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PII: S0141-3910(16)30389-5

DOI: [10.1016/j.polymdegradstab.2016.12.010](https://doi.org/10.1016/j.polymdegradstab.2016.12.010)

Reference: PDST 8131

To appear in: *Polymer Degradation and Stability*

Received Date: 19 August 2016

Revised Date: 8 December 2016

Accepted Date: 20 December 2016

Please cite this article as: Salazar R, Domenech S, Plessis C, Ducruet V, Quantitative determination of volatile organic compounds formed during polylactide processing by MHS-SPME, *Polymer Degradation and Stability* (2017), doi: 10.1016/j.polymdegradstab.2016.12.010.

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Comment citer ce document :

Salazar Gonzalez, R., Domenech, S., Plessis, C., Ducruet, V. (Auteur de correspondance) (2017). Quantitative determination of volatile organic compounds formed during polylactide processing by MHS-SPME. *Polymer Degradation and Stability*, 136, 80-88. DOI : 10.1016/j.polymdegradstab.2016.12.010

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

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Abstract

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

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

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1. Introduction

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

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

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

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

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

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

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

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

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

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

2. Materials and methods

2.1 Materials and processing

2.1.1 Reagents and SPME fibers

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

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

The solid phase micro extraction in headspace mode was carried out using carboxen/polydimethylsiloxane (CAR/PDMS) and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fibres of 75 μm of thickness, needle size 24 ga (Supelco).

2.1.2 Poly(D,L-lactide) pellets

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

2.1.3 Extrusion and thermoforming of PLA samples

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

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

2.2 Methods

2.2.1 Equipment and gas chromatographic conditions

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

2.2.2 MHS-SPME procedure

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

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

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

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

2.3 Statistical analysis

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

3. Results and Discussion

3.1 Optimization of MHS-SPME method

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

3.1.1 Screening of SPME fibre

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

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

3.1.2 PLA grades

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

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

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

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

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

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

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

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

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

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

3.1.3 Incubation temperature

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

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

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

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

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

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

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 25.7 mg/kg, respectively. Acetaldehyde could migrate in mineral water packed in PET bottles 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 storage at room and cause sensorial defect [43], that could be explained because the values are between 80 and 884 times higher than the sensorial threshold value of acetaldehyde in mineral water (0.01 – 0.02 ppm) [38]. Finally, to the best of our knowledge, no data were reported previously about the acetaldehyde concentration in PLA and considering the low residual content, PLA may likely present lower sensorial problem than PET associated to the migration of this molecule into the food in contact.

4. Conclusions

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

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

Acknowledgements

The authors would like to acknowledge the help of Alain Guinault in preparation of PLA films. Rómulo Salazar acknowledges SENESCYT of Ecuador for funding.

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503 Tables

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

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Compound	IK cal ^c	IK ref ^d	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

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

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

Compounds	Studied range (µg)	Linear range (µg)	LOQ (µg)	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

*in hexadecane; ** in propyleneglycol.

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

Compounds	KI cal ^c	KI ref ^d	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

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

Table 4. Concentrations of VOCs (μg of compound/g of sample) in PLA2003D samples (200 mg) obtained by MHS-SPME before and after storage at room temperature in capped vials.

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

* LOQ = limit of quantification (μg of compound/g of sample); ** determined in a PLA samples of 1g; ^a different letters indicate significant differences at $p < 0.05$ (Duncan).

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

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a) Thermal degradation mechanism of PLA

b) Degradation mechanism of PLA by hydrolysis.

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