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Abstract

The use of fully bio-based and biodegradable materials for massive applications, such as food packaging, is an emerging tendency in polymer research. But the formulations proposed in this way should preserve or even increase the functional properties of conventional polymers, such as transparency, homogeneity, mechanical properties and low migration of their components to foodstuff. This is not always trivial, in particular when brittle biopolymers, such as poly(lactic acid) (PLA), are considered. In this work the formulation of innovative materials based on PLA modified with highly compatible plasticizers, i.e. oligomers of lactic acid (OLAs) is proposed. Three different synthesis conditions for OLAs were tested and the resulting additives were further blended with commercial PLA obtaining transparent and ductile materials, able for films manufacturing. These materials were tested in their structural, thermal and tensile properties and the best formulation among the three materials was selected. OLA with molar mass (M_n) around 1,000 Da is proposed as an innovative and fully compatible and biodegradable plasticizer for PLA, able to replace conventional plasticizers (phthalates, adipates or citrates) currently used for films manufacturing in food packaging applications.

Keywords (separated by '-')

Lactic acid - PLA - Plasticizers - Ductile properties - Glass transition temperature

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2 Synthesis and Characterization of Lactic Acid Oligomers: 3 Evaluation of Performance as Poly(Lactic Acid) Plasticizers

4 Nuria Burgos · Daniel Tolaguera · Stefano Fiori ·
5 Alfonso Jiménez

6
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8 **Abstract** The use of fully bio-based and biodegradable
9 materials for massive applications, such as food packaging,
10 is an emerging tendency in polymer research. But the
11 formulations proposed in this way should preserve or even
12 increase the functional properties of conventional poly-
13 mers, such as transparency, homogeneity, mechanical
14 properties and low migration of their components to
15 foodstuff. This is not always trivial, in particular when
16 brittle biopolymers, such as poly(lactic acid) (PLA), are
17 considered. In this work the formulation of innovative
18 materials based on PLA modified with highly compatible
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20 posed. Three different synthesis conditions for OLAs were
21 tested and the resulting additives were further blended with
22 commercial PLA obtaining transparent and ductile mate-
23 rials, able for films manufacturing. These materials were
24 tested in their structural, thermal and tensile properties
25 and the best formulation among the three materials was
26 selected. OLA with molar mass (M_n) around 1,000 Da
27 is proposed as an innovative and fully compatible and
28 biodegradable plasticizer for PLA, able to replace con-
29 ventional plasticizers (phthalates, adipates or citrates)
30 currently used for films manufacturing in food packaging
31 applications.

32
33 **Keywords** Lactic acid · PLA · Plasticizers · Ductile
34 properties · Glass transition temperature

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Introduction

Since the introduction of synthetic polymers, they have
been extensively used as packaging materials by their
advantageous properties, such as softness, lightness and
transparency [1]. Over the last decade, environmental,
economic and safety challenges have induced the use of
biodegradable polymers to partially replace conventional
petrochemical-based materials in packaging applications
[2].

Poly(lactic acid) (PLA) is one of the most studied bio-
degradable polymers, since it is a compostable and non-
toxic thermoplastic polyester obtained from the controlled
polymerization of lactic acid [1]. PLA shows excellent
biocompatibility, processability, it is less energy-dependent
and provides excellent properties at a competitive price
in packaging, consumer goods, fibers and in biomedical
devices [3, 4].

Poly(lactic acid) is classified as GRAS (Generally
Recognized As Safe) by the US Food and Drug Adminis-
tration (FDA) for food packaging applications [1]. It is
currently commercially available only in form of rigid cups
and containers for short shelf-life food, since some poor
properties, such low glass transition temperature, weak
thermal stability and high brittleness limit its use in flexible
films manufacturing. Several modifications have been
proposed to overcome this drawback, such as copolymer-
ization, blending with other polymers or plasticization.
The addition of plasticizers to PLA has been subject of
numerous studies and maybe it is an economical way to
increase the flexibility of PLA [2–4]. Concerning food
contact materials, there are several requirements to be
satisfied by additives, such as being non-toxic substances,
showing good miscibility with the polymer, providing high
tensile strength, ductility, and suitable thermal properties.

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69 Besides transparency, low volatility and low migration into
70 foodstuff are also relevant properties [2].

71 Some compounds have been tested as potential plasti-
72 cizers for PLA, such as triacetin, citrate esters [5–7], glu-
73 cose monoesters, partial fatty acid esters [8], glycerol,
74 poly(ethylene glycol) [9], poly(propylene glycol) [10] or
75 polyadipates [11, 12], but their compatibility with PLA
76 is limited and the possibility of incorporation with no
77 phase separation is restricted to concentrations lower than
78 20 wt% limiting their potential properties in food pack-
79 aging. In general, it has been accepted that amounts from
80 10 to 20 wt% of plasticizers are required to provide a
81 substantial reduction of the PLA glass transition tempera-
82 ture (T_g) as well as to obtain adequate mechanical prop-
83 erties for films manufacturing. The ideal approach to
84 increase miscibility between PLA and potential plasticizers
85 would be to add a compound with similar chemical
86 structure and a relatively high molar mass to reduce
87 migration rate and detrimental changes in the material
88 properties over time.

89 The possibility of synthesizing oligomers of lactic acid
90 (OLA) from the monomer, changing the polymerization
91 conditions to obtain compounds with different molar
92 masses, could be an alternative to get plasticizers with high
93 compatibility with PLA by their close chemical structure.
94 Martin and Avérous [9] made a preliminary study of
95 oligomeric lactic acid as a PLA plasticizer at 20 wt%
96 content. They reported an improvement in ductility with a
97 significant decrease in T_g , but the low T_g limits the appli-
98 cability of the blend and could affect the stability over
99 time, resulting in a loss of mechanical properties.

100 Some authors have studied the synthesis of lactic acid
101 oligomers and their application to some fields, in particular
102 biomedical. These OLAs, with molar masses lower than
103 10 kDa are typically produced by direct polycondensation
104 [13, 14]. The preparation and characterization of polydis-
105 perse and monodisperse OLAs and their ability to form
106 stereocomplexes to increase the yield of their synthesis
107 reactions has been fully described [15] and a minimum
108 amount of lactate (either in D- or L-form) was obtained by
109 following specific routes that will be further described in
110 the experimental section.

111 In the present work three oligomers based on D,L-lactic
112 acid were first synthesized under different conditions and
113 then were blended with commercial PLA forming fully-
114 biodegradable films. The efficiency of these biocompatible
115 plasticizers was evaluated in order to obtain PLA-based
116 formulations with adequate properties for flexible films
117 manufacturing. This innovative approach results in fully
118 biodegradable films for food packaging with improved
119 mechanical and functional properties reached by the high
120 compatibility between the PLA matrix and plasticizer.

Experimental

Materials

123 Three oligomers of lactic acid (OLA's) with M_n between
124 670 and 1,000 Da were synthesized by using the following
125 reagents: D,L-lactic acid (90 wt% L-LA) (D,L-LA) kindly
126 supplied by PURAC BV (Gorinchem, The Netherlands); a
127 commercial mixture of linear alcohols (*n*-octanol/*n*-deca-
128 nol with 45/55 v/v ratio) called Nafol[®]810D obtained from
129 Sasol Ltd (Johannesburg, South Africa); 1,4-cyclo-hexan-
130 edimethanol and two class of catalysts [methanesulfonic
131 acid, CH₃SO₃H, and dioctyl(maleate)tin oxide, C₁₆H₃₄OSn
132 (DOTO)] were purchased from Sigma-Aldrich Chemical
133 Co (Móstoles, Spain). These reagents were selected in
134 consideration of their potential use at industrial scale in the
135 OLAs synthesis. Poly(lactic acid) (PLA Ingeo[™] 2003D;
136 $M_n = 108$ kDa; 4 wt% D-isomer) from NatureWorks LLC
137 (Minnetonka, MN, USA) was used as polymeric matrix.

Synthesis of Oligomers (OLAs)

139 Lactic acid oligomers from D,L-LA were synthesized by
140 direct polycondensation with the commercial mixture of *n*-
141 octanol and *n*-decanol above described as the chain ter-
142 minator, while DOTO was used as the polycondensation
143 reaction catalyst. A previously proposed method was used
144 in these syntheses [16]. A simplified mechanism for the
145 polymerization of D,L-LA to form linear monosubstituted
146 oligomers is shown in Fig. 1. Linear monosubstituted
147 oligomers (named as OLA 00A/5 and 00A/8) were first
148 synthesized by following the above-indicated route and
149 further blended with PLA. D,L-LA was added along with
150 0.05 wt% DOTO as the catalyst and the chain terminator at
151 different D,L-LA/Nafol[®]810D ratios (approximately 70/30
152 for 00A/5; 70/20 for 00A/8) to a 1 L round bottom glass
153 reactor fitted with a multiconnection glass hat joined by a
154 silicon gasket under mechanical stirring and pure nitrogen
155 atmosphere. The temperature was slowly increased up to
156 110 ± 1 °C at atmospheric pressure and held for 30 min in
157 order to eliminate the condensation water formed during
158 the esterification reaction. The temperature was raised up
159 to 160 ± 1 and 175 ± 1 °C for OLA 00A/5 and OLA 00A/
160 8, respectively and pressure was decreased down to 1 kPa
161 for 10 min. At this point, the temperature was increased to
162 180 ± 1 °C in order to eliminate the excess of alcohol and
163 side reaction products and the pressure was further
164 decreased down to 0.5 kPa for 15 additional minutes. In all
165 cases pressure was decreased by using an oil vacuum pump
166 controlled by an electronic vacuumeter to ±0.1 kPa.
167 Finally, when the desired parameters were reached, the
168 product was unloaded from the reaction vessel and further

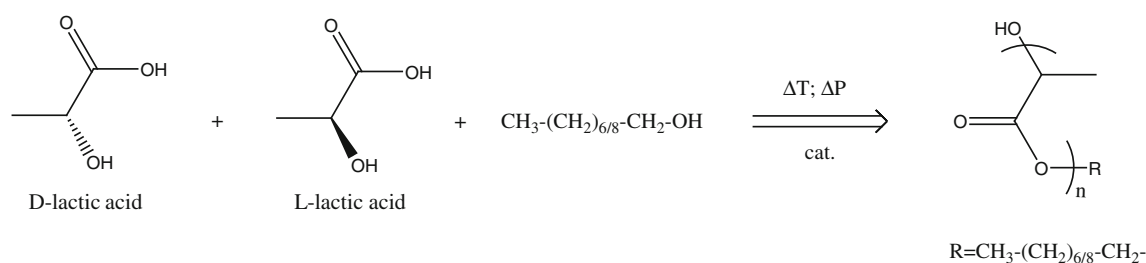


Fig. 1 Reaction scheme of the polymerization of D,L-LA to form linear monosubstituted oligomers

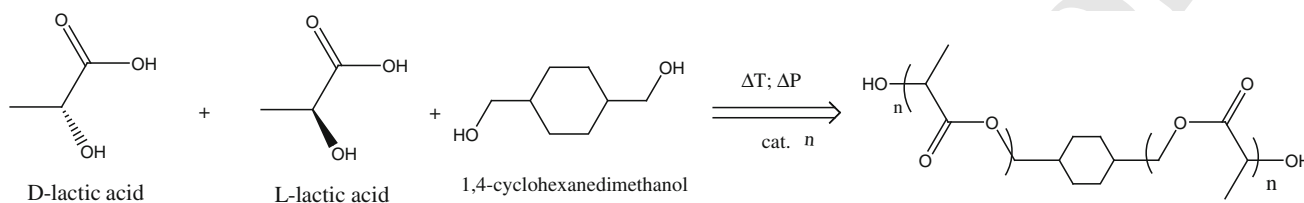


Fig. 2 Reaction scheme between D,L-LA and 1,4-cyclohexane-dimethanol

169 characterized in their chemical parameters. The average
170 yield percentage achieved for the reaction was 96 %.

171 However, some preliminary results showed that OLA
172 00A/5 had some residual lactic acid that could result in
173 significant differences in crystallinity of the oligomer and
174 consequently on properties after blending with PLA.
175 Therefore, a third OLA (named OLA 09A/5) was synthe-
176 sized with the same experimental conditions than OLA
177 00A/5 (D,L-LA/Nafol®810D ratio, pressures and tempera-
178 tures) but with the addition of 1,4-cyclohexane-dimethanol
179 (1.5 wt%) to permit the residual LA to be eliminated by
180 following the route shown in Fig. 2. Polymerization cata-
181 lyst was also changed (methanesulfonic acid, 0.05 wt%) in
182 this synthesis route.

183 Preparation of PLA-OLAs Films

184 Poly(lactic acid) pellets were dried under vacuum over-
185 night at 80 °C and milled with a RETSCH ZM200 Ultra
186 Centrifugal Mill (Haan, Germany) to a final particle size of
187 approximately 1 mm, using liquid nitrogen to avoid ther-
188 momechanical degradation. Milled PLA and oligomeric
189 plasticizers (15 wt%) were mixed at ambient temperature
190 by manual shaking until homogeneous mixtures were
191 obtained. They were further melt-blended in a Haake
192 PolyLab QC, ThermoFisher Scientific (Waltham, USA) at
193 50 rpm during 8 min.

194 The temperature was set at 160 °C but it increased to
195 170 °C upon mixing. This blending procedure for plasti-
196 cized PLA was previously optimized and reported else-
197 where [11, 12]. Blends were then processed into films
198 (14.0 × 14.0 cm² and 220 ± 5 μm thickness) by com-
199 pression molding at 170 °C in a Carver Inc. Hot Press

(Wabash, IN, USA), keeping the material between the 200
plates at atmospheric pressure for 5 min until melting and 201
then gradually increasing the pressure during 2 min up to 202
5 MPa, maintained for 5 min. 203

Material Characterization 204

205 Several physical and chemical properties of the synthesized
206 oligomers were determined immediately after their synthe-
207 sis by using standard test methods: hydroxyl number
208 (I_{OH}, ASTM E1899-08) [17]; Gardner Color Scale (ASTM
209 D1544-04) [18]; kinematic viscosity at 25 °C (ν, ASTM
210 D445-09) [19]; refractive index (N) and density (ρ) at
211 25 °C (ASTM D1045-08) [20].

212 Average molar masses of plasticizers were characterized
213 by Size Exclusion Chromatography (SEC) measurements
214 using a Shimadzu liquid chromatograph (Kyoto, Japan)
215 equipped with a RID-10A refractive index detector. The
216 columns set used was composed of a 50 mm PLgel Guard
217 5 μm column, two 300 mm PLgel MIXED-C 5 μm columns
218 and a 300 mm PLgel 5 μm-100 Å column. Chloroform was
219 used as the mobile phase and analyses were carried out at
220 25 °C with a solvent flow rate of 0.8 mL min⁻¹. Calibration
221 was carried out with polystyrene standards from 580 to
222 1.6 × 10⁶ g mol⁻¹.

223 Wide angle X-ray scattering (WAXS) of materials was
224 performed on a Bruker D8-Advance (Madison, WI, USA)
225 diffractometer, equipped with a Cu Kα radiation source
226 (λ = 1.546 Å), operating at 40 kV and 40 mA as the applied
227 voltage and current, respectively. The incidence angle (2θ)
228 was varied between 2° and 90° at a scanning rate of 2° min⁻¹.

229 TGA tests were performed on a TGA/SDTA 851e Mettler
230 Toledo thermal analyzer (Schwarzenbach, Switzerland).

231 Samples of approximately 7 mg were heated from room
232 temperature to 700 °C at 10 °C min⁻¹ under a nitrogen gas
233 flow rate of 50 mL min⁻¹. Two replicates were scanned for
234 each formulation and errors were lower than 3 % in all
235 cases.

236 DSC tests were performed on a TA Instruments DSC
237 Q2000 (New Castle, DE, USA) under a dry nitrogen gas
238 flow rate of 50 mL min⁻¹. OLAs (4–6 mg) were sealed in
239 aluminium pans and subjected to the following thermal
240 cycles: first heating from –90 to 150 °C at 10 °C min⁻¹,
241 followed by 5 min at 150 °C (in order to erase the thermal
242 history), quenching to –90 °C and a second heating up to
243 150 °C at 10 °C min⁻¹. Two replicates were tested for
244 each formulation and errors were lower than 1 % in all
245 cases. PLA plasticized films were analysed from –30 to
246 180 °C at 10 °C min⁻¹, followed by quenching to –30 °C
247 and further heating up to 180 °C at 10 °C min⁻¹. Glass
248 transition temperatures (T_g) were determined in the second
249 heating scan as the inflection point of the region where a
250 shift in the signal baseline was detected.

251 Elongation at break (% ϵ_{tB}), tensile strength (TS) and
252 elastic modulus (E) of PLA–OLA films were determined at
253 a crosshead speed of 10 mm min⁻¹ using a universal test
254 machine IBERTEST ELIB 30 (Ibertest, Madrid, Spain),
255 equipped with a 5 kN load cell. Tests were performed
256 according to ASTM D 882-01 standard²¹, with rectangular
257 probes (100 × 10 mm²) and an initial grip separation of
258 50 mm. All values were the average of five measurements
259 (\pm standard deviation).

260 A JEOL model JSM-840 (Jeol USA Inc., Peabody, MA,
261 USA) scanning electron microscope, operated at 12 kV,
262 was used to observe the surface and cross-sections of
263 plasticized PLA films. Samples were previously sputtered
264 with gold to turn them in conductive materials with a
265 metallizer (Au)/Evaporator (C) Balzers, model SCD 004
266 (Oerlikon Balzers, Liechtenstein).

267 Results and Discussion

268 Characterization of Synthesized Oligomers of Lactic 269 Acid (OLAs)

270 Some physical and chemical properties of the synthesized
271 oligomers are summarized in Table 1, while SEC analysis
272 was used to determine their average molar masses (M_n and
273 M_w) and results are shown in Table 2. No significant dif-
274 ferences between all OLAs were observed in their refrac-
275 tive index and density values determined at 25 °C. It was
276 observed that OLA 09A/5 showed the highest hydroxyl
277 index (I_{OH}) since shorter chains with –OH end groups were
278 obtained, in comparison with 00A/8 whose lowest I_{OH}

Table 1 Some physico-chemical properties of synthesized oligomers

OLA	I_{OH} (mg KOH g ⁻¹)	Color G	ν (m ² s ⁻¹) × 10 ⁴ 25 °C	N 25 °C	ρ (g cm ⁻³) 25 °C
00A/5	76	1	2.70	1.448	1.08
00A/8	55	4	38.9	1.448	1.10
09A/5	138	2	3.30	1.452	1.07

index was given by the minor proportion of chain termi- 279
nator. It was also observed that all the oligomers showed a 280
slightly yellowish color, as indicated by the Gardner Color 281
Scale. These results are important for the use as a potential 282
plasticizer for PLA where the use of colorless additives is 283
normally preferred from the industrial point of view to 284
avoid the modification of the polymer natural color. On the 285
other hand, the kinematic viscosity of 00A/8 is clearly 286
higher than values for the other two OLAs, which is con- 287
sistent with its higher molar mass (Table 2). This is an 288
important parameter for further blending with PLA. In 289
general, higher viscosities result in more difficulties during 290
blending, but it should be pointed out that the obtained 291
value for this parameter ranges in the same order to those 292
normally presented by polyadipates, which were success- 293
fully blended with PLA in previous works [11, 12]. 294

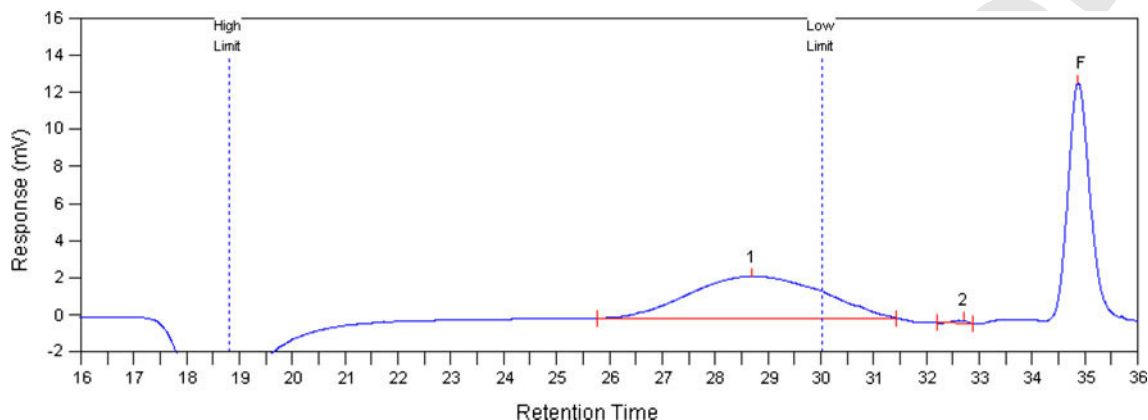
The number-average molar mass (M_n) of OLAs ranged 295
from 671 to 957 Da, with polydispersity indexes below 1.5 296
in all cases (Table 2). This is an indication of the suc- 297
cessful synthesis of these compounds with a relatively low 298
dispersion in the length of macromolecular chains. Fig- 299
ure 3 shows a representative SEC curve obtained for OLA 300
00A/8. A peak with low intensity (<2 % of the total area of 301
the chromatogram) was observed in all oligomers at high 302
retention times with an average M_n around 170 g mol⁻¹. 303
This peak could be attributed either to the formation of a 304
certain amount of the lactic acid dimer ($M_n = 162$ g mol⁻¹) 305
during polymerization or to the presence of some residual 306
chain terminator. It is noteworthy that the 00A/8 oligomer 307
differed from the rest of synthesized OLAs because of its 308
higher average molar mass that could be due to the higher 309
temperature used in the reaction [23]. Besides, if compared 310
with 00A/5, the formation of longer chains in 00A/8 is 311
consistent with the lower proportion of chain terminator 312
used in the synthesis. 313

The determination of the degree of polymerization (DP) 314
of these OLAs is necessary to calculate solubility param- 315
eters. DP was calculated on the basis of the oligomers 316
chemical structures (Fig. 1), being lactate the repeating 317
unit (molar mass, $M = 72$ g mol⁻¹) and Nafol®810 the 318
chain terminator ($M \sim 146$ g mol⁻¹), according to the 319
following Eq. (1): 320

Table 2 Average molar masses (M_w , M_n), polydispersity index (PDI) and degree of polymerization (DP) determined by SEC relative to PS standards, and solubility parameters (δ) for all materials

Material	M_w (Da)	M_n (Da)	PDI = M_w/M_n	DP	δ ((J cm ⁻³) ^{1/2})*
00A/5	904	706	1.28	8	17.5
00A/8	1,346	957	1.41	11	17.7
09A/5	863	671	1.29	7	17.3
PLA	220×10^3	108×10^3	2.04	1,500	19.5

* Calculated with group molar attraction constants from Small [22]

**Fig. 3** SEC pattern of lactic acid oligomer 00A/8, using PS standards in the calibration

$$DP = \frac{M_n - M_{chain\ terminator}}{M_{lactate\ unit}} \quad (1)$$

322 The selection of a plasticizer to be used in specific PLA
 323 compositions requires that this compound should present
 324 low volatility, resistance to migration, lack of toxicity and
 325 plasticizer efficiency resulting in a significant increase in
 326 ductile properties. This efficiency is mostly related to their
 327 chemical structure and to the compatibility between the
 328 plasticizer and the polymer matrix [7]. In general,
 329 plasticizers reduce the polymer chain-to-chain interactions
 330 by distributing homogeneously within the polymer,
 331 increasing the free volume [24]. It should be considered
 332 that the most effective plasticizers for a specific polymer
 333 could be those with similar structure to the matrix and this is
 334 characterized by their close solubility parameters [25].

335 In order to predict PLA–OLAs compatibility, their sol-
 336 ubility parameters were determined by the group contri-
 337 bution, according to the Small's cohesive energies
 338 calculated according to Eq. (2) [22].

$$\delta = \frac{\rho \sum G}{M_n} \quad (2)$$

340 where δ is the solubility parameter, ρ is the density, M_n is
 341 the number-average molar mass and $\sum G$ is the sum of the
 342 molar attraction constants estimating the contribution of
 343 each group in their chemical structure. As shown in
 344 Table 2, all the synthesized OLAs had solubility

Table 3 Thermal degradation parameters, glass transition temperature (T_g) of raw oligomeric lactic acids and PLA, determined under nitrogen atmosphere by TGA and DSC, respectively

Material	T_5 (°C)	T_{max} (°C)	T_{95} (°C)	T_g (°C)
00A/5	189	287	297	-60.4
00A/8	214	291	326	-40.4
09A/5	179	259	268	-60.0

parameters close to PLA, which indicates that they should
 be miscible at least up to a certain concentration of oli-
 gomer, having a plasticizing effect in their blending with
 PLA. Slight differences were observed in solubility
 parameters between oligomers that could be mainly ascri-
 bed to their different polymerization degree and molar
 mass.

Thermal stability of OLAs was studied by TGA under
 nitrogen atmosphere. Table 3 shows the initial decompo-
 sition temperature (T_5), defined as the temperature at which
 5 % of the total mass has been lost; the temperature at the
 maximum degradation rate (T_{max}), determined as the peak
 maximum from the first derivative of TGA curves and the
 final decomposition temperature (T_{95}), corresponding to
 the temperature at which 95 % of the total mass has been
 lost.

It was observed in TGA curves (not shown) that thermal
 degradation of all OLAs occurred in a single step.

363 Intermolecular and intramolecular trans-esterification
 364 reactions could occur during thermal degradation, such as
 365 in the case of PLA, resulting in the formation of the
 366 monomer and low molar mass lactides [26, 27].

367 When comparing TGA results for the three studied
 368 OLAs, 00A/8 exhibited the highest thermal stability, since
 369 T_5 value was 25 and 35 °C higher than those calculated for
 370 00A/5 and 09A/5, respectively (Table 3). Moreover, a clear
 371 relation between the thermal stability and the average
 372 molar mass of the oligomers was observed. When compar-
 373 ing thermal degradation parameters with SEC results
 374 (Table 2) it could be concluded that an increase in molar
 375 mass produced a more stable material upon heating.
 376 Besides, in the case of 00A/5 and 09A/5, shorter chains
 377 were obtained since a higher proportion of alcohol was
 378 used in their syntheses. The presence of hydroxyl end
 379 groups in the PLA oligomer chains was found to be critical
 380 for degradation, initiating the chain-scission and decreasing
 381 the thermal stability [28, 29]. In the case of 09A/5, the
 382 highest number of hydroxyl end groups derived from 1,4-
 383 cyclohexanedimethanol could explain the low thermal
 384 stability compared with 00A/5 and 00A/8 (with T_5 value 10
 385 and 35 °C lower, respectively). On the other hand, T_{max}
 386 values for 00A/8 and 00A/5 were very similar, just slightly
 387 higher for 00A/8; while 09A/5 showed a T_{max} value 32 °C
 388 lower than 00A/8. A similar behavior was observed for the
 389 final decomposition temperature (T_{95}), but differences
 390 between oligomers were even higher. While 00A/8 showed
 391 the highest T_{95} , 00A/5 and 09A/5 showed T_{95} values 29
 392 and 58 °C lower than 00A/8, respectively.

393 In summary, the higher thermal stability of 00A/8 is an
 394 advantage when considering its potential use as PLA
 395 plasticizer, since it could avoid an important mass loss
 396 during processing at high temperatures. This hypothesis
 397 will be discussed later.

398 Only one glass transition temperature (T_g) was observed
 399 for each OLA during the second heating scan in DSC
 400 analysis (Table 3) indicating the high homogeneity of all
 401 materials and the success in the synthesis strategies. As
 402 expected, the T_g values of each OLA increased with their
 403 molar mass. The two lower molar mass compounds (00A/5
 404 and 09A/5) showed similar T_g values, 20 °C lower than the
 405 observed result for 00A/8. On the other hand, DSC curves
 406 (not shown) did not reveal any endothermic (melting) or
 407 exothermic transitions (cold crystallization) during the first
 408 heating scan, giving a clear indication of the amorphous
 409 nature of all raw materials. This result is in agreement with
 410 PLA that is either amorphous or semicrystalline at room
 411 temperature depending on the amount of L-lactide in its
 412 structure. PLA containing 50–93 % L-lactide is strictly
 413 amorphous whereas PLA with >93 % L-lactide is semi-
 414 crystalline [35]. The amorphous structure of OLAs indi-
 415 cated in DSC analysis was confirmed in XRD patterns

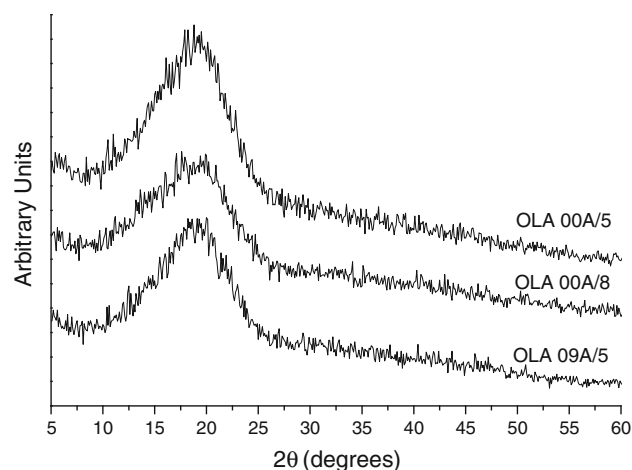


Fig. 4 WAXS patterns obtained for 00A/8, 00A/5 and 09A/5

(Fig. 4) since no diffraction peaks were observed but only
 an amorphous halo.

Characterization of PLA–OLAs Films

In order to evaluate the ability of OLAs as potential
 plasticizers for PLA, films with OLAs (15 wt%) and the
 un-plasticized PLA matrix were prepared by compression
 molding after melt-blending. Processing conditions were
 those previously optimized for PLA-polyadipate blends
 and reported elsewhere [11] in order to avoid the plasticizer
 loss as well as thermal degradation of materials during
 melt-blending at high temperatures. However, a significant
 release of vapors was detected during blending of PLA
 with 00A/5 and 09A/5 oligomers, suggesting that there was
 some volatilization of these compounds during processing.
 It should be noted that temperatures as high as 170 °C were
 registered in some moments of the melt-blending process.
 This is in agreement with TGA analysis of raw OLAs,
 since at such temperature, 00A/5 and 09A/5 showed a mass
 loss of 2.5 and 2.9 %, respectively. However, no vapors
 were observed during melt-blending of PLA with 00A/8,
 also in agreement with TGA results, showing the stability
 of this compound at 170 °C with no apparent mass losses.

It should be pointed out that all films were transparent
 with homogeneous morphologies. Typical micrographs of
 fracture surfaces of these plasticized materials are shown in
 Fig. 5. These results suggest that no further evaporation of
 plasticizers during the formation of films at high temper-
 atures and pressures was observed or at least that the vapor
 release from PLA-00A/5 and PLA-09A/5 blends was not
 enough to generate a porous morphology in these films. No
 apparent differences were observed when comparing with
 the PLA-00A/8 film.

The effect of plasticizers on the thermal stability of PLA
 was evaluated by performing TGA tests. The main thermal

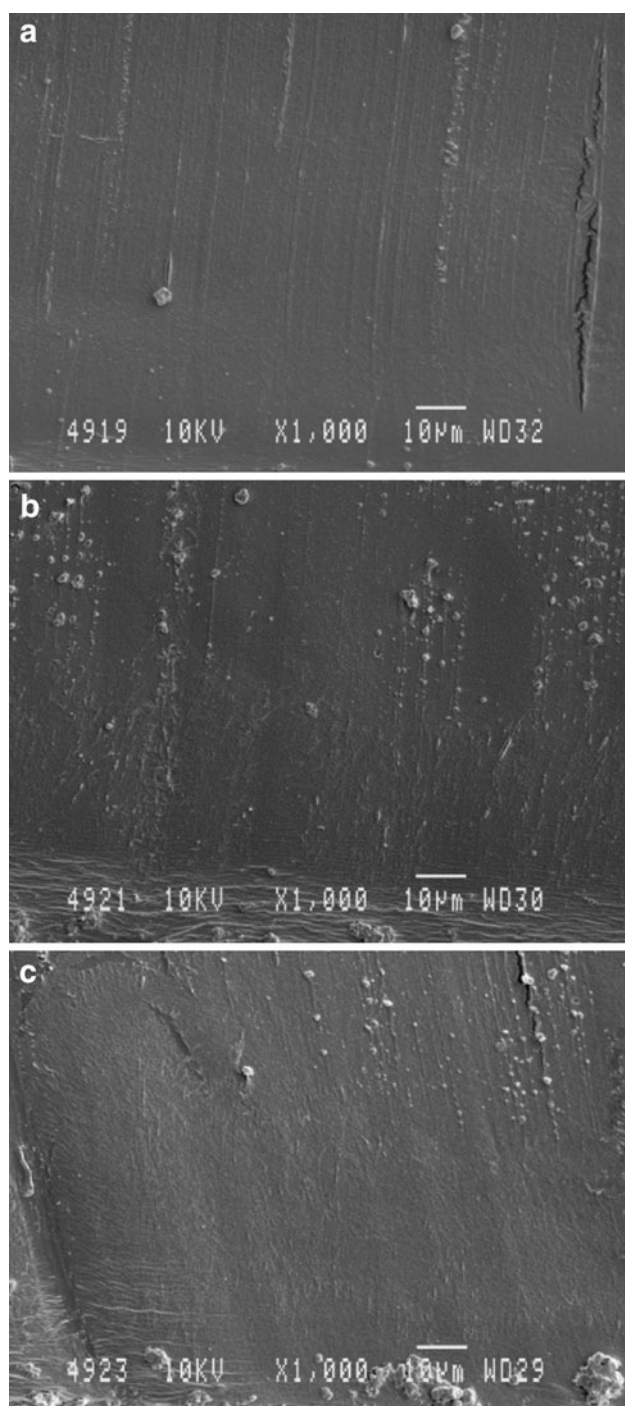


Fig. 5 SEM micrographs of fracture surfaces ($\times 1,000$) of PLA-00A/5 (a), PLA-09A/5 (b) and PLA-00A/8 (c) films

parameters obtained from this study are shown in Table 4. PLA-OLA films showed a single step degradation process in all cases, with T_{\max} values similar to those of the neat polymer, which was 365 °C, in agreement with previously reported values [11, 31, 32]. However, the thermal stability of these materials was reduced by the addition of OLAs.

Table 4 Thermal data obtained by TGA and DSC analysis of neat PLA and PLA-OLA (15 wt%) films

Film	T_5^* (°C)	T_{\max}^* (°C)	T_g^{**} (°C)	$T_{g, \text{Fox}}$ (°C)	T_{cc}^{**} (°C)	T_m^{**} (°C)
Neat PLA	339	365	58.8	—	—	150.6
PLA-00A/5	266	361	35.8	33.1	98.6	135.5–145.5
PLA-00A/8	278	363	39.3	38.9	102.1	136.9–146.6
PLA-09A/5	254	364	36.0	33.2	97.7	135.1–145.2

* Determined by TGA analysis at 10 °C min⁻¹ in N₂ atmosphere

** DSC data determined from the second heating scan

The low molar mass of these compounds produced a decrease in the initial decomposition temperature (T_5) of blends, compared to results for neat PLA. Since 09A/5 is more volatile than 00A/5 and 00A/8, a higher decrease in the thermal stability of the PLA-09A/5 film was observed. As expected, these T_5 values were higher than those observed for the pure oligomers (Table 3). This fact could be explained by the superposition of two factors. The first one would be the high miscibility of the blend components due to the strong interactions between them. The second reason would be a protective effect of the matrix on the additives that are homogeneously distributed, delaying their degradation.

DSC tests were carried out to investigate the thermal transitions of plasticized PLA films and the main results are also indicated in Table 4. As expected from the solubility parameters previously calculated and discussed in this work and their similar chemical structures, all OLAs showed good miscibility with PLA at 15 wt% content since only one T_g value was observed in the DSC thermograms of all blends. Since T_g is an excellent indicator of the chain mobility, the efficiency of OLAs as potential PLA plasticizers was evaluated by determining the decrease of T_g compared to its value for the neat PLA matrix. It was previously reported that the addition of 10–20 wt% of OLA to PLA induced a significant decrease in T_g values (from 58 to 37 °C and 18 °C, respectively) by increasing molecular mobility, showing their plasticizing effect on the matrix [9]. As expected from T_g values of pure OLAs (Table 3), this effect was clearly less pronounced for PLA-00A/8 blends due to its higher molar mass. It should be emphasized that the reduction in T_g values for these PLA-OLA blends was higher than those reported for PLA-polyadipates and PLA-citrates formulations at the same concentration levels [6, 32].

The evaluation of the incorporation of OLAs to the PLA matrix in the blends was carried out by comparison of the experimental T_g values determined from DSC curves with the theoretical values expected for binary miscible blends, calculated by following the Fox Eq. (3) [33].

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (3)$$

497 where w is the weight fraction of the blend components (1
498 and 2) and T_g values of the pure components are those
499 obtained from DSC tests (Table 3). Results are also shown in
500 Table 4. The slight deviations observed between predicted
501 and experimental data could be mainly due to the OLAs
502 evaporation at the blending temperature. It is noticeable that
503 theoretical and experimental T_g values approached as the
504 molar mass of OLAs increased, confirming the above-
505 mentioned assumption. As can be observed in Table 4, the
506 experimental T_g value obtained for PLA-00A/8 blends is in
507 good agreement with the theoretical prediction (only 0.4 °C
508 difference), suggesting once again the excellent compati-
509 bility of 00A/8 with PLA. However, for PLA-00A/5 and
510 PLA-09A/5 blends, there were differences of 2.7 and 2.8 °C
511 between experimental and theoretical T_g values respec-
512 tively. This result is in agreement with the vapors release
513 observed during processing, leading to the decrease in OLA
514 concentration in the final material.

515 Figure 6 shows the DSC curves of neat PLA and PLA-
516 OLA films during the second heating scan. The increased
517 chain mobility of PLA due to the plasticizing effect
518 induced by OLAs resulted in crystallization and further
519 melting during heating, which was not observed in the case
520 of the neat polymer. The two endothermic thermal transi-
521 tions observed between 120 and 155 °C in PLA-OLA
522 formulations provided evidence of the presence of different
523 PLA crystals. According to the literature, both melting
524 peaks are considered to be related with the melting phe-
525 nomenon of α homocrystals developed in PLLA during
526 heating [30, 34, 35]. The total enthalpy (ΔH_{total}), calculated
527 as the addition of melting and crystallization peak areas in
528 the range between 80 and 155 °C, provides a method for
529 determining the original crystallinity of materials, since it
530 is assumed that continuous transitions are occurring in this
531 interval [34]. The ΔH_{total} values determined during the first
532 DSC heating scan were close to zero in all cases (data not
533 shown), indicating that crystallization exotherms and
534 melting endotherms had similar heat contents. Therefore, it
535 can be concluded that the cooling rate used during pro-
536 cessing was high enough to get samples mainly amorphous.
537 It was also found that, among the PLA-OLA blends, the
538 cold crystallization temperature (T_{cc}) was higher with
539 increasing plasticizer molar mass.

540 The main goal of the addition of plasticizers to polymer
541 matrices is to get an improvement in ductile properties for
542 flexible films manufacturing. In the case of PLA it is
543 known that the neat polymer shows brittle behavior at room
544 temperature with a small elongation at break (ϵ_{tB} %) (around
545 4 %), and high elastic modulus ($E = 2.5$ GPa) and tensile
546 strength ($TS = 56$ MPa). Table 5 shows these

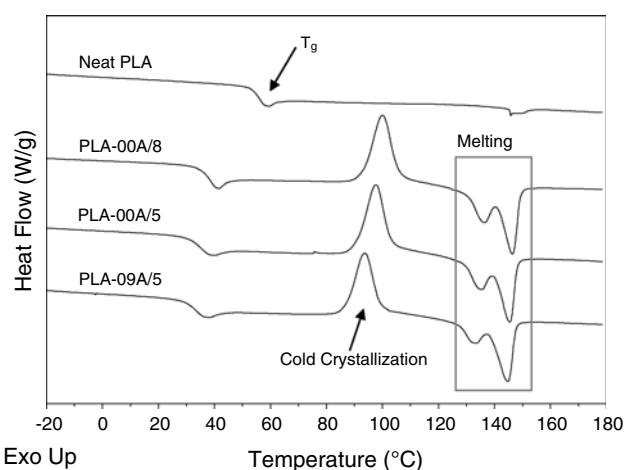


Fig. 6 DSC thermograms during the second heating scan at 10 °C min⁻¹ of PLA films after processing

Table 5 Elastic modulus (E), tensile strength (TS) and elongation at break (ϵ_{tB}) of PLA films calculated from tensile tests according to ASTM D882-91 [21]

Film	E (GPa)	TS (MPa)	ϵ_{tB} (%)
Neat PLA	2.5 ± 0.1	56 ± 5	4 ± 1
PLA-00A/5	1.3 ± 0.1	21 ± 3	235 ± 20
PLA-00A/8	1.8 ± 0.1	16 ± 5	204 ± 27
PLA-09A/5	1.3 ± 0.1	22 ± 5	243 ± 17

Results are given as average ± standard deviation

547 values as well as those obtained for tensile properties of
548 PLA-OLA formulations.

549 The addition of OLAs (15 wt%) lead to the expected
550 decrease in values for tensile strength and elastic modulus.
551 This result could be explained by considering the lower
552 macromolecular chain cohesion produced when plasticizers
553 penetrate through the polymer chains [36]. The elongation
554 at break of PLA-OLA films was strongly increased
555 (200–240 % for all plasticizers), showing an important
556 enhancement in ductility of blends. This result is well
557 correlated with the decreases in T_g observed for all for-
558 mulations permitting to conclude that OLAs used in this
559 work can be considered adequate plasticizers for com-
560 mercial PLA. Moreover, the decrease in rigidity for the
561 plasticized compositions was well evidenced by the lower
562 elastic moduli, with the highest reduction around 48 %
563 obtained for PLA-00A/5 and PLA-09A/5. It should be
564 pointed out that the PLA-00A/8 blend showed a lower
565 decrease in the elastic modulus (28 %) due to the highest
566 T_g value and molar mass of 00A/8.

567 It should be also emphasized that the increases in
568 elongation at break for PLA-OLA films were higher than
569 those obtained for PLA plasticized with polyadipates, DOA
570 and glycerol [7, 32] at the same concentration levels. All

571 these results confirmed again the excellent plasticizing
572 effect induced by the addition of OLAs, without significant
573 differences between them regarding tensile properties.

574 Conclusions

575 The use of oligomers of lactic acid (OLAs) as potential
576 plasticizers for PLA was evaluated for three compounds
577 based on D,L-lactic acid (90 wt% L-LA). OLAs were syn-
578 thesized by following a common route but other reagents,
579 catalysts and experimental conditions were modified to
580 obtain compounds with high compatibility with commercial
581 PLA to form transparent and flexible films. Some differences
582 in properties of these films were observed, mainly caused by
583 the effect of the OLA molar mass. All these OLAs, in par-
584 ticular the one with the higher molar mass (called 00A/8),
585 could lead to good performance in terms of ductility of their
586 blends with PLA and finally to permit the preparation of fully
587 biodegradable films based on PLA and an environmentally
588 friendly plasticizer for several applications, particularly for
589 food packaging.

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