, which represents a tangible upgrading in starch barrier properties.

593 Finally, it must be emphasized that these formulations met the barrier requirements for

594 food packaging. As for WVP, all the formulations are within the requirement range for

595 meat and MAP products (10-50 g water vapour$\cdot$m$^{-2}\cdot$day^{-1}) according to what reported

596 by Schmid *et al*., 2012. In addition, the oxygen permeability of each starch-based

597 formulation cover the highest requirements for food packaging (less than 1 cm^3

598 oxygen·m^{-2}·day^{-1}·bar^{-1}, Schmid *et al.*, 2012). The investigated materials show oxygen

599 barrier properties comparable to Polyethylene Terephthalate (PET) and Ethylenevinyl

600 alcohol (44% ethylene content -EVOH) and their WVTR is close to that of Polystyrene

601 (PS) and PET (Schmid *et al.*, 2012). Nevertheless, although their excellent barrier

602 properties, the overall migration in different food simulants must be assessed, according

603 to the migration limits established by regulation for plastic materials in contact with

604 food.

605

4. CONCLUSIONS

607 The aim of this work was to carry out two different strategies as to circumvent the

608 incompatibility between starch and PCL, in order to obtain biodegradable starch based

609 films, able to meet food packaging requirements. The first approach was to prepare

610 binary blends by directly melt blending PCL grafted with GMA (PCL$_G$) or both MA

611 and GMA (PCL$_{MG}$) with starch macromolecular backbone. The second strategy

612 consisted of adding PCL$_G$ and PCL$_{MG}$ as compatibilizers in starch-PCL ternary blends.

613 The interfacial adhesion between polymers was improved in presence of functionalized

614 PCL, particularly concerning ternary blends. Compatibilizers acted as nucleating agents

615 for PCL crystallization, affecting the crystallization degree of blends. Morphological

616 and mechanical properties were particularly enhanced in ternary blends, where only

617 2.5% or 5 wt% of gPCL, were used as compatibilizers in a cost-effective way. The films

618 showed gas and water vapour barrier properties comparable to some synthetic plastics

619 commonly used for food packaging. The overall migration in different food simulants

620 must be assessed, according to the migration limits established by regulation for plastic

15

materials in contact with food. Likewise, the stability of films over the storage time

must be more deeply investigated in order to assess their potential application as new

eco-sustainable and cost-effective food packaging biodegradable plastic films.

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