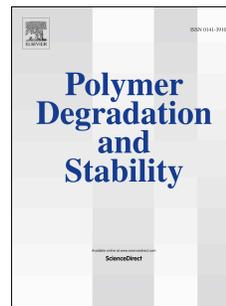


Accepted Manuscript

Characterization and degradation characteristics of poly(ϵ -caprolactone)-based composites reinforced with almond skin residues

Arantzazu Valdés García, Marina Ramos Santonja, Ana Beltrán Sanahuja, María del Carmen Garrigós Selva



PII: S0141-3910(14)00093-7

DOI: [10.1016/j.polymdegradstab.2014.03.011](https://doi.org/10.1016/j.polymdegradstab.2014.03.011)

Reference: PDST 7272

To appear in: *Polymer Degradation and Stability*

Received Date: 8 December 2013

Revised Date: 12 February 2014

Accepted Date: 4 March 2014

Please cite this article as: García AV, Santonja MR, Sanahuja AB, Selva MdCG, Characterization and degradation characteristics of poly(ϵ -caprolactone)-based composites reinforced with almond skin residues, *Polymer Degradation and Stability* (2014), doi: 10.1016/j.polymdegradstab.2014.03.011.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

1 **Characterization and degradation characteristics of poly(ϵ -caprolactone)-based**
2 **composites reinforced with almond skin residues.**

3 Arantzazu Valdés García*, Marina Ramos Santonja, Ana Beltrán Sanahuja, María del
4 Carmen Garrigós Selva.

5
6 *Analytical Chemistry, Nutrition & Food Sciences Department, University of Alicante,*
7 *03080, Alicante, Spain.*

8
9
10
11
12
13
14
15
16 *All correspondence should be addressed to this author:

17 Arantzazu Valdés García

18 *Analytical Chemistry, Nutrition & Food Sciences Department, University of Alicante,*
19 *03080, Alicante, Spain.*

20 Tel: +34 965903400. Ext 1187. Fax: +34 965903527.

21 E-mail: arancha.valdes@ua.es

26 **ABSTRACT**

27 Poly(ϵ -caprolactone), PCL, degradation by microorganisms is a very interesting feature
28 for its potential use in massive applications, such as food packaging. Blends of PCL
29 with natural fibres, such as those from agricultural and food processing wastes, have
30 proved effective by permitting a substantial reduction of the material costs, but also
31 playing a role as reinforcement in mechanical properties. This study is focused on the
32 evaluation of morphological, mechanical, thermal, barrier properties and degradation in
33 composting environment of new bio-composites based on PCL and almond skin (AS)
34 filler at different contents (0, 10, 20 and 30 wt%). Results showed a clear improvement
35 in mechanical properties, corresponding to a gain in elastic modulus of 17% at 10 wt%
36 particle loading. Lower melting and crystallization enthalpies and higher crystallinity
37 values were obtained for bio-composites compared with neat PCL. Some decrease in
38 thermal stability and increase in oxygen and water vapour barrier properties were also
39 observed for composites with increasing filler content. PCL/AS composites showed
40 higher biodegradability than pure PCL, which can be explained in terms of the
41 depressed crystallization enthalpy of the polymer matrix and improved hydrophilicity.
42 PCL-based composites reinforced with almond skin filler at 10 wt% loading have
43 shown as promising environmentally-friendly materials for food packaging showing a
44 high disintegration rate, increasing the added-value potential of agricultural wastes and
45 reducing the packaging cost.

46

47

48 **Keywords:** Bio-composites, Degradation, Poly(ϵ -caprolactone), Almond skin,
49 Reinforcement.

50

51 1. Introduction

52 Nowadays there is a growing interest in the development of biodegradable
53 polymers to reduce the dependence on fossil fuels and to change to sustainable
54 materials. Poly(ϵ -caprolactone), PCL, is a biodegradable semicrystalline and linear
55 aliphatic polyester produced by chemical synthesis from crude oil via the ring opening
56 polymerization of caprolactone monomer. PCL has shown degradation by the action of
57 aerobic and anaerobic microorganisms that are widely distributed in various
58 ecosystems, being its biodegradation very slow and leading to the formation of carbon
59 dioxide, water, methane, biomass and mineral salts [1-3]. However, large-scale
60 application of PCL has been limited because of its relative high price (ranging 4.50-6.00
61 € per kg) [4], as well as some intrinsic inferior properties [5].

62 PCL is one of the most widely studied biopolymers and has FDA approval in
63 various devices for medical applications [6]. The use of PCL for food packaging
64 applications has been recently reported by several authors, since the main commercial
65 application of PCL is in the manufacture of biodegradable bottles and compostable bags
66 [7]. In this sense, Martinez et al. suggested that the combination of cold storage with
67 PCL incorporating cinnamaldehyde, as a natural biocide agent, could be suitable for
68 the controlled diffusion of this agent extending the shelf-life of packaged food products
69 [8]. Antimicrobial PCL nanocomposites with thymol were also developed by Sánchez et
70 al [9]. On the other hand, Pérez et al. [10] developed an interesting storage system for
71 refrigeration by using PCL and encapsulated dodecane obtaining coating materials with
72 energy storage capacity. Blends of chitosan and PCL were studied by Swapna et al.
73 showing good tensile strength and low water vapour permeability, for the potential
74 application in fruits and vegetables packaging to extended their storage life [11].

75 Ludueña et al. also studied PCL with different lignocellulosic fillers for food packaging
76 applications [12].

77 Blending PCL with other materials, such as natural fibres, has proved to be an
78 effective method to reduce the final price of the material and enhance the
79 biodegradability of the resulting composites. Natural fibres also act as reinforcement by
80 improving mechanical properties, expanding the application areas of the obtained
81 composites. The main advantages of such fibres are their good mechanical performance,
82 low cost, renewability and biodegradability [12]. In general, natural fibres are suitable
83 for reinforcing plastics due to their relatively high strength, stiffness and low density
84 [13]. Agricultural by-products are alternative lignocellulosic materials, which are
85 produced in large quantities every year [5]. Different types of cellulose based natural
86 fibres and agricultural by-products (such as wood fibre [3]; agricultural cotton, cellulose
87 and hydrolyzed-cellulose [12]; flax and rami fibres [14,15]; nanocrystalline cellulose
88 from bleached softwood kraft pulp [7]; rice husk; abaca fibres; wood flour, lignin and
89 wheat gluten [16]) have been successfully incorporated as fillers into PCL to obtain
90 biodegradable composites.

91 Almond (*Prunus amygdalus L.*) is an important crop cultivated in countries such
92 as USA, Spain, Morocco, Iran and Turkey, with a worldwide production about 2.3
93 million tones in 2009 [17]. Industrial processing of almonds starts with the removal of
94 the external coating, with the skin contributing to around 6.0-8.4 % of the seed [18].
95 This biodegradable residue is considered to have one of the highest fibre contents of all
96 edible nuts (around 12%), among other interesting compounds such as flavonoids and
97 phenolic acids with high antioxidant activity [19]. The percentage of by-products
98 obtained from industrial processing of almonds is consequently very high and industries
99 are forced to consider ways of treating or using them. Up to now, the application of

100 these agricultural residues has not received enough attention, causing potential disposal
101 problems; and most of them are just incinerated or dumped without control causing
102 several environmental problems [20] or used as animal feeds [5]. For this reason, the
103 incorporation of low-cost almond skin (AS) residues into a biodegradable polymer
104 (such as PCL) is an attractive alternative to transform agricultural residues into useful
105 industrial resources, with a positive benefit on environment, energy and economy.

106 The research on almond reinforced composites from the literature is not very
107 extensive and it is limited to the use of almond shell as filler. Pirayesh and col. studied
108 the suitability of using almond and walnut/almond shells in wood-based composite
109 manufacturing, significantly reducing the formaldehyde emissions as well as highly
110 improving water resistance of the panels [21,22]. Regarding polymer-based composites,
111 Gürü et al. used almond shells as a filler material for urea-formaldehyde-based
112 composites [23]. Finally, almond shells particles were used as reinforcement in a
113 thermoplastic matrix as polypropylene, with and without different compatibilizers, by
114 using various particle contents up to 30 wt% [24]; obtaining a clear improvement in
115 mechanical and rheological properties.

116 To the best of our knowledge, there is no information in the literature on using
117 almond skin (AS) in the production of PCL bio-composites. Therefore, the aim of this
118 work is the development and characterization of novel PCL/AS bio-composites with
119 different AS residue contents (0, 10, 20 and 30 wt%), giving some added-value to
120 agricultural wastes. Special effort will be focused in evaluating the effect of the filler
121 addition on the morphological, mechanical, thermal, barrier properties and the
122 degradation behaviour in composting conditions of the obtained bio-composites. All
123 these properties are relevant aspects for packaging applications.

124

125 2. Experimental

126 2.1. Materials

127 Poly(ϵ -caprolactone) (PCL, CAPA®6800) commercial grade (pellets, $M_n =$
128 80.000, density = 1.1 g cm^{-3}) was kindly supplied by Perstorp Holding AB (Sweden).

129 Almond skins used as filler were supplied by “Almendras Llopis” (Alicante,
130 Spain) as an industrial by-product. They were grounded with a high speed rotor mill
131 (Ultra Centrifugal Mill ZM 200, RETSCH, Haan, Germany) equipped with a 1 mm
132 sieve size. The AS fraction obtained was then dried in a laboratory oven at $100 \text{ }^\circ\text{C}$ for
133 24 h to moisture content of 0-1 %. The particle size of the resulting AS filler was
134 determined by optical microscopy at 50x magnification with a mean diameter of $50 \text{ }\mu\text{m}$.

136 2.2. Bio-composites preparation

137 PCL/AS composites were processed by melt blending in a Haake PolyLab QC
138 mixer (ThermoFischer Scientific, Waltham, MA, USA) at $80 \text{ }^\circ\text{C}$ for 5 min at 100 rpm.
139 Before processing, PCL was left in an oven at $50 \text{ }^\circ\text{C}$ for 20 h to eliminate moisture. Four
140 different formulations were obtained by adding to the polymer different AS filler
141 contents (0, 10, 20 and 30 wt%). The 50 cm^3 mixing chamber was filled with 50 g total
142 mass.

143 Films were obtained by compression-moulding at $120 \text{ }^\circ\text{C}$ in a hot-plate hydraulic
144 press (Carver Inc, Model 3850, USA). Materials were kept between the plates at
145 atmospheric pressure for 5 min until melting and then they were successively pressed
146 under 2 MPa (1 min), 3 MPa (1 min) and finally 5 MPa (5 min) to liberate the trapped
147 air bubbles. The average thickness of the obtained films was $210 \pm 1 \text{ }\mu\text{m}$ measured with
148 a 293 MDC-Lite Digimatic Micrometer (Mitutoyo, Japan) at five random positions,
149 after 48 h of conditioning at 50 % relative humidity (RH) and $23 \text{ }^\circ\text{C}$. The obtained

150 composite films were named as PCL, PCL10%, PCL20% and PCL30%; where the
151 number is the percentage filler content by weight.

152

153 2.3. Bio-composites characterization

154 2.3.1. Morphological analysis

155 The cryo-fractured surfaces of bio-composite films were analyzed by using a
156 JEOL JSM-840 scanning electron microscope (Peabody, MA, USA) under an
157 acceleration voltage of 15 kV. Samples were coated with gold under vacuum using a
158 SCD 004 Balzers sputter coater (Bal Tec. AG, Fürstentum, Lichtenstein) prior to
159 scanning in order to increase their electrical conductivity. Images were registered at
160 magnifications 500x in order to study the filler dispersion.

161

162 2.3.2. Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

163 ATR-FTIR spectra were collected by using a Bruker Analytik IFS 66 FTIR
164 spectrometer (Ettlingen, Germany) equipped with a DTGS KBr detector, a Golden Gate
165 Single Reflection Diamond ATR accessory (incident angle of 45°), and OPUS 3.1 data
166 collection software program. Films ($1 \times 1 \text{ mm}^2$) were directly placed on the ATR crystal
167 area. Spectra were recorded in the absorbance mode from 4.000 to 600 cm^{-1} , using 64
168 scans and 4 cm^{-1} resolution, and corrected against the background spectrum of air. Two
169 spectra replicates were obtained for each sample.

170

171 2.3.3. Mechanical properties

172 Tensile tests were performed using a 3340 Series Single Column System Instron
173 Instrument, LR30K model (Fareham Hants, UK) equipped with a 2 kN load cell. Tests
174 were performed in rectangular probes ($100 \times 10 \text{ mm}^2$), an initial grip separation of 60

175 mm and crosshead speed of 25 mm min⁻¹. Before testing, all samples were equilibrated
176 for 48 h at 50 % RH. Percentage elongation at break and elastic modulus were
177 calculated from the resulting stress-strain curves according to ASTM D882-09 standard
178 [25]. Tests were carried out at room temperature. Five repetitions were performed for
179 each film composition, and mean values were reported.

180

181 2.3.4. Barrier properties

182 Water absorption by bio-composite films was determined in triplicate according
183 to UNE-EN ISO 62:2008 standard [26]. Samples (8 cm length x 1 cm width x 4 mm
184 thick) were dried in a vacuum oven at 23 °C for 4 h, cooled in a desiccator, and then
185 immediately weighed to the nearest 0.001 g. Thereafter, samples were immersed in
186 distilled water and maintained at 23 °C and 50 % RH. Finally, samples were taken out at
187 different times, wiped out properly and then reweighed. Water absorption was
188 calculated according to the formula:

$$189 \quad (W_t - W_0)/W_t \times 100\% \quad (1)$$

190 where W_0 was the sample weight prior to water adsorption experiment and W_t was the
191 final mass at the pre-determined time t .

192 Water vapour permeability (WVP) was determined in triplicate according to UNE
193 53097:2002 standard [27] by using the Desiccant Method (CaCl_2). Samples of 95 mm
194 diameter were fixed with paraffin on the top of aluminium capsules containing CaCl_2 ,
195 and they were placed in a climate chamber (Dycometal, Barcelona, Spain) at 20.0 ± 0.1
196 °C and 50 ± 2 % RH. Capsules were periodically weighed until the steady state was
197 reached and no significant changes in mass were noticed.

198 Oxygen transmission rate (OTR) tests were carried out with an oxygen
199 permeation analyzer (8500 model Systech Instruments, Metrotec S.A, Spain). Bio-

200 composite films were cut into 14-cm diameter circles for each formulation and they
201 were clamped in the diffusion chamber at 25 ± 1 °C. Tests were carried out by
202 introducing O₂ (99.9% purity) into the upper half of the diffusion chamber while N₂ was
203 injected into the lower half, where an oxygen sensor was located. Tests were performed
204 in triplicate and were expressed as oxygen transmission rate per film thickness (OTR·e).

205

206 2.3.5. Thermal properties

207 Differential scanning calorimetry (DSC) tests were conducted in triplicate by
208 using a TA DSC Q-2000 instrument (New Castle, DE, USA) under inert N₂ atmosphere
209 (50 mL min^{-1}). Films (3.0 ± 0.1 mg) were introduced in aluminium pans and were
210 submitted to the following thermal program: heating from -80 °C to 160 °C (3 min
211 hold), cooling to -80 °C (3 min hold) and heating to 160 °C, all steps at 10 °C min^{-1} .
212 Calorimetric curves were analysed using the Universal Analysis TM Software (TA
213 Instruments, New Castle, DE) to obtain crystallization and melting parameters which
214 were determined from the second heating scan. The degree of crystallinity (χ_c) of each
215 material was calculated by equation (2):

$$216 \quad X_c = \frac{\Delta H_m}{w \cdot \Delta H_m^0} * 100 \quad (2)$$

217 where ΔH_m is the experimental melting enthalpy of the sample, w is the PCL weight
218 fraction in the bio-composite film and ΔH_m^0 is the melting enthalpy of 100 % crystalline
219 PCL (136 J g^{-1}) [12].

220 Thermogravimetric analysis (TGA) was performed in a TGA/SDTA 851 Mettler
221 Toledo (Schwarzenbach, Switzerland) thermal analyzer. Films (4.0 ± 0.1 mg) were
222 weighed in alumina pans and were heated from 30 °C to 700 °C at 10 °C min^{-1} under N₂
223 atmosphere (50 mL min^{-1}). Analyses were performed in triplicate and two parameters
224 were determined: initial degradation temperature, T_i (°C), calculated at 5 % of weight

225 loss; and temperature of maximum degradation, T_{\max} (°C), corresponding to the
226 maximum decomposition rate.

227

228 2.3.6. Disintegration tests

229 Disintegration tests in composting conditions were carried out as reported by
230 Ludeña et al. and following ISO 20200 standard method using commercial compost
231 with certain amount of sawdust, rabbit food, starch, oil and urea [12,28]. Tested samples
232 were obtained from the previously prepared films, which were cut in square pieces (15 x
233 15 x 0.2 mm³), buried at 5 cm depth in perforated boxes and incubated at 25 °C. The
234 aerobic conditions were guaranteed by mixing the compost softly and by the periodical
235 addition of water according to the standard requirements.

236 After disintegration experiments (0, 7, 10, 15, 30, 45, 60 and 75 days), samples
237 were removed from the compost and immediately washed with distilled water to
238 remove traces of compost extracted from the container and to stop any further microbial
239 reaction. Then, samples were dried at 23 °C and 50 % RH for 24 h before gravimetical
240 analysis. The disintegrability value for each burial sample was obtained by using
241 equation (3):

$$242 \text{ Disintegrability (\%)} = [(w_0 - w_t)/w_0] \cdot 100 \quad (3)$$

243 where w_0 is the initial mass and w_t is the remaining mass at different stages of
244 incubation. All results are the average of two replicates.

245 Evaluation of degradation was completed by taking photographs of samples for
246 visual evaluation of physical alterations with disintegration time. DSC tests, as
247 previously described in section 2.3.5, were used in order to establish changes in the
248 structure of the degraded composite films.

249

250 2.4. Statistical analysis

251 Statistical analysis of results was performed with SPSS commercial software
252 (Version 15.0, Chicago, IL). A one-way analysis of variance (ANOVA) was carried out.
253 Differences between means were assessed on the basis of confidence intervals using the
254 Tukey test at a $p \leq 0.05$ significance level.

255

256 **3. Results and discussion**

257 3.1. Morphological analysis

258 The surface morphology of neat PCL and PCL/AS composite films was studied
259 by scanning electron microscopy (Fig. 1). As it can be seen, regions with dispersed filler
260 and some others with agglomerates were observed, being more evident in PCL with 30
261 wt%. As a result, the dispersion of AS particles inside the PCL matrix was less efficient
262 for the higher weight fraction samples, such as 20 and 30 wt% formulations. Similar
263 results were reported by Ludueña et al. for PCL based composites containing different
264 lignocellulosic filler types and contents [12]. This fact could be attributed to the high
265 hydrophilicity of the filler, and hence poor polymer/filler compatibility since PCL is
266 strongly hydrophobic; as well as to the incremented filler exposed surface area that
267 promotes the formation of hydrogen bonds between the individual hydrophilic fibres.

268

269 3.2. Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

270 Fig. 2 shows the ATR-FTIR spectra obtained for neat PCL and PCL30%
271 composite. The observed features are characteristic of PCL polymer and similar results
272 have been reported by other authors [29,30]. Table 1 shows the average of the main
273 significant bands observed for each sample in the spectra.

274 Significant differences were observed between neat PCL and the obtained bio-
275 composite films as a result of the addition of the AS residue regarding the wavenumber

276 and maximum absorbance values of the wide band appearing at 3400 cm^{-1} which is
277 characteristic of the O-H bonds ($p < 0.05$). As a result, a significant increase in
278 absorbance was obtained for this band with increasing AS weight fraction in the
279 formulations ($p < 0.05$). This band is characteristic of the AS residue spectrum (Fig.
280 2.b), and it could be related with stretching vibrations of the hydroxyl groups of
281 carbohydrates such as glucose, galactose and manose as major components present in
282 AS [19,24]; which are formed by carbon, hydrogen and oxygen with general formula
283 $(\text{CH}_2\text{O})_n$.

284 In addition, statistical significant differences between neat PCL and bio-
285 composites were observed regarding the wavenumber value of the band observed at
286 $2940\text{-}2870\text{ cm}^{-1}$ ($p < 0.05$) (Fig. 2.c). In this case, as filler content increased, the
287 intensity of the band observed at 2943 cm^{-1} tended to decreased. This fact could be due
288 to a lower PCL content in the composites [29].

289 Significant differences between samples were also found regarding the peak at
290 1724 cm^{-1} due to the C=O bonding [31]. In this sense, the increment of AS content in
291 the bio-composites is expected to increase the attached C=O functional groups while
292 decreasing the free ones, which are related to the decrease in the band intensity
293 observed at 1724 cm^{-1} (Fig. 2.d) [31,32]. Finally, the absorbance of the bands
294 corresponding to the C–O lactones stretching (1180 cm^{-1}), and C-O-C stretching (1045
295 cm^{-1}) also decreased when polymer content was reduced [31,32].

296

297 3.3. Mechanical properties

298 The incorporation of AS particles clearly influenced the mechanical properties of
299 pure PCL matrix with increasing weight fraction (Table 2). As a result, a significant
300 increase in the elastic modulus of these samples was observed with the addition of the

301 almond residue ($p < 0.05$) for PCL10% and PCL20%. This fact is due to the high tensile
302 modulus of particles compared with neat PCL and indicates that the rigidity of the
303 material increased with the addition of the filler [24]. The highest elastic modulus value
304 was obtained at 10% loading, in contrast with PCL30% which showed lower value than
305 neat PCL. These results are in agreement with the filler dispersion inside the matrix
306 previously analyzed by SEM; where higher filler dispersion and better adhesion
307 between AS residue and PCL matrix was observed for PCL10% whereas some
308 agglomeration of the filler takes place for PCL30% (Fig. 1).

309 The incorporation of the filler also drives to a significant decrease in the
310 elongation at break with increasing AS content ($p < 0.05$). As it can be seen (Table 2),
311 all bio-composite films containing the AS residue showed lower values of elongation at
312 break than neat PCL, obtaining the lowest value at 30% loading. The decreased in
313 elongation at break values may be related to the increased stiffness of composite films
314 by the addition of the AS residue because the fibre restricted the polymer chain
315 elongation [33-35]. The elongation at break is affected by the volume fraction of the
316 added reinforcement, the dispersion in the matrix and the interaction between the
317 reinforcement and the matrix [36]. The effectiveness of composites material largely
318 depends on their ability to transfer stress from the polymer matrix (continuous phase) to
319 fillers (dispersed phase) [24]. In this sense, low interactions between filler and matrix
320 are responsible for an effect of stress concentration, and they generate the beginning of
321 the fracture [37]. The decrease in of elongation at break with the addition of fibres is
322 commonly observed in thermoplastic composites, where the addition of stiff
323 reinforcements causes stress concentrations [36]. In this case, higher AS loading in PCL
324 composite films results in poor compatibility between phases, in agreement with the
325 obtained SEM results, causing substantial local stress concentrations, accelerating

326 failure and sample break. Similar results were obtained by Ludueña et al. when studying
327 the mechanical behaviour of PCL composites containing different lignocellulosic fillers
328 at different concentrations [12].

329 These results clearly suggest that AS residues could act as reinforcement agents
330 in PCL composite films at 10 wt% loading [34]. In general, the mechanical properties of
331 fibres-polymer composites are a consequence of the combination of different
332 parameters: particle size, highest or lowest chemical compatibility, interfacial strength,
333 filler dispersion and filler aspect ratio and particle loading [12,24].

334

335 3.4. Barrier properties.

336 Results obtained for oxygen transmission rate per film thickness (e), $OTR \cdot e$, for
337 PCL and PCL/AS composite films are shown in Table 2. As it can be seen, bio-
338 composite films containing AS showed significant higher $OTR \cdot e$ values ($p < 0.05$)
339 compared with neat PCL. No significant differences were observed by comparing
340 $OTR \cdot e$ results for films containing 10 and 20 wt% of filler ($p > 0.05$). However,
341 PCL30% films showed a great increase in $OTR \cdot e$ values suggesting a possible filler
342 agglomeration in films with higher fibre loading; as it was already observed by SEM.

343 Table 2 also shows the WVP values obtained for PCL and PCL/AS composites.
344 Slightly higher values were observed for PCL20% and PCL30% formulations compared
345 to the neat matrix ($p < 0.05$). However, no significant differences were found for neat
346 PCL and PCL10% composite ($p > 0.05$). In general, results observed for OTR and WVP
347 values increased with the filler content, which can be attributed to agglomeration
348 causing a reduction in the matrix homogeneity and cohesion and leading to preferential
349 penetrant paths and to detrimental effects in barrier properties [38].

350 When considering barrier properties, a balance between different mechanisms has
351 been reported to be responsible of the final behaviour of composites [12]: (1) the
352 crystallinity degree of the matrix goes down by the presence of the filler, making the
353 matrix more permeable to water or oxygen molecules; (2) the presence of the filler
354 increases the tortuosity of the pathway for water or oxygen molecules to pass through
355 the film; (3) weak interfacial strength and agglomeration of the filler promotes the
356 generation of voids in the polymer/filler interface making easier the transport of the
357 water or oxygen molecules through these regions.

358 Regarding water absorption, Fig. 3 compares the curves obtained for neat PCL
359 and PCL/AS composites at 23 °C and 50 % RH. As it was expected, higher water
360 absorption values for samples with increased AS residue contents were obtained,
361 showing the neat matrix the lowest value. Water absorption largely depends on the
362 hygroscopic components present in the biocomposite; so, if the polymer matrix is
363 hydrophobic it may act as a semipermeable membrane. Moisture penetration into
364 composite materials has been reported to be conducted by three different mechanisms:
365 (1) diffusion of water molecules inside the microgaps between polymer chains and
366 natural fillers; (2) capillary transport into the gaps and flaws at the interfaces between
367 fibres and polymer because of incomplete wettability and impregnation; (3) transport
368 through microcracks in the matrix, formed during the compounding process.
369 Accordingly, water absorption in biocomposites can be influenced by several factors,
370 such as fibre loading (higher fibre content should contribute to higher moisture
371 absorption), the chemical nature of lignocellulosic fillers, fibre geometry, and,
372 especially, the compatibilization between matrix and fillers (improved interfacial
373 adhesion would result in fewer and smaller microgaps where water uptake may occur)
374 [1].

375

376 3.5. Thermal properties

377 3.5.1. DSC analysis

378 Fig. 4 shows the thermograms, corresponding to the second heating scan, of neat
379 PCL and PCL/AS composites. All materials exhibited two energy transitions: an
380 exothermic crystallization around 30 °C and an endothermic melting at approximately
381 55 °C, characteristics of PCL by its semi-crystalline structure. A significant decrease in
382 melting parameters (temperature and enthalpy) ($p < 0.05$) was observed for PCL30%
383 (Table 3). In this sense, the incorporation of the AS residue can restrict the periodic
384 arrangements of PCL chains into its lattice, leading to some loss in the polymer
385 crystallinity in bio-composites than in neat PCL, resulting in decreased melting
386 parameters [5]. Regarding crystallization parameters, the observed decrease in ΔH_c and
387 increase in T_c in PCL30% (Table 3) ($p < 0.05$) suggested a decrease on the extent and
388 crystallization kinetics of PCL upon heating, probably due to highly restricted
389 segmental motions at the organic–inorganic interface. Indeed, the glass transition
390 temperature (T_g) of this material increased about 5 °C (Table 3), thus confirming the
391 occurrence of restricted polymer chain movements after the addition of AS particles
392 [39]. These results are in agreement with those reported in a previous work when
393 studying the effect of cellulose nanocrystals incorporation obtained by acid hydrolysis
394 of *Luffa cylindrica* fibres as reinforcing phase in PCL nano-biocomposites. In this
395 sense, it was suggested that T_g values displacement could be related to the restriction of
396 the rotational backbone motions of PCL polymer chains through the establishment of
397 hydrogen bonding forces between individual fibres into the polymer matrix [32].

398 Finally, the crystallinity degree obtained for all materials are also shown in Table
399 3. Previous studies demonstrated that PCL is a partial crystalline polyester with

400 crystallinity between 40–60% [5]. As it can be seen from Table 3, the crystallinity of the
401 PCL/AS composites increased at higher AS loading. These results are consistent with
402 those found by Chun et al. when studying cocoa pod husk-filled polypropylene
403 composites and this behaviour is due to the nucleating effect of the AS residue
404 modifying the crystallisation by increasing the number of nucleating sites [40]. For
405 PCL30% this phenomena could be restricted in some extent by filler agglomeration
406 with reduces the filler exposed surface area [12].

407

408 3.5.2. Thermal stability (TGA)

409 The thermal stability of the AS residue was studied by TGA. The DTG curve
410 obtained for AS particles (Fig. 5) showed an initial step between 40 and 150 °C as the
411 result of the loss of volatile compounds and water [41]. Three main thermal degradation
412 peaks were observed. A similar DTG profile was observed by Essabir et al. when
413 studying the thermal stability of almond shells particles used as reinforcement in
414 polypropylene matrices. The first peak observed between 285 °C and 320 °C was
415 attributed to the thermal depolymerisation of hemicelluloses, and the second peak which
416 occurs in the 320–400 °C range corresponded to the cellulose degradation. Finally, the
417 third stage is associated to the degradation of lignin at 420 °C, which occurs slowly in
418 the temperature range due to its complex structure [24].

419 In the case of PCL, thermal degradation in inert atmosphere takes place through
420 the rupture of the polyester chains via ester pyrolysis reaction with the release of CO₂,
421 H₂O and formation of carboxylic acid groups. Pyrolysis provokes chain cleavages
422 randomly distributed along the chain and when two pyrolysis reactions occur with
423 neighbouring ester functions, one of the reaction products is 5-hexenoic acid [39].

424 Fig. 5 also shows DTG curves obtained for neat PCL and PCL/AS in nitrogen. As
425 it can be seen, at low filler contents (10 wt%) the thermal stability of the PCL matrix
426 was not significantly affected by the presence of the filler, showing initial and
427 maximum degradation temperatures around 385 and 415 °C, respectively (Table 3).
428 However, since filler loading increased some extra peaks related to the thermal
429 degradation of the AS residues were observed, being more evident for the PCL30%
430 film. This behaviour is related to the lower matrix homogeneity of this formulation.
431 Similar results were obtained by Ludueña et al. for the incorporation of some
432 lignocellulosic fillers into PCL at different concentrations [12]. As a result, some
433 decrease in thermal stability was observed for PCL20% and PCL30% composites
434 regarding T_{ini} and T_{max} values (Table 3).

435 In conclusion, the addition of AS particles to the polymer matrix at 20 and 30
436 wt% may promote earlier degradation of the overall material. This behaviour was also
437 reported by Jiménez et al. when preparing mixtures based on PCL with different natural
438 fillers; since they found that the early formation of acidic products from cellulose and
439 hemicellulose decomposition promoted the random scission of ester linkages in a PCL
440 matrix reinforced with sisal fibres [42,43].

441

442 3.6. Disintegration tests

443 The effect of the addition of natural fibres on the biodegradation process of
444 biocomposites is an active topic of research. In general, the presence of lignocellulosic
445 reinforcements enhances the microbial attack and the biodegradation rates by promoting
446 biofouling and the adhesion of microorganisms to the surface. The kinetics of the
447 biodegradation process depends on different factors, such as the susceptibility of the
448 different components of the biocomposites; the interfacial adhesion by selecting the

449 type of natural filler that exhibits higher fibre-fibre and fibre-matrix interactions; the
450 hydrophilic nature of the polymeric matrix; and crystallinity. In this sense, PCL
451 biocomposites may exhibit slower biodegradation rates than other biopolymer-based
452 composites, due to their tailored semicrystalline structure and relative hydrophobicity
453 [1].

454

455 3.6.1. Physical alterations

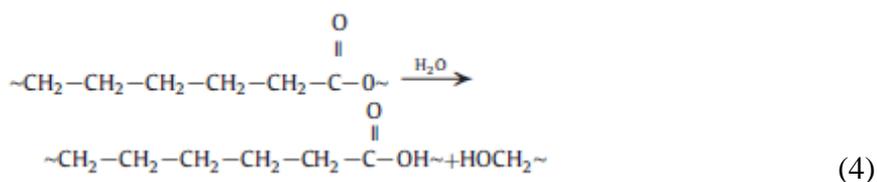
456 The visual evaluation of physical alterations of all samples at different
457 degradation times (0, 30 and 75 days) in composting conditions at 25 °C is shown in
458 Fig. 6. All samples showed considerable changes in their morphology after 30 days of
459 the disintegration study with a general roughing and holes formation. These
460 modifications were indicative of the beginning of the polymer hydrolytic degradation
461 process, which was related to the moisture absorption by the polymer matrix. In this
462 sense, the incorporation of AS residue accelerated the water intake as fibres facilitated
463 the access of water into the PCL matrix of the bio-composite films, and the
464 disintegration rate of PCL matrix became more pronounced with the increasing fibre
465 contents [16]. Results obtained at longer testing times showed that physical degradation
466 progressed with burial time resulting in the complete loss of their initial morphology
467 and general fragmentation after 75 days.

468 Fig. 7 shows the evolution of the disintegrability (%) as function of time for neat
469 PCL and PCL/AS composites in composting conditions. Before 15 days of treatment,
470 no significant differences were observed between all samples, showing a similar weight
471 loss ($p > 0.05$). However, significant differences between neat PCL and the rest of bio-
472 composites were observed after 15 testing days ($p < 0.05$). These differences could be
473 related to the presence of the fibre which can produce strong interactions during the

474 initial period due to the formation of H-bonds, producing a physical network which
 475 prevents the water uptake, and thus reducing the accessibility to soil microflora [35]. In
 476 this sense, the diffusivity of water is strongly influenced by the material's
 477 microstructure as well as porosity and water affinity of the polymer components. These
 478 kind of interactions between cellulose fibres and polymer matrices were reported by
 479 Dufresne et al. [44,45] for systems composed by thermoplastic starch and microfibrils
 480 obtained from potato pulp, observing a decrease in water uptake by increasing the
 481 cellulose contents. This phenomenon was ascribed to the formation of a microfibril
 482 network, which prevented the swelling of the biocomposite and water absorption.

483 The end of the disintegration study was 75 days, when PCL/AS bio-composites
 484 were considered to be totally disintegrated, according to the ISO 20200 standard
 485 requirements [28], which states 90 % disintegration for a biodegradable material. At that
 486 time, bio-composites containing 10-30 wt% of AS showed higher disintegration values
 487 that neat PCL. In this sense, it was reported that the addition of natural fillers, such as
 488 rice husk fibres, into PCL increased the disintegration rate as they could facilitate the
 489 access of water into the polymer matrix [16]; as water absorption tests have shown in
 490 this study. A similar tendency was also observed by other researchers for neat PCL and
 491 PCL-based composites in natural media, such as soil [5,12,37].

492 According to Fukushima, et al. [46] the main mechanism of PCL degradation
 493 involves the scission of PCL ester bonds by enzyme-catalyzed hydrolysis due to
 494 microorganisms present in the compost with the formation of alcohol and carboxylic
 495 acid groups, as shown in Scheme 4.



497 PCL degradation proceeds in two stages: random hydrolytic ester cleavage and
498 weight loss through the diffusion of oligomeric species from the bulk [47]. Then, the
499 biodegradation process is dependent on the water bio-availability that promotes the
500 microbial attack and the matrix hydrolysis. PCL exhibits high hydrophobicity, which
501 can inhibit the access of water to the polymer matrix during the degradation, and thus
502 retard the hydrolysis of ester bonds. The hydrophobicity of poly(ϵ -caprolactone) could
503 lead to surface erosion/degradation [47]. In contrast, AS is highly hydrophilic due to the
504 structure with multiple hydroxyl groups of carbohydrates. Therefore, the incorporation
505 of the AS can facilitate the access of water to the PCL matrix, leading to accelerated
506 degradation. Due to the natural origin of the AS, its presence can favour the enzymes
507 binding onto the material surface, thereby promoting the degradation of the
508 neighbouring PCL matrix [5]. Both effects are expected to be enhanced with increasing
509 AS loading.

510 The following characteristics of these fibres and their effect on the properties of
511 the polymer matrix have been reported to simultaneously affect the biodegradation
512 process of the composites [12]:

513 (1) The high hydrophilicity of natural fibres promotes the water intake and provides a
514 rougher support for microbial growth. Then, the presence of microorganisms in soil,
515 which are relatively active in hemicelluloses under suitable temperature and humidity
516 conditions, could accelerate the degradation process [35]. In later stages, cellulose
517 chains breakdown may contribute to the higher weight loss suffered by the bio-
518 composites.

519 (2) Fibre agglomerates can form micro-cavities promoting the water uptake, but also
520 drastically diminish the contact surface between the fibre and the polymer diminishing
521 the effect mentioned in Section (1).

522

523 3.6.2. Thermal analysis (DSC)

524 Fig. 8 shows the thermograms obtained for neat PCL and PCL/AS composites
525 corresponding to the second heating after 0, 15, 30 and 75 days of degradation in
526 compost. After 15 days, as the filler content increased composites showed a
527 considerable decrease in crystallization and melting enthalpies as the consequence of
528 the formation of less perfect crystals due to polymer chain scission during the hydrolytic
529 degradation [39]; being more noticeable for PCL20% and PCL30% after 30 days as
530 these energy transitions were no longer visible. These results are consistent with the
531 high extent of polymer degradation evidenced by the visual observations and
532 disintegrability analysis. They are probably related to the scission of polymer chains
533 preventing the formation of stable crystalline structure and to the mixing upon heating
534 of PCL with the enzymes secreted by microorganisms from compost (amorphous
535 macromolecules) [39]. No significant differences were observed in crystallization and
536 melting enthalpy values for neat PCL after 75 days, indicating the lower extent of
537 polymer degradation when compared to PCL/AS composites, in particular at high filler
538 loading. This was expected for a semicrystalline polymer such as PCL, since crystalline
539 regions show the tendency to retard water uptake [47].

540 It is well known that crystallinity plays an important role in the degradation
541 behaviour of the aliphatic polyesters [5]. The observed modifications on crystallization
542 enthalpy values (ΔH_c) for PCL-AS films during biodegradation are shown in Fig. 9. No
543 significant differences in ΔH_c ($p > 0.05$) were observed for neat PCL up to 30 testing
544 days. However, PCL containing 10 wt% of AS residue did not show significant
545 differences in ΔH_c values ($p > 0.05$) up to 15 days, in contrast to 20 and 30 wt%
546 formulations which showed a significant decrease with disintegration time ($p < 0.05$). It

547 can be concluded that the incorporation of almond skin led to reduction in crystallinity
548 of the polymer matrix accelerating the degradation process [12].

549

550 **4. Conclusions.**

551 Novel biodegradable composites based on poly(ϵ -caprolactone) (PCL) and
552 almond skin residues (AS) were produced. A remarkable improvement in mechanical
553 properties with the addition of AS particles was obtained indicating the potential use of
554 this residue as reinforcement agent in PCL composites. Furthermore, the presence of AS
555 filler accelerated the degradation of the PCL matrix in the composite films, being this
556 effect more pronounced with the increase in AS contents. This effect was explained in
557 terms of the reduction in crystallinity of the polymer matrix and the high hydrophilicity
558 of the natural fibres, promoting the water uptake and, consequently, the microbial attack
559 and hydrolysis of the PCL matrix.

560 The best performance regarding the studied properties was found for composite
561 films with 10 wt% AS loading. In this sense, mechanical properties were improved with
562 good adhesion between the AS residue and the PCL matrix, as observed by SEM. No
563 significant differences were observed regarding thermal degradation and barrier
564 properties compared to neat PCL. In conclusion, this formulation can be an interesting
565 environmentally-friendly material to be used for food packaging applications showing a
566 biodegradable nature and increasing the added-value potential of almond agricultural
567 wastes. In this sense, it is clear that some reduction in transparency of the polymer
568 matrix will be obtained with the AS filler incorporation, but the obtained formulation
569 could be suitable for the development of sustainable food trays and similar containers
570 where transparency is not an issue. Finally, an additional advantage is the reduction of
571 the packaging cost by adding this residue.

572

573 **Acknowledgements**

574 Authors would like to thank “Almendras Llopis S.A” for kindly providing the
575 almond skin by-product as well as to Spanish Ministry of Economy and
576 Competitiveness for financial support (MAT-2011-28468-C02-01). Arantzazu Valdés
577 acknowledges Conselleria de Educación (Spain) for ACIF/2010/172 Predoctoral
578 Research Training Grant.

579

580 **References**

- 581 [1] Vilaplana, F, Strömberg, E, Karlsson, S. Environmental and resource aspects of
582 sustainable biocomposites. *Polymer Degradation and Stability* 2010; 95: 2147-2161.
- 583 [2] Tokiwa, Y, Calabia, B, Ugwu, C, Aib, S. Biodegradability of Plastics. *International*
584 *Journal of Molecular Sciences* 2009; 10: 3722-3742.
- 585 [3] Bikiaris, DN, Papageorgiou, GZ, Achilias, DS, Pavlidou, EZ, Stergiou, A.
586 Miscibility and enzymatic degradation study of poly (ϵ -caprolactone)/poly(propylene
587 succinate) blends. *European Polymer Journal* 2007; 43:2491-2503.
- 588 [4] <http://www.bio-plastics.org> Last access December, 2013.
- 589 [5] Zhao Q, Tao J, Yam RCM, Mok ACK, Li RKY, Song C. Biodegradation behavior
590 of polycaprolactone/rice husk ecomposites in simulated soil medium. *Polymer*
591 *Degradation and Stability* 2008; 93:1571-1576.
- 592 [6] Woodruff, M., Werner, D. The return of a forgotten polymer-polycaprolactone in the
593 21st century. *Progress in Polymer Science* 2010; 35: 1217–1256.
- 594 [7] Khan, R, Beck, S, Dussault, D, Salmieri, S, Bouchard, J, Lacroix, M. Mechanical
595 and Barrier Properties of Nanocrystalline Cellulose Reinforced Poly(caprolactone)

- 596 Composites: Effect of Gamma Radiation. *Journal of Applied Polymer Science* 2013;
597 3038-3046.
- 598 [8] Martínez-Abad, A., Sánchez, G., Fuster, V., Lagarón, JM. Antibacterial performance
599 of solvent cast polycaprolactone (PCL) films containing essential oils. *Food Control*
600 2013; 34: 214-220.
- 601 [9] Sánchez-García, MD., Ocio, MJ., Gimenez, E., Lagarón, JM. Novel
602 Polycaprolactone Nanocomposites Containing Thymol of Interest in Antimicrobial Film
603 and Coating Applications 2008; 24: 239-251.
- 604 [10] Perez-Masia, R., Lopez-Rubio, A., Fabra, MJ., Lagarón, JM. Biodegradable
605 Polyester-Based Heat Management Materials of Interest in Refrigeration and Smart
606 Packaging Coatings. *Journal of applied polymer science* 2013; 130: 3251-3262.
- 607 [11] Swapna Joseph, C., Prashanth, H., Rastogi, NK., Indiramma, AR., Reddy, Y.,
608 Raghavarao, KSMS. Optimum Blend of Chitosan and Poly-(ϵ -caprolactone) for
609 Fabrication of Films for Food Packaging Applications. *Food Bioprocess Technol*
610 2011; 4: 1179–1185.
- 611 [12] Ludueña L, Vázquez A, Alvarez V. Effect of lignocellulosic filler type and content
612 on the behavior of polycaprolactone based eco-composites for packaging applications.
613 *Carbohydrate Polymers* 2012; 87:411– 421.
- 614 [13] Faruk O, Bledzki AK, Fink H-P, Sain M. Biocomposites reinforced with natural
615 fibers: 2000–2010. *Progress in Polymer Science* 2012; 37:1552– 1596.
- 616 [14] Arbelaiz A, Fernández B, Valea A, Mondragón I. Mechanical properties of short
617 flax fibre bundle/poly(ϵ -caprolactone) composites: influence of matrix modification and
618 fibre content. *Carbohydrate Polymers*, 2006; 64:224-232.

- 619 [15] Xu H, Wang I, Teng C, Yu M. Biodegradable composites: ramie fibre reinforced
620 PLLA-PCL composite prepared by in situ polymerization process. *Polymer Bulletin*
621 2008; 61:663-670.
- 622 [16] Wahit MU, Akos NI, Laftah WA. Influence of Natural Fibers on the Mechanical
623 Properties and Biodegradation of Poly(lactic acid) and Poly(ϵ -caprolactone)
624 Composites: A Review. *Polymer Composites* 2012; 1045-1053.
- 625 [17] Food and Agriculture organization of the United Nations. (FAOSTAT Database):
626 <http://faostat.fao.org/> Last access November, 2013
- 627 [18] Garrido I, Monagas M, Gómez-Cordovés C, Bartolomé B. Polyphenols and
628 antioxidant properties of almond skins: Influence of industrial processing. *Journal of*
629 *Food Science* 2008; 73(2):106-115.
- 630 [19] Mandalari G, Tomaino A, Arcoraci T, Martorana M, Turco VL, Cacciola F, Rich
631 GT, Bisignano C, Saija A, Dugo P, Cross KL, Parker ML, Waldron KW, Wickham M
632 SJ. Characterization of polyphenols, lipids and dietary fibre from almond skins
633 (*Amygdalus communis* L.). *Journal of Food Composition and Analysis* 2010;
634 23(2):166-174.
- 635 [20] Deniz F. Dye removal by almond shell residues: Studies on biosorption
636 performance and process design. *Materials Science and Engineering* 2013; C 33:2821–
637 2826.
- 638 [21] Pirayesh H, Khazaeian A. Using almond (*Prunus amygdalus* L.) shell as a bio-
639 waste resource in wood based composite. *Composites: Part B* 2012; 43:1475–1479.
- 640 [22] Pirayesh H, Khanjanzadeh H, Salari A. Effect of using walnut/almond shells on
641 the physical, mechanical properties and formaldehyde emission of particleboard.
642 *Composites: Part B* 2013; 45:858–863.

- 643 [23] Gürü M, Tekeli S, Bilici I. Manufacturing of urea-formaldehyde-based composite
644 particleboard from almond shell. *Materials and Design* 2006; 27:1148–51.
- 645 [24] Essabir H, Nekhlaoui S, Malta M, Bensalah MO, Arrakhiz FZ, Qaiss A, Bouhfid R.
646 Bio-composites based on polypropylene reinforced with Almond Shells particles:
647 Mechanical and thermal properties. *Materials and Design*, 2013; 51:225–230.
- 648 [25] ASTM D882-09. Standard test method for tensile properties of thin plastic
649 sheeting. 468 Annual Book of ASTM Standards. Amer. Soc. for Testing and Materials,
650 Philadelphia, PA.
- 651 [26] ISO 62:2008 Plastics: Determinations of water absorption- Determination of water
652 absorbed content after immersion into water at 23 °C.
- 653 [27] UNE 53097:2002 Sheet materials – Determination of water vapour transmission
654 rate – Gravimetric (dish) method.
- 655 [28] UNE-EN. ISO 20200:2006. Plastics - Determination of the degree of disintegration
656 of plastic materials under simulated composting conditions in a laboratory-scale test
657 (ISO 20200:2004). 2006.
- 658 [29] Hoidy WH, Al-Mulla EAJ, Al-Janabi KW. Mechanical and Thermal Properties of
659 PLLA/PCL Modified Clay Nanocomposites. *Journal of Polymers and the Environment*
660 2010; 18(4):608-616.
- 661 [30] Salmieri S, Lacroix M. Physicochemical Properties of Alginate/Polycaprolactone-
662 Based Films Containing Essential Oils. *Journal of Agricultural and Food Chemistry*
663 2006; 54:10205-102014.
- 664 [31] Sadeghi M, Mehdi Talakesh M, Ghalei B, Shafiei M. Preparation, characterization
665 and gas permeation properties of a polycaprolactone based polyurethane-silica
666 nanocomposite membrane. *Journal of Membrane Science* 2013; 427(0):21-29.

- 667 [32] Siqueira G, Brasa J, Follain N, Belbekhouche S, Marais S, Dufresnea A. Thermal
668 and mechanical properties of bio-nanocomposites reinforced by *Luffa cylindrica*
669 cellulose nanocrystals. *Carbohydrate Polymers*, 2013; 91:711– 717.
- 670 [33] Reixach R, Espinach F, Franco-Marqués E, Ramirez de Cartagena F, Pellicer N,
671 Tresserras J, Mutjé P. Modeling of the Tensile Moduli of Mechanical,
672 Thermomechanical, and Chemi-thermomechanical Pulps from Orange Tree Pruning.
673 *Polymer Composites* 2013; 1-7.
- 674 [34] Sharmin N, Khan RA, Salmieri S, Dussault D, Lacroix M. Fabrication and
675 Characterization of Biodegradable Composite Films Made of Using Poly(caprolactone)
676 Reinforced with Chitosan. *Journal of Polymer Environmental* 2012; 20:698–705.
- 677 [35] Di Franco CR, Busalmen JP, Ruseckaite RA, Vázquez A. Degradation of
678 Polycaprolactone/starch blends and composites with sisal fibre. *Polymer Degradation*
679 *and Stability* 2004; 86:95-103.
- 680 [36] Fortunati E, Armentano I, Zhou Q, Iannoni A, Saino E, Visai L, Berglund LA,
681 Kenny JM. Multifunctional bionanocomposite films of poly(lactic acid), cellulose
682 nanocrystals and silver nanoparticles. *Carbohydrate Polymers* 2012; 87:1596-1605.
- 683 [37] España, JM., Smaper, MD., Fages, E., Sánchez, LN, Balart, R. Investigation of the
684 Effect of Different Silane Coupling Agents on Mechanical Performance of Basalt Fiber
685 Composite Laminates with Biobased Epoxy Matrices. *Polymer composites* 2013: 376-
686 381.
- 687 [38] Sanchez-Garcia MD, Gimenez E, Lagaron JM. Morphology and barrier properties
688 of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers.
689 *Carbohydrate Polymers*, 2008; 71(2): 235–244.

- 690 [39] Fukushima K, Tabuani D, Abbate C, Arena M, Rizzarelli P. Preparation,
691 characterization and biodegradation of biopolymer nanocomposites based on fumed
692 silica. *European Polymer Journal* 2011; 47:139–152.
- 693 [40] Chun KS, Husseinsyah S, Osman H. Modified Cocoa Pod Husk-Filled
694 Polypropilene Composites by using Methacrylic Acid. *BioResources* 2013; 8 (3): 3260-
695 3275.
- 696 [41] Valdés A, Beltrán, A, Garrigós, MC. Characterization and Classification of
697 Almond Cultivars by Using Spectroscopic and Thermal Techniques. *Journal of Food*
698 *Science* 2013; 78 (2):C138-C144.
- 699 [42] Jiménez A, Ruseckaite R. Binary mixtures based on polycaprolactone and cellulose
700 derivatives. *Journal of Thermal Analysis and Calorimetry* 2007; 88(3):851-6.
- 701 [43] Ruseckaite RA, Jiménez A. Thermal degradation of mixtures of polycaprolactone
702 with cellulose derivatives. *Polymer Degradation and Stability* 2003; 81(2):353-8.
- 703 [44] Dufresne, A, Vignon, M. Improvement of Starch Film Performances Using
704 Cellulose Microfibrils. *Macromolecules* 1998; 31: 2693-2696.
- 705 [45] Anglés, N, Dufresne, A. Plasticized Starch/Tunicin Whiskers Nanocomposites. 1.
706 Structural Analysis. *Macromolecules* 2000; 33: 8344-8353.
- 707 [46] Fukushima K, Abbate C, Tabuani D, Gennari M, Rizzarelli P, Camino G.
708 Biodegradation trend of poly (ϵ -caprolactone) and nanocomposites. *Materials Science*
709 *and Engineering* 2010; C 30:566-574.
- 710 [47] Chouzouri G, Xanthos M. Degradation of aliphatic polyesters in the presence of
711 inorganic fillers. *Journal of Plastic Film & Sheeting* 2007; 23: 19-36.
- 712

713 **Figure Captions.**

714 **Fig. 1.** Scanning electron micrographs of the fractured surface of PCL/AS composites
715 (500x).

716 **Fig. 2.** ATR-FTIR spectra obtained for AS residue, neat PCL (—) and PCL30%
717 composite (—).

718 **Fig. 3.** Water absorption curves obtained for neat PCL and PCL/AS composites as a
719 function of time (n=3; 23 °C, 50 % RH).

720 **Fig. 4.** Melting (a) and crystallization (b) thermograms of neat PCL and PCL/AS
721 composite films, second heating.

722 **Fig. 5.** DTG curves obtained for AS residue, neat PCL and PCL/AS composites in nitrogen.

723 **Fig. 6.** Physical disintegration of PCL and PCL/AS composite films after 0, 30 and 75
724 days of disintegration in composting conditions at 25 °C.

725 **Fig. 7.** Disintegrability (%) of neat PCL and PCL/AS composite films as a function of
726 degradation time in composting conditions at 25 °C (n=2).

727 **Fig. 8.** DSC thermograms of PCL and PCL/AS composites at 0, 15, 30 and 75 days of
728 degradation in compost, second heating.

729 **Fig. 9.** Crystallization enthalpy values (ΔH_c) of neat PCL and PCL/AS composite films
730 as a function of degradation time in composting conditions at 25 °C (n=2).

731

732 **Table 1.** Main significant FTIR bands observed for PCL and PCL/AS composites.

Band (cm ⁻¹)	Structural group
3450	O-H stretching vibrations of hydroxyl groups
2943	Symmetric C-H stretching vibrations
2866	Asymmetric C-H stretching vibrations
1724	C=O lactones stretching
1470	Asymmetric COO- stretching
1365	Symmetric COO- stretching and O-H bending
1180	C-O lactones stretching
1045	C-O-C stretching

733

734

735 **Table 2.** Mechanical (mean \pm SD, n = 5) and barrier properties (mean \pm SD, n = 3)
 736 obtained for neat PCL and PCL/AS composites. Different superscripts within the same
 737 row indicate statistically significant different values ($p < 0.05$).

Parameter	Formulation			
	PCL	PCL 10%	PCL 20%	PCL 30%
Elastic Modulus (MPa)	335 \pm 8 ^a	392 \pm 8 ^b	365 \pm 4 ^c	280 \pm 4 ^d
Elongation at break (%)	68 \pm 7 ^a	38 \pm 1 ^b	24 \pm 1 ^c	18 \pm 1 ^d
OTR.e (cm ³ mm m ⁻² day)	90 \pm 11 ^a	173 \pm 8 ^b	160 \pm 10 ^b	554 \pm 20 ^c
WVP x 10 ⁻¹⁴ (Kg m Pa ⁻¹ s ⁻¹ m ⁻²)	2.5 \pm 0.5 ^a	2.2 \pm 0.1 ^a	3.1 \pm 0.7 ^b	3.2 \pm 0.3 ^c

738

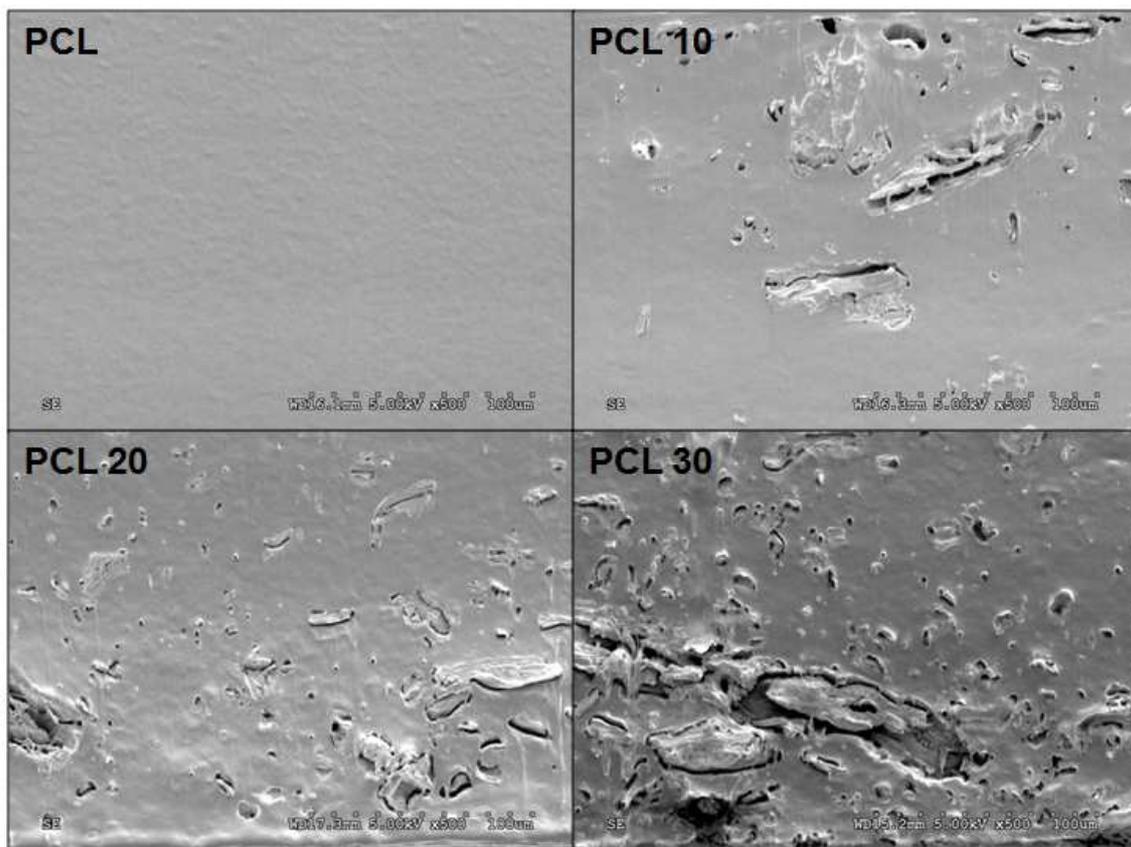
739

740 **Table 3.** Thermal properties (mean \pm SD, n = 3) obtained for neat PCL and PCL/AS
 741 composites. Different superscripts within the same column indicate statistically
 742 significant different values ($p < 0.05$).

Formulation	ΔH_c (J g ⁻¹)	T _c (°C)	ΔH_m (J g ⁻¹)	T _m (°C)	χ_c (%)	T _g (°C)	T _{ini} (°C)	T _{max} (°C)
Control	59 \pm 1 ^a	30 \pm 1 ^a	59 \pm 1 ^a	55 \pm 1 ^a	43 \pm 1 ^a	-61 \pm 2 ^a	385 \pm 2 ^a	415 \pm 1 ^a
PCL 10%	55 \pm 5 ^a	30 \pm 1 ^a	55 \pm 6 ^a	55 \pm 1 ^a	45 \pm 5 ^a	-60 \pm 1 ^a	381 \pm 2 ^a	415 \pm 1 ^a
PCL 20%	57 \pm 2 ^a	32 \pm 1 ^b	54 \pm 2 ^a	55 \pm 1 ^a	50 \pm 2 ^a	-57 \pm 1 ^b	292 \pm 7 ^b	411 \pm 3 ^b
PCL 30%	54 \pm 1 ^b	33 \pm 1 ^b	44 \pm 1 ^b	44 \pm 1 ^b	46 \pm 1 ^b	-56 \pm 1 ^b	272 \pm 5 ^c	404 \pm 5 ^c

743

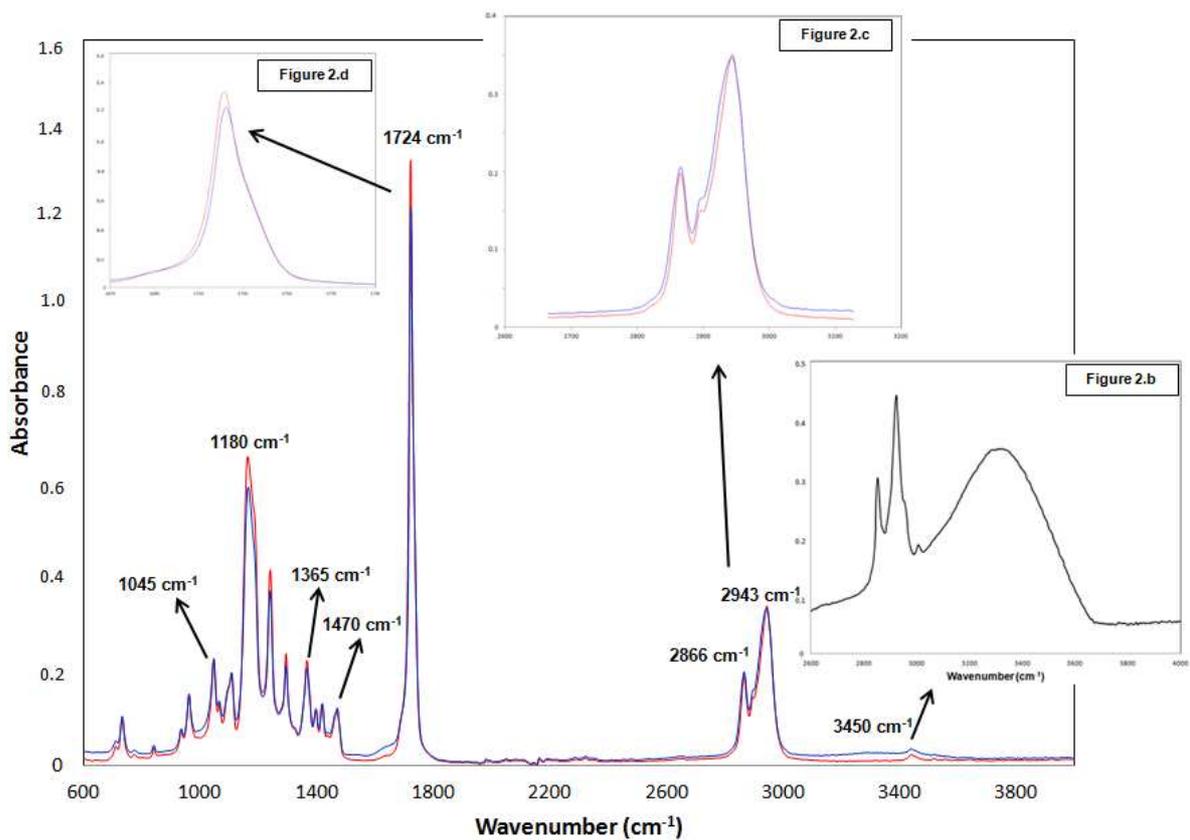
744



745

746 **Fig. 1.** Scanning electron micrographs of the fractured surface of PCL/AS composites

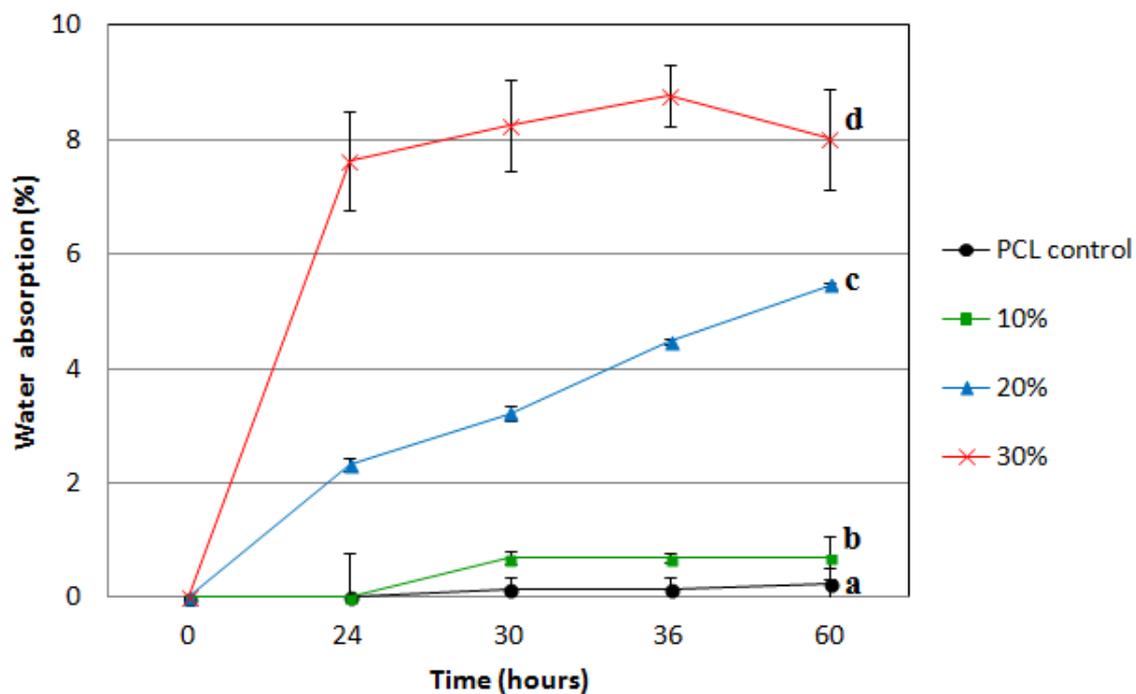
747 (500x).



748

749 **Fig. 2.** ATR-FTIR spectra obtained for AS residue, neat PCL (—) and PCL30%
 750 composite (—).

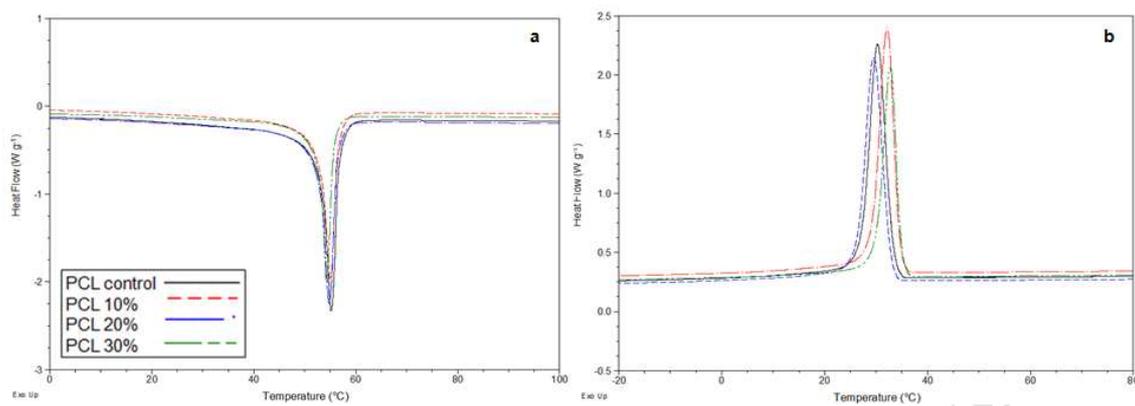
751



752

753 **Fig. 3.** Water absorption curves obtained for neat PCL and PCL/AS composites as a
754 function of time (n=3; 23 °C, 50 % RH).

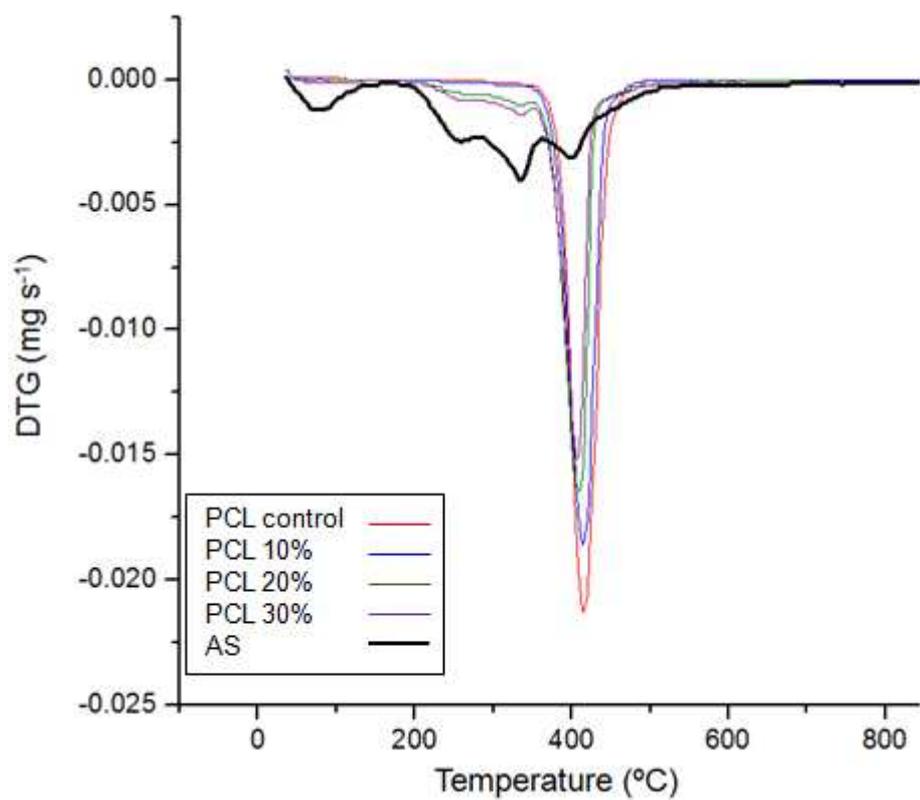
755



756

757 **Fig. 4.** Melting (a) and crystallization (b) thermograms of neat PCL and PCL/AS
758 composite films, second heating.

759



760

761 **Fig. 5.** DTG curves obtained for AS residue, neat PCL and PCL/AS composites in
762 nitrogen.

763

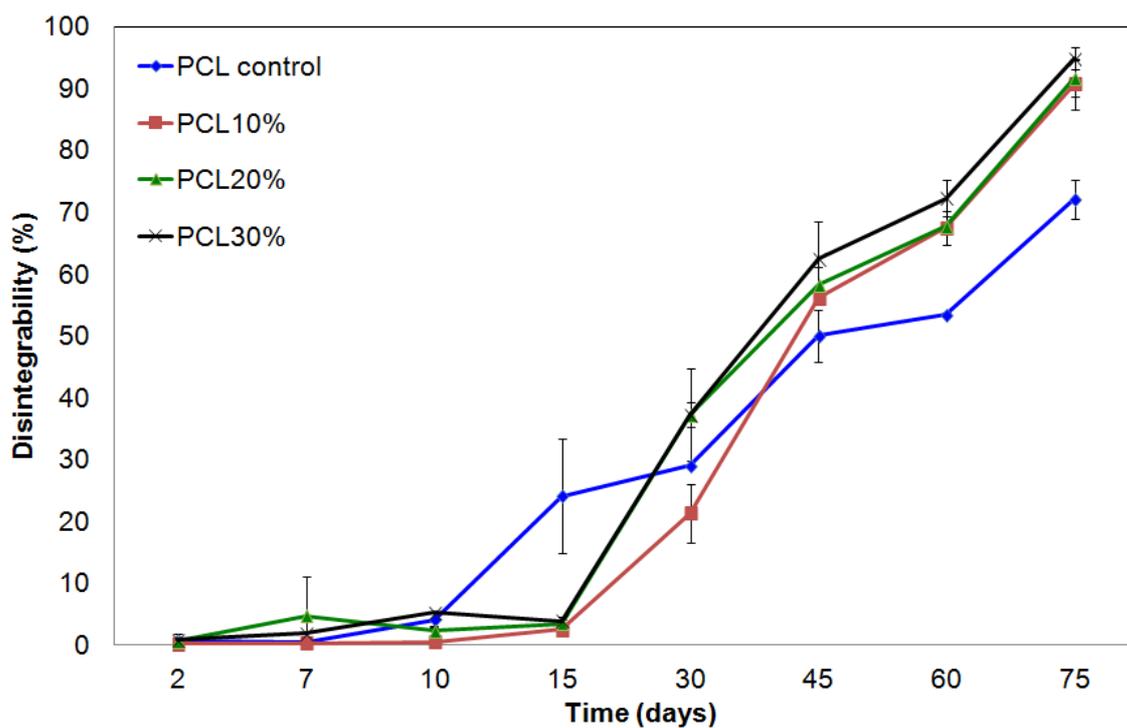


764

765 **Fig. 6.** Physical disintegration of PCL and PCL/AS composite films after 0, 30 and 75

766 days of disintegration in composting conditions at 25 °C.

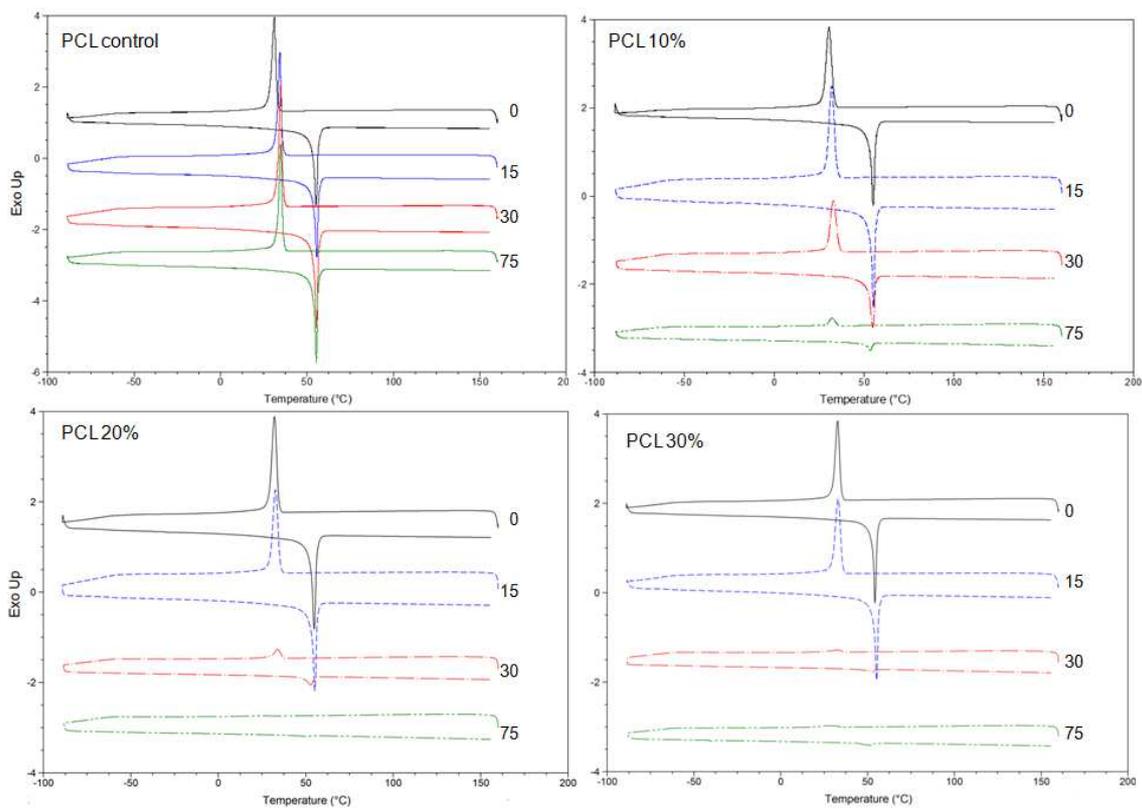
767



768

769 **Fig. 7.** Disintegrability (%) of neat PCL and PCL/AS composite films as a function of
770 degradation time in composting conditions at 25 °C (n=2).

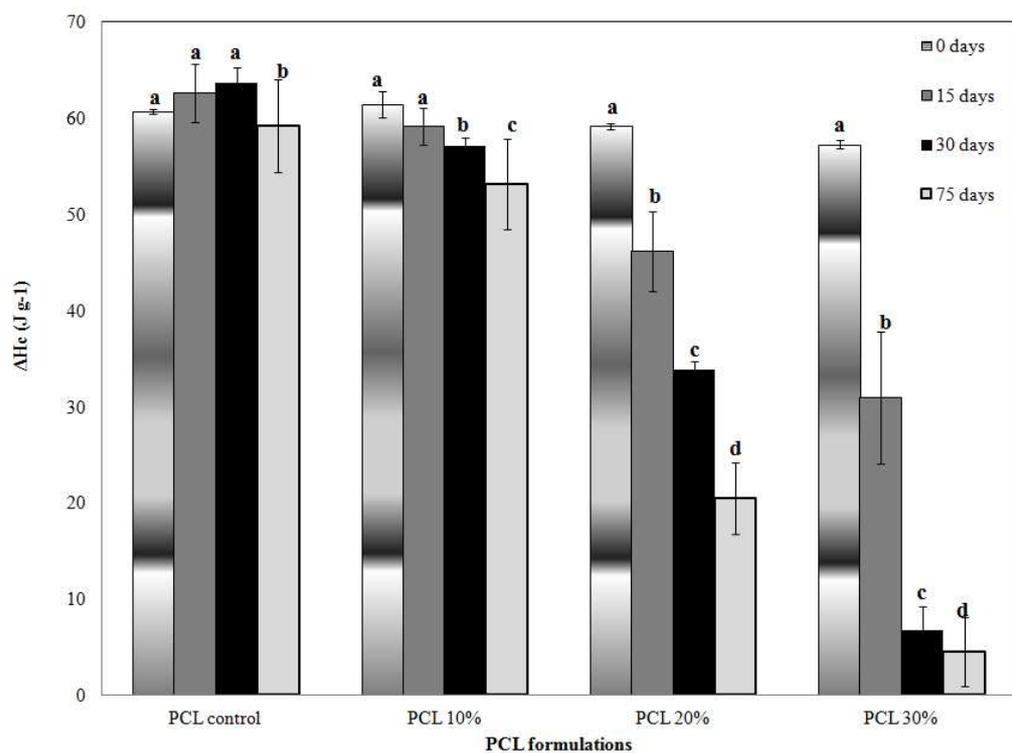
771



772

773 **Fig. 8.** DSC thermograms of PCL and PCL/AS composites at 0, 15, 30 and 75 days of
774 degradation in compost, second heating.

775



776

777 **Fig. 9.** Crystallization enthalpy values (ΔH_c) of neat PCL and PCL/AS composite films

778 as a function of degradation time in composting conditions at 25 °C (n=2).