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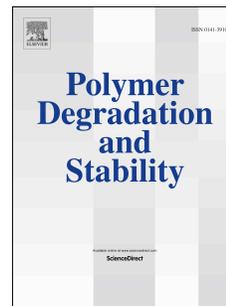
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1        **QUANTITATIVE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS**  
2        **FORMED DURING POLYLACTIDE PROCESSING BY MHS-SPME**

3  
4        Rómulo Salazar <sup>a,b</sup>, Sandra Domenek <sup>a</sup>, Cédric Plessis<sup>a</sup>, Violette Ducruet <sup>a</sup>

5  
6        <sup>a</sup> UMR Ingénierie Procédés Aliments, AgroParisTech, INRA, Université Paris-Saclay, 91300

7        Massy, France. Corresponding author: violette.ducruet@agroparistech.fr

8        <sup>b</sup> Escuela Superior Politécnica del Litoral, ESPOL, Facultad de Ingeniería en Mecánica y

9        Ciencias de la Producción, Carrera de Ingeniería en Alimentos, Campus Gustavo Galindo Km

10       30.5 Vía Perimetral, P.O. Box 09-01-5863, Guayaquil, Ecuador.

11  
12  
13

14 **Abstract**

15 Polylactide (PLA), a bio-based polyester, has been used in wide applications including food  
16 packaging. Nevertheless, it is well known that mass transfer occurs between packaging  
17 polymer and foodstuff leading to safety and quality issues. In this sense, volatile organic  
18 compounds (VOCs) present in packaging materials can migrate to the food in contact,  
19 changing its sensorial properties. Up to date, no study has focused on quantification of VOCs  
20 in PLA during its processing, which needs an optimized methodology to measure compounds  
21 at very low concentrations. In this study, different PLA samples in form of pellets, extruded  
22 films and thermoformed samples were studied in order to determine the VOCs present in each  
23 step of processing and to quantify them using headspace extraction methodology (MHS-  
24 SPME). Several volatile organic compounds were determined such as aldehydes, ethanol,  
25 acetone, acetic acid and lactides. Among the VOCs identified, three compounds were  
26 quantified: acetaldehyde; 2-methyl-2-propanol; 2,3-pentanedione. Acetaldehyde and 2,3-  
27 pentanedione increased after the extrusion and then decreased or disappeared after  
28 thermoforming. The results showed that residual acetaldehyde in PLA could be an important  
29 marker for the industry in the selection of PLA grades.

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34 **Keywords:** PLA, Polylactide, VOCs, extrusion, thermoforming, SPME.

35

ACCEPTED MANUSCRIPT

## 36 1. Introduction

37

38 Food packaging contribute to keep food safety and quality during shelf life. However,  
39 polymeric packaging materials are not inert and mass transfer occurs between packaging  
40 polymer and foodstuff [1] leading to safety and quality issues. Plastic packaging materials can  
41 absorb a significant quantity of aroma compounds from food which can involve modifications  
42 of the flavor composition, decrease of intensity, unbalance flavor and modifications of  
43 packaging material properties [2-5]. Indeed, the packaging materials contain additives to  
44 stabilize the polymer during processing or to improve its properties, such as antioxidants,  
45 ultraviolet light absorbers, slip agents and plasticizers. Other molecules may also be present in  
46 the packaging as residual monomers or low molecular weight oligomers and even non-  
47 intentionally added substances [6-8]. Moreover, volatile organic compounds (VOCs)  
48 produced during the process of forming (extrusion, thermoforming, etc.), can migrate to the  
49 food in contact [9], changing its sensorial properties by giving off-taste and/or undesirables  
50 flavors [10].

51 In the last decades, the increasing environmental problems such as the decreasing fossil  
52 resources have generated a major interest on the biopolymers. New materials from alternative  
53 resources, with lower energy consumption, biodegradable and non-toxic to the environment,  
54 have been developed [11]. One of the most promising bio-based polyesters aimed for food  
55 packaging is Polylactide (PLA) [12-14] due to its ease of processing using standard  
56 equipment and its good mechanical and barrier properties.

57 Thermal degradation of PLA is the most important degradation pathway during the forming  
58 process due to the residual moisture contained in the pellets, high temperatures of processing  
59 and shear induced by the extrusion screw. Indeed, thermal degradation of PLA is a complex  
60 phenomenon and is observed above 200 °C [15] leading to the appearance of low molecular

61 weight molecules and oligomers with different molecular weight. The main degradation  
62 mechanisms of PLA reported by literature are presented in Figure 1.

63 Thermal degradation of Polylactide has been mainly studied by pyrolysis-gas  
64 chromatography-mass spectrometry (Py-GC/MS) analysis [15-19] involving different  
65 reactions such as: Hydrolysis by trace amounts of water, leading to acid and alcohol;  
66 Intermolecular transesterification producing monomer and oligomeric esters; Intramolecular  
67 transesterification (backbiting ester interchange), resulting in formation of monomer and  
68 oligomer lactides of low Mw; Cis-elimination, leading to acrylic acid and acyclic oligomers;  
69 Radical and concerted non radical reactions, producing acetaldehyde, carbon monoxide and  
70 methylketene; Unzipping depolymerisation, leading to lactides; and Oxidative, random main-  
71 chain scission, leading to lactides.

72 Depolymerization by back-biting (intramolecular transesterification) is considered the  
73 dominant degradation pathway at the temperature range of 270 °C - 360 °C [15].  
74 Nevertheless, degradation occurs by different coupled mechanisms leading to the formation of  
75 different molecules, which depend on the temperature. They are primary degradation products  
76 such as acetaldehyde, lactides and ring-formed oligomers of different sizes then secondary  
77 degradation products are formed due to oxidation, hydrolysis and cross reaction between  
78 primary products, such as carbon dioxide, carbon monoxide, methane, 2,3-butanedione, 2,3-  
79 pentanedione, acrylic acid, acyclic oligomers, methylketene (fragmentation product), ethylene  
80 and propylene [15, 17].

81 Despite literature about VOCs identification during thermal degradation of PLA has been  
82 reported [15-19], to our best knowledge, no literature is available on the VOCs concentrations  
83 during PLA processing. The identification of VOCs is possible when using high sensitive  
84 analytical methods, such as gas chromatography-mass spectrometry (GC-MS); however, the  
85 VOCs concentration is difficult to establish due to their low concentration levels, which

86 challenges analytical methods. A confident identification of compounds analyzed by GC-MS,  
87 can be achieved with mass spectra and Kovats retention index that closely match those given  
88 in the literature [7] or by injection of standards. The Kovats retention index of a compound  
89 for a given GC stationary phase is a characteristic value obtained by interpolation, relating the  
90 adjusted retention time of the molecule to the adjusted retention time of two alkanes eluted  
91 before and after the peak of the sample component.

92 Multiple headspace extraction (MHE) by dynamic gas extraction carried out stepwise on a  
93 sample is an absolute quantitative method, whose theoretical explanation has been widely  
94 supported to assess volatiles in solid matrix [10, 20]. A methodology used to quantify the  
95 concentration of volatile organic compounds and aroma compounds into solid matrix is  
96 multiple headspace – solid phase micro extraction (MHS-SPME) gas chromatography [21-  
97 25], which allows avoiding matrix effect, use of solvent and concentration like MHE but due  
98 to trapping of volatiles by SPME fibre, MHS-SPME allows the determination of volatile  
99 compounds with a concentration 100 times smaller than by MHE [23].

100 In this context, the aim of this work is to quantify the VOCs produced by PLA packaging  
101 samples during processing, using an optimized multiple headspace – solid phase micro  
102 extraction (MHS-SPME) gas chromatography/mass spectrometry (GC-MS). For that, some  
103 commercial types of Poly(D,L-lactide) were studied and the VOCs formed after extrusion  
104 and after thermoforming were identified and then quantified.

105

## 106 **2. Materials and methods**

107

### 108 **2.1 Materials and processing**

#### 109 **2.1.1 Reagents and SPME fibers**

110 Acetaldehyde (>99.5%), 2-methyl 2-Propanol (>99.5%), 2,3-Pentanedione ( $\geq 96\%$ ), pentane

111 (98%), hexadecane (97%) were purchased from Sigma-Aldrich. Propylene glycol (>99.5%)  
112 was provided by Fluka. A standard mixture of alkanes C6 to C19 in pentane was used to  
113 calculate the Kovats indices.

114 The solid phase micro extraction in headspace mode was carried out using carboxen/  
115 polydimethylsiloxane (CAR/PDMS) and divinylbenzene/carboxen/polydimethylsiloxane  
116 (DVB/CAR/PDMS) fibres of 75  $\mu\text{m}$  of thickness, needle size 24 ga (Supelco).

### 117 2.1.2 Poly(D,L-lactide) pellets

118  
119 PLA2002D, PLA2003D, PLA3251D, PLA4042D and PLA7000D were provided by  
120 NatureWorks® LLC (NE, USA) in pellet form. The content of D-lactic acid present in  
121 materials was between 4% and 4.5% for PLA2002D and PLA2003D [16, 26, 27],  
122 approximately 1.4% for PLA4042D [28] and about 6.4 % for PLA7000D [29]. In the case of  
123 PLA3251D, the exact proportion of D, L monomer was not specified in the manufacturer's  
124 datasheet.

### 126 2.1.3 Extrusion and thermoforming of PLA samples

127 Before extrusion, pellets of PLA2002D and PLA2003D were dried in a SOMOS® dryer  
128 (MANN+HUMMEL ProTec) at 80 °C for 8 h and 60 °C for 24 h, respectively. The residual  
129 moisture in pellets after drying was 700 ppm in PLA2002D, and be lower than to 350 ppm  
130 using an Aboni FMX Hydrotracer (France) in PLA2003D. Extrusion conditions of both PLA  
131 grades were described in our previous work [24]. Following that procedure, we obtained a  
132 film of 100 mm in width and approximately 65  $\mu\text{m}$  in thickness for PLA2002D. In the case of  
133 PLA2003D, we obtained a film of 120 mm wide and about 60  $\mu\text{m}$  thick.

134 Trays from PLA2003D film were made at 90 °C for 15 seconds using a thermoforming  
135 machine (Formech 660, UK) and a semi-hemispheric mold of 0.5 H/D. Trays had a thickness  
136 of 20 µm.

137

## 138 2.2 Methods

### 139 2.2.1 Equipment and gas chromatographic conditions

140 An Agilent Technologies 6890 GC/FID coupled with a mass spectrometer 5975 INSERT and  
141 an Autosampler MPS2 GERSTEL, which allows automated MHS-SPME injections, were  
142 used. The chromatographic column was an Agilent J&W Scientific DB5-MS capillary  
143 column (30 m length x 0.32 mm inner diameter x 0.5 µm film thickness). The carrier gas was  
144 He at 1.4 ml/min. The oven temperature program began with an initial temperature of 30 °C  
145 for 5 min and then temperature increased at a rate of 5 °C/min up to 230 °C, maintained 5  
146 min. Split/splitless injector and detector temperatures were 250 °C. The parameters of mass  
147 spectrometer used for identification of VOCs were: electron impact ionization; electron  
148 energy, 70 eV; ion source, 230 °C; electron multiplier voltage, 1470 eV; transfer line, 270 °C;  
149 scanning, between 29 and 400 amu. The data were recorded by MSD ChemStation software  
150 and the identification of the constituents was achieved using mass spectral matches with  
151 Wiley7 NIST 05 mass spectra database. Kovats indices were determined to confirm  
152 identification. For that, a standard mixture of alkanes C6 to C19 in pentane was analyzed  
153 under the same conditions as the samples.

154

### 155 2.2.2 MHS-SPME procedure

156 The MHS-SPME method used for VOCs quantification was described in our previous work  
157 [24]. Samples of about 0.2 or 1 g were sealed in 20 ml glass vials with silicon/PTFE septa. In  
158 the case of films and trays, samples were taken and sealed as soon as finished the extrusion

159 and thermoforming steps, then they were stored at room temperature before to be analyzed  
160 within the next seven days. Three vials of each sample were prepared.

161 The sample vials were incubated at 30 °C for 30 min. MHS-SPME was performed for 15 min  
162 at 30 °C using a 75 µm CAR-PDMS fibre. Desorption time was 5 min into the injector port.  
163 After injection, the SPME fiber was conditioned at 300 °C for 10 minutes. Total peak area of  
164 each compound sorbed was calculated according methodology described by Salazar et al.  
165 (2012) [24]. The calibration was carried out by external standard. For that, a solution of a mix  
166 of organic compounds previously identified was prepared in hexadecane or propylene glycol  
167 (10000 ppm each). Dilutions of 1 to 50 µg/g were used for acetaldehyde, 2-methyl 2-  
168 Propanol, 2,3-Pentanedione. Twenty µl of the diluted solution were introduced in a 20 ml  
169 glass vial sealed with silicon/PTFE septa and a steel cap. Three vials were prepared for each  
170 dilution, each vial was sampled four times and total peak area of each compound was  
171 calculated using the same methodology as PLA samples.

172 The limit of detection (LOD) was calculated as the quantity of compound producing a signal  
173 exceeding the average background signal by three standard deviations of the signal-to-noise  
174 ratio in the lowest concentration standard, divided by the slope of the corresponding analytical  
175 curve [30]. The limit of quantification (LOQ) was obtained as the quantity of compound that  
176 is 10 standard deviations above the average background signal, divided by the slope of the  
177 corresponding calibration curve [31].

178

### 179 2.3 Statistical analysis

180 The statistical analysis of data was performed through one-way analysis of variance  
181 (ANOVA) using XLSTAT-Pro 7.0 software (Addinsoft, Paris, France).

## 182 3. Results and Discussion

183

### 184 3.1 Optimization of MHS-SPME method

185 Preliminary experiments were carried out to optimize the MHS-SPME method to quantify the  
186 VOCs present in PLA.

187

#### 188 3.1.1 Screening of SPME fibre

189 The type of fibre coating to be used depends on the chemical nature of the target analytes.  
190 With the purpose of selecting the appropriate SPME fibre, we compared the results obtained  
191 in preliminary experiments using CAR/PDMS and DVB/CAR/PDMS fibres on samples of 1  
192 g approximately of PLA2002D pellets. Samples were incubated for 25 min at 70°C, a  
193 temperature higher than the glass transition of PLA (between 55 and 65 °C), to promote the  
194 volatilization of organic compounds from pellets. The results are shown in Figure 2.

195 As expected according to literature [10, 32], the CAR/PDMS fibre provided better results for  
196 compounds with low molecular weight, while DVB/CAR/PDMS was better for the  
197 compounds with high molecular mass (Figure 2) and also polar compounds such as  
198 carboxylic acids. Both types of fibre allowed identifying also some semi-volatile compounds  
199 such as lactides, which were separated by GC using a DB5 capillary column in two peaks, the  
200 first one is meso-lactide and the second one is a mix of L,L and D,D-Lactide, which are co-  
201 eluted. Van Aardt et al. [33] reported the use of CAR/PDMS solid phase microextraction in  
202 static headspace at 45 °C for 15 min as an effective method for the recovery of acetaldehyde  
203 in milk and water media with detection levels as low as 200 and 20 ppb, respectively. So, as  
204 our principal aim was quantifying the high volatile organic compounds, the CAR/PDMS fibre  
205 was selected for the next phases of our study.

206

## 207 3.1.2 PLA grades

208

209 With the purpose of identifying the VOCs in pellets of different PLA grades, sample vials of  
210 PLA2003D, PLA3251D, PLA4042D and PLA7000D were incubated at 70°C (higher than T<sub>g</sub>,  
211 between 55 and 65 °C) for 25 min using a CAR/PDMS fiber. The results obtained are shown  
212 in Figure 3.

213 The results mainly showed the presence of lactides. Meso-lactide, L,L- and D,D-lactide can  
214 be produced by the reactions of degradation of PLA such as the simple depolymerization  
215 reaction by intramolecular ester exchange [15, 17]. Additionally, several volatile organic  
216 compounds whatever the PLA sample, thus aldehydes, alcohols, acetone, acetic acid, 2,3-  
217 Pentanedione were identified due mainly to transesterification and side-reactions [34, 35].  
218 Kotliar [34] and Porter & Wang [35] showed that intra and inter transesterification of  
219 polyesters occur rapidly in molten state during processing but take place below the melting  
220 point of the polymer. Monomers which are results of transesterification of a single chain may  
221 become distribute over all the chains in the system. Transesterification undergoes the scission  
222 and recombination reactions, including acidolysis and alcoholysis. Kinetics of  
223 transesterification showed that breaking and making of bonds occur simultaneously. In this  
224 context, the hydroxyl end group in PLA mainly participates to the degradation of the polymer  
225 leading to molecular and radical reactions [15, 17].

226 Literature reported the formation of volatile compounds in PLA samples exposed to outdoor  
227 soil environment during two years [36]. The authors used solid phase microextraction  
228 (SPME) coupled to gas chromatography and mass spectrometry to monitor the volatile  
229 compounds. They reported the presence of lactic acid, lactide and lactoyl lactic acid in unaged  
230 and aged films. Khabbaz et al. [37] studied the biotic and abiotic degradation of polylactide  
231 (PLLA) using fractionated Py-GC-MS at 400 and 500°C. At these temperatures, they

232 identified acetaldehyde, acrylic acid, lactoyl acrylic acid, two lactide isomers and cyclic  
233 oligomers up to the pentamer as thermal decomposition products of PLA, as well as some  
234 other not completely identified products [37].

235 In our study, the most volatile compound acetaldehyde was identified. Acetaldehyde can be  
236 produced by different pathways during PLA processing, mainly by reactions of trans-  
237 esterification [17]. Acetaldehyde has a distinct fruity odor and taste (irritant at high  
238 concentration) and has a low sensory detection threshold level especially in mineral water  
239 where its migration is detectable at low concentrations of 10–20 ppb [38]. Consequently, the  
240 residual acetaldehyde in PLA could be an important marker for the industry in the selection of  
241 PLA grades as shown in the PET industry. Removing acetaldehyde from PLA is important as  
242 this aroma compound can migrate from PLA leading to sensorial deterioration to foods or  
243 beverages in contact. Others aldehydes identified as hexanal, heptanal, octanal, nonanal and  
244 decanal, could be produced from the reactions of trans-esterification.

245 Another compound identified in PLA2002D, PLA2003D and PLA3251D was 2,3-  
246 Pentanedione, which may be produced by the radical reaction between acetaldehyde and  
247 propen-1-one [17] and has a buttery – cheesy odor.

248 Hydrolysis of ester groups could explain the presence of alcohols such as 2-methyl-2-  
249 propanol, which is the simplest tertiary alcohol with a camphor – like odor. Pentanoic,  
250 hexanoic and nonanoic acids are present in pellets only for some PLA grades (PLA4042D and  
251 PLA7000D). They could be secondary reaction products by cis-elimination reactions on short  
252 chains oligomers of the PLA.

253 Acetone and acetic acid have been already reported in literature about PLA degradation [15];  
254 however, alkanes identified in our study, such as 2,2,4,6,6-pentamethyl-heptane remain  
255 unexplained. Considering that no studies about PLA degradation reported their presence, thus  
256

257 they could be degradation products from additives or processing aids. Literature reported the  
258 presence of some additives in pellets of five different PLA commercial grades [39]. After  
259 extraction of additives by dissolution/precipitation (dichloromethane-ethanol) method, the  
260 authors used gas chromatography - flame ionization detector (FID), GC-MS and nuclear  
261 magnetic resonance (NMR) to identify additives in all samples studied. They reported the  
262 presence of plasticizers (Polyethylene glycol and adipate derivatives) and slip agents  
263 (Erucamide) in samples [39].

264 Finally, although that results showed no main differences in VOCs between PLA grades  
265 studied, PLA2003D grade presented higher peaks of small volatile compounds than others  
266 grades studied, such as acetaldehyde, 2-methyl-2-propanol and 2,3-pentanedione. So,  
267 PLA2003D grade was selected for the next steps of our study.

268

### 269 3.1.3 Incubation temperature

270

271 To have a representative view of the volatile compounds present in the PLA matrix, the HS-  
272 SPME procedure should be optimized but the limits of this methodology are well-known in  
273 the literature. At room temperature, the highly volatile compounds can be easily released from  
274 polymers; nevertheless, the extraction of semi-volatile compounds is lower [40]. Increasing  
275 temperature allowed the release of semi-volatile compounds [40] from the solid matrix but  
276 modified the partition coefficient between the SPME fibre and the headspace and led to their  
277 desorptions [41]. Moreover, a too elevated temperature causes a saturation into the headspace  
278 above the matrix, in particular for the highly volatile compounds and affects the extraction  
279 rate [40, 41]. So, due to these drawbacks for semi-volatile compounds determination, we  
280 focused our study on the quantification of the high volatile compounds and we selected a  
281 temperature of 30 °C (room temperature) for extraction by SPME.

282

## 283 3.1.4 Effect of processing

284 To evaluate the effect of processing on the VOCs formed in PLA, we analyzed samples of  
285 PLA2003D in different forms, as pellets, extruded films and thermoformed samples. The  
286 results of VOCs identified at 30 °C in these samples are shown in Table 1. The results  
287 showed the presence of eight compounds, six of them already identified in pellets samples at  
288 70 °C (see Figures 2 and 3) and two new compounds that were identified in film and  
289 thermoformed samples. The new compounds identified were 2,4-dimethyl-2-pentanol and  
290 2,3,4-trimethyl-hexane. The former compound is an alcohol whose presence could be  
291 explained by the hydrolysis of ester groups. The latter compound is an alkane which presence  
292 remains unexplained and it could be a degradation product from additives. Moreover, the  
293 semi-volatile compounds previously identified at 70 °C, such as lactides, were not extracted at  
294 30 °C, which is in agreement with SPME literature [40]. Additionally, four compounds  
295 (acetic acid, 2,3-pentanedione, 2,4-dimethyl-2-pentanol and 2,3,4-trimethyl-hexane) were  
296 identified only in processed PLA2003D samples. So, these compounds could be thermo-  
297 formed during the extrusion process, whose final temperature was 200 °C.

## 298 3.2 Quantification of VOCs

299 Comparing the three forms of PLA2003D studied (see Table 1), it is clear that volatile  
300 compounds in extruded film samples were present in higher amount than in thermoformed  
301 and pellets samples. To quantify the VOCs present into PLA samples by MHS-SPME, firstly  
302 it is necessary to demonstrate that an exponential decrease of GC peak areas of VOCs is  
303 achieved with good correlation coefficients ( $R^2 \geq 0.99$ ) and secondly it needs to obtain  
304 calibration curves of the VOCs following the same procedure. So, after first trials for the  
305 optimization of the MHS-SPME methodology, three compounds were selected as markers  
306 because they presented a linear response with good correlation coefficients of the exponential

307 decay during four successive extractions by MHS-SPME: acetaldehyde ( $R^2 = 0.9983$ ); 2-  
308 methyl-2-propanol ( $R^2 = 0.9921$ ); 2,3-pentanedione ( $R^2 = 0.9937$ ).

309 For these three compounds, calibration curves of standards in hexadecane were carried out  
310 according to the testing conditions selected previously. Table 2 shows the characteristics of  
311 method using standard solutions. We originally assumed that all compounds selected would  
312 present larger linear ranges in the calibration curves, however only acetaldehyde and 2-methyl  
313 2-propanol, presented a linear response to ratio between total peak area and compound mass,  
314 whereas 2,3-pentanedione was co-eluted with a minor compound present in hexadecane. For  
315 that, new solutions of 2,3-pentanedione in propyleneglycol (>99.5%, Fluka) were carried out  
316 and a good linearity in decay for 2,3-pentanedione was obtained under chromatographic  
317 conditions already used. Since the calibration curves were achieved, quantifications of the  
318 three compounds in extruded films and thermoformed samples of PLA2003D were carried  
319 out. The analyses were performed in triplicate using samples of 0.2 g each one. In the case of  
320 2,3-pentanedione, total peak areas obtained by MHS-SPME were below the linear range of its  
321 calibration curve and consequently, we used 1 g PLA samples to quantify this compound.

322 Additionally, the change in VOCs of PLA2003D as film or thermoformed samples was  
323 assessed after six months of storage at room temperature in capped vials. The VOCs  
324 identified in these samples are shown in Table 3 and the concentrations of three of them are  
325 presented in Table 4. The results of VOCs identified in PLA2003D samples after storage  
326 (Table 3) showed the presence of six compounds, all of them already identified in samples  
327 before storage (see Table 1), with exception of ethanol. The presence of this molecule can be  
328 explained by hydrolysis of ester groups. In addition, the peak areas of the VOCs identified  
329 after storage were lower than the peak areas determined in samples before storage. In contrast,  
330 the results found in thermoformed samples after storage showed the presence of only three  
331 compounds (ethanol, acetone and 2-methyl 2-propanol) of six compounds identified in

332 extruded films. Therefore, on the basis of these results, it is clear that the storage of samples  
333 decreased the presence of VOCs in PLA samples.

334  
335 For freshly new thermoformed PLA samples in comparison with extruded film (Table 4), the  
336 concentration of acetaldehyde decreased and 2,3-pentanedione disappeared. The process of  
337 thermoforming is carried out at 90 °C during 15 seconds that could cause the loss of these two  
338 compounds, which cannot contribute to produce further degradation of PLA. After storage,  
339 the acetaldehyde concentration was lower than LOQ in extruded films and was not at all  
340 found in thermoformed samples. 2,3-pentanedione was no present in all PLA samples after  
341 storage. Hence, it seems that these molecules were degraded during storage at ambient  
342 conditions. 2,3-Pentanedione could have been degraded by photolysis leading to radical  
343 reactions, such as literature have reported [42].

344 In the case of 2-methyl-2-propanol, before storage, no significant difference was found  
345 between the concentration determined in films and thermoformed samples (Table 4). After 6  
346 months of storage in capped vials, the concentrations were lower than the LOQ of the method.  
347 Under our experimental conditions, it is however difficult to propose a PLA degradation  
348 pathway in extrusion and thermoforming that explains the production of this molecule or that  
349 allows knowing if this molecule is produced from the secondary reactions of primary  
350 products.

351 From a commercial perspective, these results are of interest because they show that there is  
352 not VOCs production in PLA samples during storage at room temperature, but during the  
353 forming at higher temperatures.

354  
355 Extruded samples of PLA in our work showed acetaldehyde concentrations between 3.6 and  
356 18 times lower than those reviewed by Mutsuga et al. [38] in PET bottles from Europe, North

357 America and Japan, ranging from 5.0 to 13.1 mg/kg, from 9.1 to 18.7 mg/kg and from 8.4 to  
358 25.7 mg/kg, respectively. Acetaldehyde could migrate in mineral water packed in PET bottles  
359 at a level from 1.62 to 2.22 ppm and from 13.94 to 17.68 ppm, after 1 day and 90 days of  
360 storage at room and cause sensorial defect [43], that could be explained because the values are  
361 between 80 and 884 times higher than the sensorial threshold value of acetaldehyde in mineral  
362 water (0.01 – 0.02 ppm) [38]. Finally, to the best of our knowledge, no data were reported  
363 previously about the acetaldehyde concentration in PLA and considering the low residual  
364 content, PLA may likely present lower sensorial problem than PET associated to the  
365 migration of this molecule into the food in contact.

366

#### 367 4. Conclusions

368

369 Several organic volatile compounds were identified by HS-SPME in PLA samples along the  
370 forming process and analysis conditions used in this work, being consequently a powerful  
371 tool for the screening of VOCs. Three volatile organic compounds of PLA2003D samples  
372 were quantified using MHS-SPME method. Acetaldehyde and 2,3-pentanedione  
373 concentrations increased after the extrusion and then decreased or disappeared after  
374 thermoforming, which can be explained by evaporation due to process temperature (90 °C).  
375 PLA2003D samples showed acetaldehyde concentrations lower than PET. Thus, residual  
376 acetaldehyde in PLA could be an important marker for the industry in the selection of PLA  
377 grades as shown in the PET industry. Thermoforming step didn't promote the degradation of  
378 PLA, on the contrary this step allowed a loss of the most volatile molecules, and thus  
379 positively influenced the sensorial quality of the packaging. Additionally, after 6 months of  
380 PLA storage at ambient conditions, the concentrations of these compounds decreased and  
381 were lower than the LOQ of the method or even absent. Consequently, from a commercial

382 point of view, these results are of interest for storage of PLA because they showed that there  
383 was not production of VOCs in PLA samples during storage at room temperature, but only  
384 during the forming at higher temperature.

385

### 386 **Acknowledgements**

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503 Tables

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505

506 **Table 1.** GC peak areas<sup>a</sup> of compounds identified by HS-SPME extraction<sup>b</sup> from 1 g of  
 507 PLA2003D samples analyzed at 30 °C × 30 minutes of incubation using a CAR/PDMS SPME  
 508 fibre.

509

Compound	IK cal <sup>c</sup>	IK ref <sup>d</sup>	Mw	CAS	Pellets	Extruded film	Thermoformed
Acetaldehyde	nd	~427	44	75-07-0	692500 ± 55400	12445800 ± 501500	233800 ± 15500
Acetone	500	500	58	67-64-1	272900 ± 35100	1132500 ± 48100	477600 ± 26100
2-methyl-2-propanol	524	526	74	75-65-0	225800 ± 5200	5624400 ± 72000	3833400 ± 84600
Acetic acid	603	~600	60	64-19-7	-	777900 ± 30000	-
2,3-pentanedione	703	697	100	600-14-6	-	1068700 ± 20000	-
2,4-dimethyl-2-pentanol	804	-	116	625-06-9	-	759300 ± 11500	362600 ± 13300
2,3,4-trimethyl- hexane	870	~850	128	921-47-1	-	151200 ± 35100	-
2,2,4,6,6-pentamethyl- heptane	1005	997	170	13475-82-6	456600 ± 72400	923600 ± 5800	542400 ± 39900

510

511 <sup>a</sup> peak area values are the mean and standard deviation of three replicates; <sup>b</sup> SPME extraction time = 15 min, desorption time = 5 min; <sup>c</sup>  
 512 Kovats index calculated in a DB5 column; <sup>d</sup> from NIST available in <http://webbook.nist.gov/chemistry/cas-ser.html> for DB5 column; nd =  
 513 not determined; - means not present.

514

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516

517 **Table 2.** Features of MHS-SPME method using standard solutions.

518

Compounds	Studied range ( $\mu\text{g}$ )	Linear range ( $\mu\text{g}$ )	LOQ ( $\mu\text{g}$ )	Calibration curve equation	$R^2$
Acetaldehyde*	0.016 - 1.524	0.077 - 0.757	0.077	$y = 68437528x$	0.98
2-methyl-2-Propanol*	0.016 - 1.524	0.016 - 0.762	0.016	$y = 92508061x$	0.98
2,3-Pentanedione**	0.007 - 0.589	0.031 - 0.243	0.031	$y = 45791165x - 2013666$	0.99

519 \*in hexadecane; \*\* in propyleneglycol.

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522

523

524 **Table 3.** GC peak areas<sup>a</sup> of VOCs identified in PLA2003D samples (200 mg) after 6 months  
 525 of storage in capped vials using MHS-SPME<sup>b</sup> at 30 °C × 30 minutes of incubation and a  
 526 CAR/PDMS SPME fibre.

527

Compounds	KI cal <sup>c</sup>	KI ref <sup>d</sup>	Mw	CAS	Extruded film	Thermoformed
Acetaldehyde	Nd	~427	44	75-07-0	2722000 ± 74400	not present
Ethanol	nd	459	46	64-17-5	368600 ± 8600	327400 ± 22700
Acetone	nd	500	58	67-64-1	581300 ± 214200	623700 ± 117900
2-methyl-2-Propanol	525	526	74	75-65-0	1634300 ± 491600	566000 ± 22800
2,4-dimethyl 2-Pentanol-	804	-	116	625-06-9	197400 ± 32100	not present
2,2,4,6,6-pentamethyl-Heptane	1005	997	170	13475-82-6	164700 ± 25000	not present

528 <sup>a</sup> peak area values are the mean and standard deviation of three replicates; <sup>b</sup> SPME extraction time = 15 min, desorption time  
 529 = 5 min; <sup>c</sup> Kovats index calculated in a DB5 column; <sup>d</sup> from NIST available in [http://webbook.nist.gov/chemistry/cas-](http://webbook.nist.gov/chemistry/cas-ser.html)  
 530 [ser.html](http://webbook.nist.gov/chemistry/cas-ser.html) for DB5 column; – means not present.

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532  
533534 **Table 4.** Concentrations of VOCs ( $\mu\text{g}$  of compound/g of sample) in PLA2003D samples (200  
535 mg) obtained by MHS-SPME before and after storage at room temperature in capped vials.  
536

Compounds	LOQ <sup>*</sup>	Before storage		After 6 months	
		extruded film	thermoformed	extruded film	thermoformed
Acetaldehyde	0.385	$1.40 \pm 0.18$	< LOQ	< LOQ	not present
2-methyl 2-propanol	0.080	$0.39 \pm 0.08^a$	$0.48 \pm 0.04^a$	< LOQ	< LOQ
2,3-pentanedione	0.069	$0.074 \pm 0.003^{**}$	not present	not present	not present

537 \* LOQ = limit of quantification ( $\mu\text{g}$  of compound/g of sample); \*\* determined in a PLA samples of 1g; <sup>a</sup> different letters  
538 indicate significant differences at  $p < 0.05$  (Duncan).  
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541 **Figures**

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545 **Figure 1.** Main degradation mechanisms of PLA: a) Thermal degradation mechanism of  
546 PLA; b) Degradation mechanism of PLA by hydrolysis. Adapted from Nishida, 2010 [18] and  
547 Oliveira et al. 2016 [44].

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552

553 **Figure 2.** Peak areas of compounds identified in the first MHS-SPME extraction from 1g of  
554 PLA2002D pellets incubated at 70 °C for 25 min using two types of SPME fibre.

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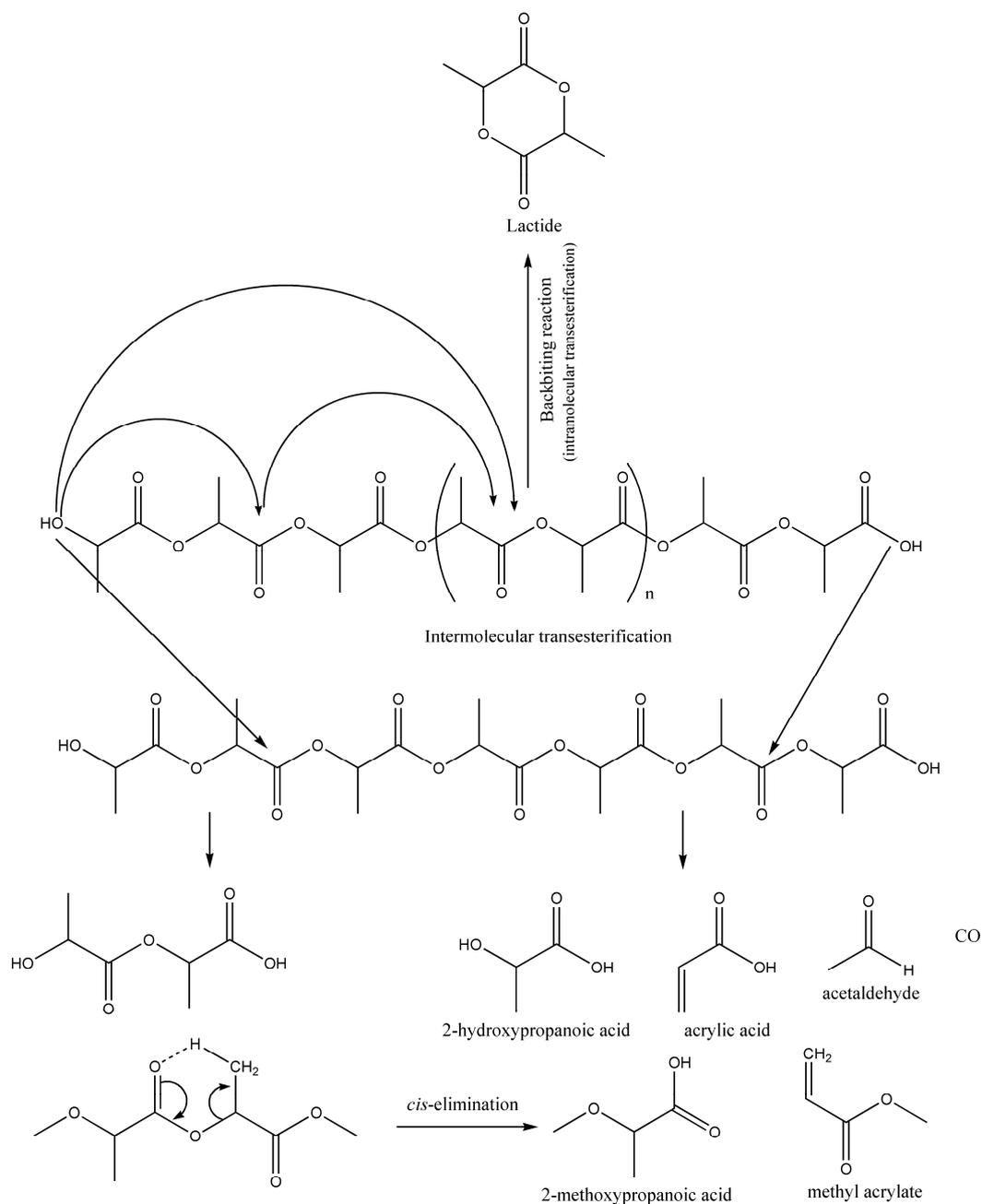
560 **Figure 3.** Peak areas of VOCs identified by HS-SPME in pellets of different PLA grades  
561 using a CAR/PDMS fibre and samples of 1 g.

562

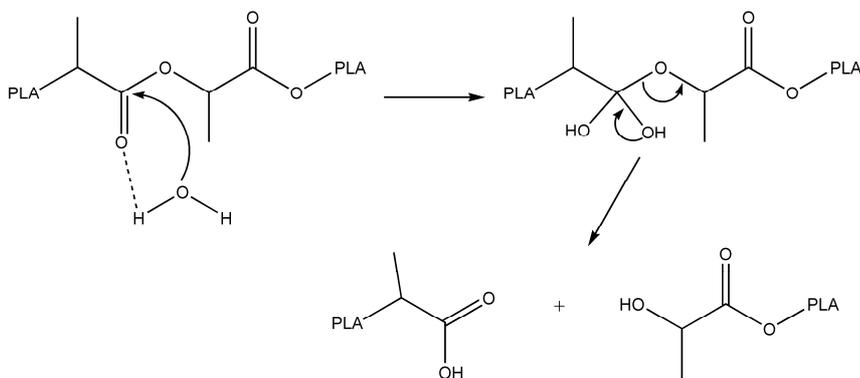
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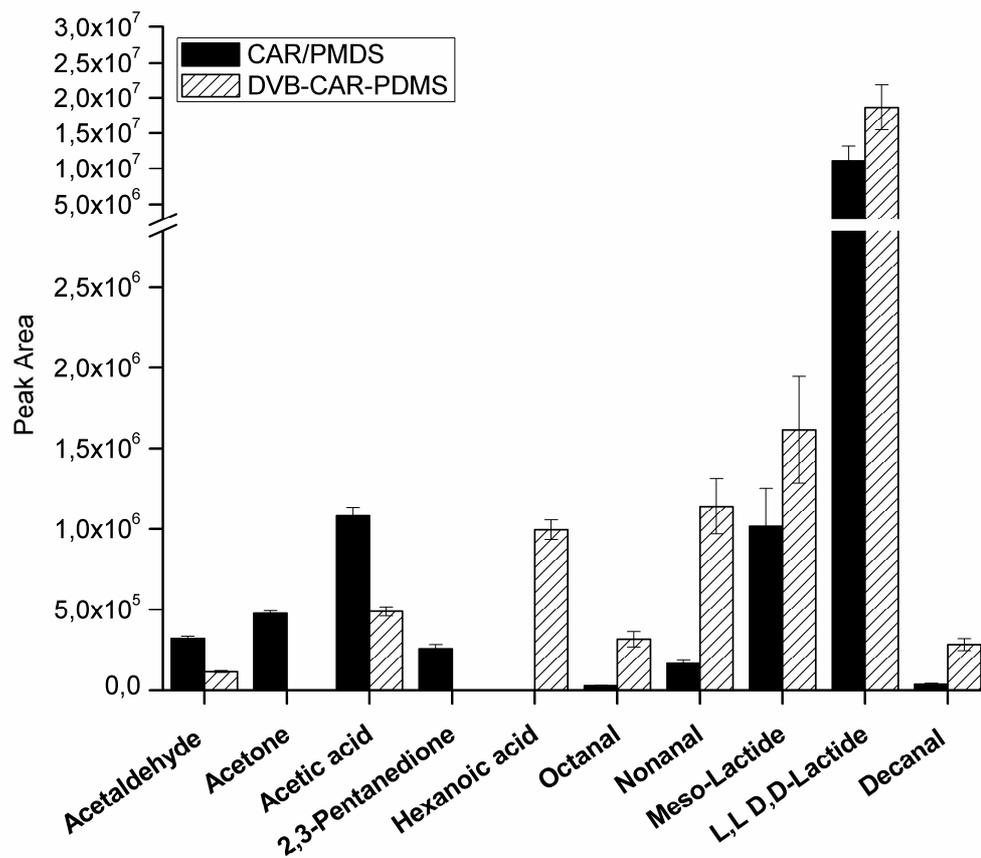
a) Thermal degradation mechanism of PLA



b) Degradation mechanism of PLA by hydrolysis.

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