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Plasticization of poly(lactide) by sorption of volatile organic compounds at low concentration

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A B S T R A C T

Poly(lactide) (PLA) is one of the most promising bio-based polyester for wide applications and in particular for food packaging. However aroma compounds can interact with packaging in contact leading to modification of its thermal properties during storage. Up to date, no study has focused on aroma sorption in PLA at realistic food packaging conditions implying low vapor activities, and thus using dedicated methodology ranging over concentrations below 200 µg of aroma compound per gram of polymer. In the present study the sorption of four ethyl esters (C4, C6, C7 and C8), benzaldehyde and 2-nonanone in three different types of poly(D,L-lactide) (PDLLA) at 25 °C was investigated in order to determine their solubility coefficients and their impacts on the thermal properties of the tested PDLLA. The sorption of aroma compounds at low vapor activities was studied using two methods of headspace extraction (MHE and MHS-SPME) after 20 days of conditioning in a hermetic flask. The results showed that PLA films studied have a very high affinity for benzaldehyde. Ethyl acetate solubility coefficient in PLA was comparatively similar to poly(ethylene terephthalate), polypropylene (PP) and low-density polyethylene (LDPE). Differential Scanning Calorimetry results showed a decrease in glass transition temperature (T_g) of PDLLA films and an increase in the crystallinity degree that depend on the concentration of the sorbed aroma compounds. It could be clearly demonstrated that plasticization of PDLLA by aroma compounds occurred at very low vapor activities (0.01) and that the importance of the effect depended on the chemical nature of the molecule.

1. Introduction

Poly(lactide) (PLA) is one of the most promising bio-based polyester for food packaging [1,2] because of its good mechanical and barrier properties and ease of processing. However, polymeric packaging materials are not inert and mass transfer occurs between packaging polymer and foodstuff [3] leading to quality issues.

Indeed, plastic packaging materials can absorb a significant quantity of aroma compounds from food which can involve modifications of the flavour composition, decrease of intensity, or unbalance flavour [4–7].

Furthermore, a number of studies showed that the sorption of flavour molecules can lead to modifications of the properties of the packaging material induced by swelling and/or plasticization. Such

phenomena can favour for example oxygen permeation which in turn can reduce the shelf-life of the product [8–10].

Most of the literature concerned with interactions between flavour molecules and polymers deals with polyolefins, polypropylene and polyethylene [11] and very few studies show results on glassy polymers such as polyesters [5,12–14] and polystyrene [15].

One of the principal difficulties in dealing with sorption studies in glassy polymers is the low mass transfer rate which challenges analytical methods. Analysis of sorbed quantities is eased when excessive aroma concentrations are employed. The drawback of this strategy is that at aroma activities sorption isotherms usually do not follow the Henry model because of modification of the polymer morphology (plasticizing, swelling...). In order to avoid this phenomenon, experiments should be conducted with low concentration of aroma compounds, ideally at infinite dilution.

Tedious methods need often to be employed to quantify the amount of flavour absorbed by the plastic materials, such like solvent extraction or supercritical solvent extraction [12,16]

followed by a careful solvent concentration [17]. Presence of oligomers and additives coming from polymer is a limiting factor in using this extraction procedure as sorbed aroma compounds can be co-extracted with these molecules leading to a complex gas chromatography profile [18,19].

For these reasons, headspace techniques such as Multiple Headspace Extraction (MHE) and Multiple HeadSpace – Solid Phase Micro Extraction (MHS-SPME) coupled to gas chromatography (GC) are promising tools for analysing flavour compound sorption in low quantity in polymeric structures without interference of non-volatile compounds. Multiple Headspace Extraction Gas Chromatography (MHE-GC) technique and Multiple headspace-solid phase micro extraction (MHS-SPME) were usually used to quantify the concentration of volatile organic compounds [17,20,21] into solid matrix. They allow avoiding matrix effect, use of solvent and concentration. The multiple headspace extraction (MHE) is an absolute quantitative method by dynamic gas extraction carried out stepwise. At each step, equilibrium conditions are established in the vial between the sample and its headspace (gas phase of the vial). Several extractions are made on one sample by automatic headspace injector. Quantities of sorbed analytes exponentially decay with the number of extractions and total quantity corresponds to the total peak area, calculated as the sum of peak areas for each extraction until the complete desorption of the volatiles. By a suitable calibration procedure, the peak area versus amount relationship can be established [22]. MHS-SPME provides more sensitivity and selectivity than MHE-GC due to the concentration step of the volatile molecules on the solid phase of a properly chosen fibre, where low concentrations can be detected and thus it is useful to extract volatile organic compounds sorbed into packaging materials [23]. It is, however, more challenging with respect to calibration issues, in particular when mixtures of volatile compounds are to be analyzed. The amount of analyte extracted by the fibre is proportional to the initial amount but also subjected to a partition coefficient [23,24].

To date, only a few studies were conducted on the sorption of aroma compounds in PLA, which is glassy at room temperature, and those mainly for ethyl acetate and D-limonene [25–27]. In the case of ethyl acetate, which is part of many fruity aroma formulations, it was shown that it had a plasticizing effect and induced crystallization in PLA, changing its properties during storage [26,27]. Auras et al. [25] studied the sorption of different volatile compounds, and showed that PLA had more affinity to more hydrophilic molecules, such as ethyl acetate, compared to hydrophobic one such as limonene. They concluded that PLA had therefore promising properties for the conservation of aroma profiles, as most of the aroma compounds are hydrophobic. The main drawback of those studies was however the high aroma compound activity. No study has focused on aroma sorption in PLA at realistic food packaging conditions where vapour activities are very low, and where the use of specific analytical methodology capable to detect concentrations even below 200 µg of aroma compound per gram of polymer is required. Under such conditions, one can assume that the aroma compounds are present in an infinite dilution. Therefore Henry's law should apply and the solubility coefficients should be independent of the partial pressure.

The present work aims to study the sorption of common aroma compounds in PLA, alone and in mixture at activities usually encountered in the headspace of food products. For that, four commercial types of poly (D,L-lactide) were put in vapor contact with six aroma compounds. Their solubility coefficients at low activities were determined and the impact of aroma sorption on the thermal properties of materials was investigated.

2. Materials and methods

2.1. Materials and processing

2.1.1. Aroma compounds

Ethyl acetate (Sigma Aldrich, >99.5%), ethyl butanoate (Aldrich, 99%), ethyl 2-methylbutanoate (Aldrich, 99%), benzaldehyde (Fluka, >99%), ethyl hexanoate (Aldrich, >99%) and 2-nonanone (Aldrich, >99%) were used. The physicochemical properties are given in Table 1. Hexadecane (Sigma Aldrich, 99%) and pentane (Aldrich, 98%) were used as solvents for the aroma solution and for the preparation of standards.

2.1.2. Poly(D,L-lactide) films samples

Extruded P(D,L-L)A Biomer L9000 (Biomer, Germany), PLA4032D (NatureWorks LLC), PLA2002D (NatureWorks LLC) and PLA Biophan 121 film (Treophan, Germany) with thickness of 120 µm, 235 µm, 65 µm and 40 µm, respectively, were studied. The content of D-lactic acid present in materials was about 1% for P(D,L-L)A Biomer L9000 [26], approximately 2% for PLA4032D [28], and between 4% and 4.5% for PLA2002D [29,30]. In the case of PLA Biophan 121, the exact proportion of D, L monomer was not specified in the manufacturer's datasheet.

Extrusion conditions of PLA Biomer L9000 were already reported by Colomines et al. [26]. In the case of PLA2002D, the films were prepared using a MAPRE single-screw extruder of 30 mm in diameter with a 33 L/D (Length on Diameter) barrel and a three section screw without mixing elements and turning at 35 rpm. The temperature profile of the six zones of the screw was 180–185–190–195–200–200 °C and the temperature of the die was 200 °C. A flat die of 200 mm in width and chill roll equipment were used to manufacture a film of 100 mm in width and approximately 65 µm in thickness. The roll temperature and roll speed were set at 25 °C and 10 m/min, respectively. The PLA4032D granulates were converted into a film using a Collin single-screw extruder with a 30 mm screw turning at 60 rpm. The temperature profile of the five zones of the screw was 190–190–190–200–200 °C and the temperature of the die was 200 °C. A flat film die with a width of 200 mm was used to produce a film of 100 mm in width and approximately 300 µm in thickness. The film was cooled by passing 2 rolls at 25 °C and 4.8 m/s.

In order to obtain very thin films three samples (30 ± 1 mg each one) of PLA4032D and PLA2002D with a thickness of 10 µm were prepared using a microtome (LKB Bromma Historange microtome 2218).

2.2. Conditioning of PLA films in aroma atmosphere

The experimental system used to conditioning of PLA samples is shown in Fig. 1. It consisted in an airtight flask equipped with a Mininert® valve which was placed in a climatic chamber for temperature control. The conditioning was carried out for 14 days (at high activities) or 20 days (at low activities) at 25 ± 0.3 °C. Three

Table 1
Physicochemical properties of the aroma compounds.

Aroma compounds	MW (g/mol)	BP (°C)	P _{vs} at 25 °C (kPa)	log P
Ethyl acetate	88.11	77.91	12.43	0.86
Benzaldehyde	106.12	16.90	0.12	1.71
Ethyl butanoate	116.16	121.79	2.07	1.85
Ethyl 2-methylbutanoate	130.18	133.00	1.10	2.12
Ethyl hexanoate	144.21	170.05	1.71	2.83
2-Nonanone	142.24	192.00	0.86	3.03

MW: molecular weight; BP: boiling point; P_{vs}: saturated vapour pressure at 25 °C; log P: octanol-water partition coefficient.

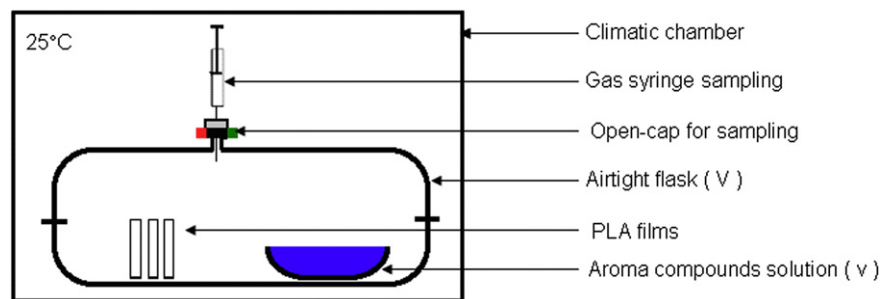


Fig. 1. System used to conditioning of PLA samples.

samples of each material were conditioned separately. Specific partial pressure of the aroma compounds in the atmosphere was generated by a solution of a mix of aroma compounds in hexadecane.

In order to measure the tightness of the system, preliminary experiments were conducted to establish the partition coefficient between headspace and aroma solution. The solutions of a mix of six aroma compounds to be used in MHE and MHS-SPME methods were put into a headspace vial of 20 ml and then sealed with silicon/PTFE septa and an aluminium cap. Three vials were prepared by each solution and they were conditioned at 25 °C. After 20 days, 0.5 ml of headspace volume was sampled using a gas syringe and injected into the gas chromatograph. One headspace injection was made per vial. The partition coefficient was calculated and the results are presented in Table 2. The same procedure was carried with the sorption system (Fig. 1) without PLA films (blank). The headspace/aroma solution partition coefficients measured (Table 2) (k) were compared to the preliminary experiments. No significant differences between the measured partition coefficients were observed. Therefore it was concluded that experimental system was tight during the 20 days of experimentation.

The concentration of the different molecules in the hexadecane solution is given in Table 3. Partial pressure (P_p) was calculated using ideal gas law. The activity of each compound was calculated as P_p/P_{sv} , where P_{sv} is the saturated vapour pressure of aroma compound at 25 °C. P_p and Activities of each aroma compound after 20 days are presented in Table 3.

For experiments at low aroma compound activities (3.4×10^{-5} – 9.06×10^{-2}), film samples were cut into rectangles with mass of 0.3 g for PLA4032D, 0.08 g for PLA2002D and 0.04 g for PLA Biophan. Three samples of each material were conditioned in a separate flask. At activities between 2.9×10^{-3} and 9.06×10^{-2} analysis of sorbed quantities in PLA was done by MHE and at vapor activities between 3.4×10^{-5} and 1.5×10^{-3} by MHS-SPME.

For the analysis of aroma compound sorption at high vapor activity between 0.1, 0.2, 0.5 and 0.9, PLA Biomer L9000 films were cut in rectangles with total mass of 1 g.

Table 2

Headspace/aroma solution partition coefficient (k) at 25 °C after 20 days of conditioning in a flask of 20 ml and in the sorption system without PLA films with the aroma solution used in MHE and MHS-SPME methods.

Aroma compound	In 20 ml flask		In sorption system	
	MHE method	MHS-SPME method	MHE method	MHS-SPME method
	k	k	k	k
Ethyl acetate	$6.63 \pm 0.62 \text{ E-}03^b$	$3.42 \pm 0.88 \text{ E-}03^a$	$8.79 \pm 0.78 \text{ E-}03^b$	$6.12 \pm 2.90 \text{ E-}03^{a,b}$
Ethyl butanoate	$1.52 \pm 0.32 \text{ E-}03^a$	$1.72 \pm 0.46 \text{ E-}03^a$	$1.32 \pm 0.14 \text{ E-}03^a$	nd
Ethyl 2-methylbutanoate	$7.32 \pm 1.61 \text{ E-}04^a$	$4.87 \pm 1.81 \text{ E-}04^a$	$6.94 \pm 0.19 \text{ E-}04^a$	$4.50 \pm 2.24 \text{ E-}04^a$
Benzaldehyde	$2.44 \pm 0.79 \text{ E-}04^a$	$3.76 \pm 1.59 \text{ E-}04^a$	$1.90 \pm 0.32 \text{ E-}04^a$	$2.90 \pm 2.18 \text{ E-}04^a$
Ethyl hexanoate	$1.19 \pm 0.49 \text{ E-}04^a$	$1.08 \pm 0.64 \text{ E-}04^a$	$9.69 \pm 3.06 \text{ E-}05^a$	$1.10 \pm 0.69 \text{ E-}04^a$
2-nonanone	$6.77 \pm 3.23 \text{ E-}05^a$	$8.24 \pm 4.12 \text{ E-}05^a$	$8.13 \pm 4.76 \text{ E-}05^a$	$9.40 \pm 5.19 \text{ E-}05^a$

k = concentration in headspace (mg/L)/concentration in solution (mg/L) nd = not determinate because it was not included in aroma solution.

^{a, b} Different letters indicate significant differences at $p < 0.05$ (Duncan). Statistical analysis was carried out separately for each aroma compounds.

2.3. Determination of the aroma partial pressure by gas chromatography

The aroma compounds concentration in the atmosphere of the airtight flask was measured after 20 days using a gas syringe. For that, 0.5 ml of the headspace of the hermetic flask were collected through the Mininert[®] valve installed on the flask and injected into a gas chromatograph (GC) Agilent Technologies, Model 6890GC/FID equipped with a DB5-MS capillary column (30 m length \times 0.32 mm, 0.5 μm film thickness, JW Scientific).

The aroma compound concentration was determined using an external calibration curve measured on the same gas chromatograph. It was carried out by injecting 2 μl of a solution of a mix of aroma compounds in pentane (10, 25, 50, 100, 500, 1000 and 5000 $\mu\text{g/g}$). The temperature of the split/splitless injector was 250 °C with a purge time of 0.5 min. The flame ionisation detector was set at 305 °C with hydrogen as carrier gas (45 ml/min). The oven temperature was programmed to increase from 30 to 230 °C at 5 °C/min.

2.4. Sorbed aroma compounds quantification

2.4.1. Quantification by headspace methods

MHE and MHS-SPME techniques are dynamic gas extractions carried out stepwise on a same sample. At each extraction step, the overall equilibrium of the analyte in the system must be first established then analyte present in the headspace volume was removed and analyzed as GC area. Various extractions of the same sample are performed in order to reach an exponential decay of the analyte present in the sample and then to calculate the total area of the analyte, according to geometric progression showed in Eq (1). It means that from a restricted number of successive measurements (ideally $N = 5$), the sum of GC areas would be calculated if carrying out the successive measurements ad infinitum [22,23].

$$A_T = \sum_{i=1}^N A_i = \frac{A_1}{1 - \beta}, \quad (1)$$

Table 3

Conditioning of the PLA samples for the three methods: Concentrations of aroma compound in solution and in headspace expressed as partial pressure and activity.

Aroma compound	Aroma solution in hexadecane (mol/L)	Concentration of aroma in headspace (mol/L)	P _p (Pa)	Activity	Method
Ethyl acetate	2.0E-04	1.6E-06	3.0	2.4E-04	MHS-SPME
	2.0E-02	1.7E-04	429.0	3.5E-02	MHE-GC
	4.2E-01	5.2E-04	1243.0	1.0E-01	Gravimetry
	8.4E-01	1.0E-03	2486.0	2.0E-01	Gravimetry
	2.3E+00	2.6E-03	6215.0	5.0E-01	Gravimetry
	5.2E+00	5.2E-03	11187.0	9.0E-01	Gravimetry
Ethyl butanoate	1.5E-02	1.9E-05	47.6	2.3E-02	MHE-GC
	1.1E-01	6.8E-05	207.0	1.0E-01	Gravimetry
	2.7E-01	1.4E-04	414.0	2.0E-01	Gravimetry
	6.6E-01	3.4E-04	1035.0	5.0E-01	Gravimetry
	1.2E+00	6.1E-04	1863.0	9.0E-01	Gravimetry
	2.0E-04	8.8E-08	0.2	2.0E-04	MHS-SPME
Benzaldehyde	2.0E-02	1.3E-05	33.0	3.0E-02	MHE-GC
	3.0E-04	7.0E-08	0.2	1.5E-03	MHS-SPME
Ethyl hexanoate	3.0E-02	4.5E-06	11.1	9.6E-02	MHE-GC
	1.8E-04	2.3E-08	0.1	3.4E-05	MHS-SPME
	1.8E-02	2.0E-06	5.0	2.9E-03	MHE-GC
2-nonanone	8.1E-01	4.5E-05	855.0	5.0E-01	Gravimetry
	1.6E+00	8.1E-05	1539.0	9.0E-01	Gravimetry
	1.7E-04	1.6E-08	0.0	4.6E-05	MHS-SPME
	1.7E-02	1.4E-06	3.4	3.9E-03	MHE-GC

In previous equation, A_T is the theoretical total GC area, A_i is the GC peak area relative to the i -th extraction, N is the total number of extractions, A_1 is the GC peak area relative to the first extraction, and β is a constant which describes the exponential decay of peak areas during the stepwise multiple headspace extraction procedure. The constant β can be obtained from the slope of the plot resulting from the next equation:

$$\ln A_i = (i - 1)\ln \beta + \ln A_1, \quad (2)$$

So, the accuracy of the measurement depends on the right linearity (depending of R^2) of the N successive extractions and not on the total extraction of the compound. Therefore, parameters like temperature and time of equilibration require to be optimized.

Then, the quantity of analyte in the sample can be calculated from the total peak area A_T using a calibration by external standard.

2.4.1.1. Multiple headspace extraction (MHE). After conditioning time, PLA samples were removed from airtight flasks and sealed in 20 ml headspace glass vials with silicon/PTFE septa and an aluminium cap. An automatic headspace sampler coupled with GC/FID (Perkin Elmer HS40 XL) was used to monitor the extraction and analysis of the released aroma compounds. The specific headspace sampler operation conditions were: head pressure (Helium) 200 kPa, equilibration temperature 60 °C, equilibration time 55 min, pressurization time 2 min, injection time 0.05 min, hold up time 0.2 min, needle temperature 110 °C, transfer line temperature 130 °C. The oven temperature was programmed at 35 °C for 2 min, 6 °C/min up to 230 °C. Injector temperature was 250 °C and its split was 15.6 ml/min. Detector temperature was 250 °C and it was set at range 1. The column was a SupelcoWax-10 capillary column (30 m length \times 0.32 mm, 0.5 μ m film thickness). The carrier gas was He at 1.8 ml/min. Three vials were prepared for each type of PLA and each vial was sampled five times at equal time intervals (55 min) at 60 °C. Total peak area of each aroma compound sorbed was calculated using Eq. (1). Calibration of each aroma compound was performed by external standards. For that, a solution of a mix of aroma compounds was prepared in hexadecane. Dilutions of 100–10,000 μ g/g in hexadecane were used. Ten μ l of the diluted solution was introduced in a 20 ml glass vial sealed with silicon/PTFE septa and an aluminium cap. Three vials were prepared for each dilution and then each vial was sampled five times following the method already described.

2.4.1.2. Multiple headspace solid-phase micro extraction (MHS-SPME). After conditioning time, samples were removed from airtight flasks and sealed in 20 ml glass vials with silicon/PTFE septa. 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 oven temperature programme 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, and then this temperature was maintained for 5 min. Split/splitless injector and detector temperatures were 250 °C. The column was a JW Scientific DB5-MS capillary column (30 m length \times 0.32 mm inner diameter \times 0.5 μ m film thickness). The carrier gas was He at 1.4 ml/min. For MHS-SPME injections, three vials were prepared for each type of PLA and each vial was sampled four times. The sample vials were incubated at 60 °C for 30 min and agitated at 250 rpm. MHS-SPME was performed for 15 min at 60 °C using a 75 μ m carboxen–polydimethylsiloxane (CAR-PDMS) fibre providing best results in terms of amount of compound extracted for low molecular mass compounds [31]. Desorption time was 5 min into the injector port. Total peak area of each aroma compound sorbed was calculated using Eq (1). The calibration was carried out by external standard in hexadecane. For that, a solution of a mix of aroma compounds was prepared in hexadecane. Dilutions of 0.5–25 μ g/g in hexadecane were used for ethyl butanoate, ethyl 2-methylbutanoate, ethyl hexanoate and 2-nonanone, whereas dilutions of 25–500 μ g/g in hexadecane were used for ethyl acetate and benzaldehyde. Twenty μ l 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 and each vial was sampled four times as described for PLA samples.

2.4.2. Gravimetric method

Once the samples were conditioned at high activity (14 days at 25 °C), they were weighed by an analytical balance (Mettler AE160, 10⁻⁴ g) to calculate the mass uptake and the solubility coefficients.

2.5. Solubility coefficient

The apparent solubility coefficient (S) of each aroma compound was calculated according to:

$$S = \frac{M_{\infty}}{M_0} \times \frac{d}{P_p} \quad (3)$$

where M_{∞} is the mass sorption after 14 or 20 days of conditioning (kg), M_0 is the initial mass of PLA sample (kg), d is the film density (kg/m^3) and P_p is the partial pressure of each aroma compound.

2.6. Thermal properties: differential scanning calorimetry (DSC)

Before and after conditioning, the thermal properties of film samples were determined in triplicate using a differential scanning calorimeter QSC 100 instrument (TA Instruments, France). Films samples were analyzed at $10^{\circ}\text{C}/\text{min}$ from -30°C to 190°C and the degree of crystallinity (X_c) of materials was calculated according to:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \quad (4)$$

where ΔH_m is the enthalpy of fusion, ΔH_{cc} is the enthalpy of cold crystallization and ΔH_m^0 is the heat of melting crystalline PLA (93 J/g) [32].

2.7. 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). When differences were significant ($p < 0.05$), Duncan's test was used to evaluate the differences between pairs of groups.

3. Results and discussion

3.1. Optimization of the headspace extraction methods

To apply the MHE technique for the extraction of aroma compounds the temperature and time of equilibration before injection have to be optimized. The temperature of equilibrium was set at 60°C , in the region of the glass transition of PDLLA in order to facilitate the extraction of all sorbed aroma compounds. For each compound the equilibration time producing stabilized and reproducible chromatographic peak areas was tested using conditioned samples of Biophan film. Furthermore, the quality of the linear decrease of peak areas during multiple headspace extraction was checked. The effect of time on the area of peaks depended on each compound, for example while the peaks of 2-nonanone still increased at 55 min, the other compounds achieved a plateau at 30 min. The incubation time of 55 min was retained as a good compromise for all aroma compounds and produced a very good linear decrease ($R^2 \geq 0.99$) during multiple extraction. Furthermore, it was in agreement with the duration of chromatographic cycle.

In order to obtain an efficient extraction of aroma compounds, 5 extraction cycles were chosen. Kolb et al., 1991 [22] showed the possible use of only 2 extraction cycles, but only for very volatile compounds. Furthermore the behaviour of compounds with a large difference in their volatilities as it is the case here (Table 1) could vary during the extraction cycles. To keep low cycle numbers, in some case authors add solvents or liquid displacers to improve extraction [33], but this strategy would have included further analytical difficulty in our case.

In the case of MHS-SPME the incubation time of the CAR-PDMS $75 \mu\text{m}$ fibre was optimized. For that, three incubation times were studied (15, 30 and 45 min) using conditioned samples of Biophan film which were placed in 20 ml headspace glass sealed vials, heated at 60°C . The fibre extraction time was set to 15 min. The peak areas showed that all compounds started to reach a plateau at

15 min. Therefore 30 min incubation time was selected as a condition for further experiments. Finally, the linearity of the relationship between the logarithm of peak area and extraction number was confirmed by finding good correlation coefficients ($R^2 \geq 0.99$). When the amount of compound in the vial is too large, exponential decay of peak area is not observed and low correlation coefficients are obtained [34]. In our study, the sample mass in the vial was different for each material due their different thickness. It did not present any effect on the correlation coefficients when we used thick PLA films; however, microtomed PLA which sorbed a higher amount of aroma compounds than thick PLA samples presented linearity but lower correlation coefficients ($R^2 \geq 0.98$) in accordance to the effects observed by Carrillo and Tena [34].

3.2. Aroma compounds sorption

The amount ($\mu\text{g/g}$) of aroma compounds sorbed in PLA samples after conditioning for 20 days and the solubility coefficients are shown in Fig. 2A and B by MHE and MHS-SPME determinations respectively. The sorption profiles are similar between the two methods, but MHE-SPME allowed for determining concentrations one hundred times lower.

The sorption of ethyl acetate in PLA is high, as already observed in literature [25,26]. The main explanation for this affinity can be sought in the quite similar molecular structure of ethyl acetate being the most hydrophilic of a homologous series of ethyl esters. The more surprising result was however the high affinity of the aromatic structure of benzaldehyde for PLA. However, those results were done on PLA samples with high thickness, and therefore the sorption equilibrium might not be reached after 20 days of conditioning. In this case, the rate of diffusion of the considered molecule into the structure might importantly change the picture, as larger molecules are known to diffuse slower. The dependence of the diffusion coefficient (D) on molecular weight is indeed very steep in the case of glassy materials as was shown by Pennarun et al. [35] for PET and probably the same for PLA under our measurement conditions.

The values of D of ethyl acetate in PLA were reported between $10^{-14} \text{ m}^2/\text{s}$ [36] and $10^{-17} \text{ m}^2/\text{s}$ [25,27]. In the hypothesis of the lower D , 20 days of conditioning of the thick PLA samples are not enough to reach thermodynamic equilibrium. For this reason, we did an experiment on microtomed samples, where the characteristic film thickness was reduced to $10 \mu\text{m}$ and sorption equilibrium could be reached in 20 days under the hypothesis of a diffusion coefficient in the order of $10^{-17} \text{ m}^2/\text{s}$.

The results of the adsorbed amount are given in Fig. 2C and D. The microtomed samples sorbed a higher quantity of aroma compound whatever the method compared with thick PLA films samples. For example, in the case of ethyl acetate and MHE method (Fig. 2C, activity 10^{-2}), concentration sorbed in microtomed samples is 10 times and 5 times higher than in thick samples of PLA2002D and PLA4032D, respectively (Fig. 2A). However, one observes a similar sorption pattern, still with a high affinity of benzaldehyde. There seemed to be a difference of the sorption of the aroma compounds for both PLA grades, but this difference depended on the activity.

To get a clearer picture on the affinity of the aroma compounds for both PLA grades, the data were normalized by the calculation of the solubility coefficient after Eq. (3). The results are given in Fig. 2E and F for both levels of activity differing by a factor of 100. The first conclusion is that S is equivalent for both activities, within a reasonable variation linked to the different experimental determination methods. Therefore, in the case of such low vapour activities, one can conclude that the sorption isotherm follows Henry's law.

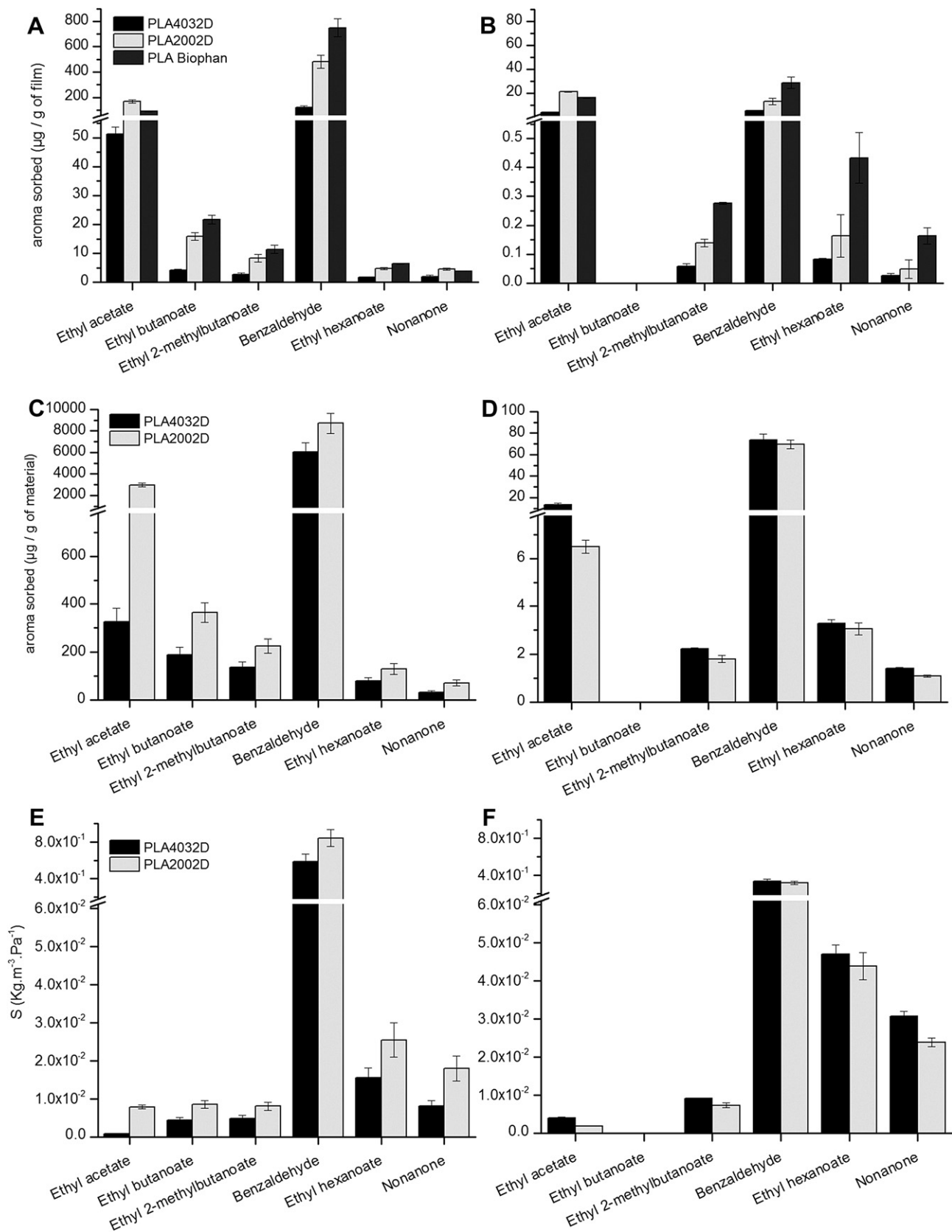


Fig. 2. Apparent sorption of aroma compounds in PLA films samples determined by (A) MHE and (B) MHS-SPME. Aroma sorption in microtomed PLA samples (thickness = 10 μm) determined by (C) MHE and (D) MHS-SPME. Solubility coefficients (S) of aroma compounds in microtomed PLA samples (thickness = 10 μm) determined by (E) MHE and (F) MHS-SPME. The ordinate is discontinuous as indicated to present all small values, $n = 3$. Partial pressures used for each method were done in Table 2.

Table 4
Values of Hansen solubility parameters (J/cm^3)^{1/2} for PLA and aroma compounds.

Compound	V (cm^3/mol)	δ_D	δ_P	δ_H	δ_T^a	$\Delta\delta^b$	Reference
PLA	47.1	18.6	9.9	6.0	21.9	–	[39]
Ethyl acetate	98.5	15.8	5.3	7.2	18.2	5.5	[38]
Ethyl butanoate	132.9	15.5	5.6	5.0	17.2	5.4	[38]
Ethyl 2-methylbutanoate		n.d.	n.d.	n.d.			
Ethyl hexanoate	149.6	15.5	3.2	5.9	16.9	7.4	[38]
Benzaldehyde	101.5	19.4	7.4	5.3	21.4	2.7	[38]
2-nonanone		n.d.	n.d.	n.d.			
PP	49.5	16.1	0.0	0.0	16.1	–	[25]
LDPE	32.8	17.9	0.0	0.0	17.9	–	[25]

n.d. No data literature available.

^a Values were calculating according to Eq (5).

^b Values were calculating according to Eq (6) between PLA and aroma compounds.

The results of the homologous series of ethyl esters show that the most hydrophobic component ethyl hexanoate had the highest solubility coefficient, most likely due to its structure similar to the PLA chain. In the case of benzaldehyde which presented the highest *S*, the high affinity may be explained by the well-known miscibility of PLA with aromatic solvents such as toluene and benzene [37]. Ethyl-2-methylbutanoate had comparable *S* compared to that of ethyl butyrate, which hints that the additional methyl group does not change the behaviour of the molecule in the polymer structure. 2-Nonanone had comparatively higher *S*, which could be compared to that of ethyl hexanoate.

The calculation of the Hansen solubility parameters is a semi-quantitative method from which the affinity of a polymer for a substance can be obtained. This affinity can be estimated from Hildebrand's theory by calculating the total solubility parameter, according Eq. (5):

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (5)$$

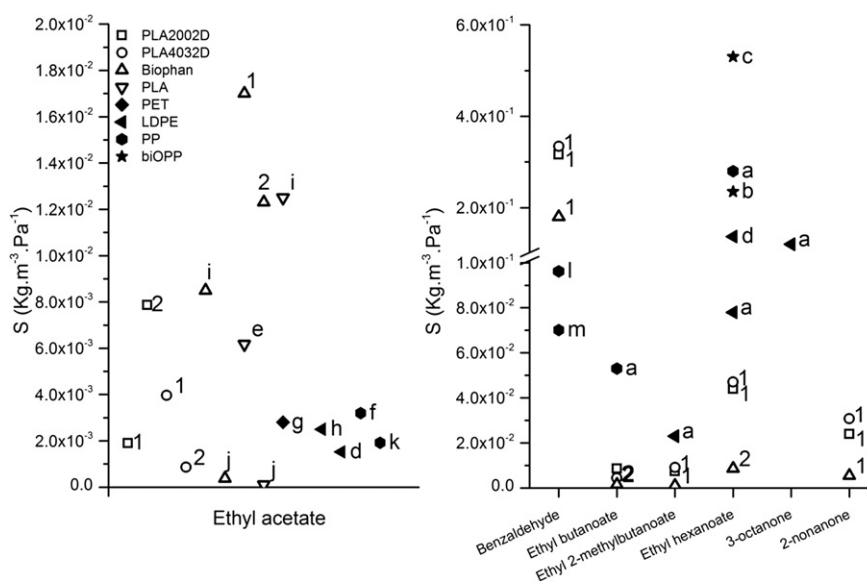


Fig. 3. Solubility coefficients of aroma compounds in plastic packaging materials. **1** this work between $0.34\text{--}14.93 \times 10^{-4}$ vapor activities (P_p between 0.039 and 3.04 Pa). **2** this work between $0.29\text{--}9.59 \times 10^{-2}$ vapor activities (P_p between 3.4 and 429 Pa) **a** at 25 °C, vapor activity not detailed, by permeation kinetic [43] **b** 0.5 vapor activity ($P_p = 855$ Pa), 25 °C and 0% RH by Micro-atmosphere-derived method [44] **c** 0.5 vapor activity ($P_p = 855$ Pa), 25 °C, 0% RH by microgravimetric method [44] **d** 0.5 vapor activity ($P_p = 855$ Pa), 25 °C, 0% RH by gravimetric method [45] **e** 0.2 vapor activity ($P_p = 3030$ Pa), 30 °C by gravimetric method – digital electrobalance [25] **f** 0.56 vapor activity ($P_p = 6088$ Pa), 22 °C by gravimetric method [16] **g** 0.6 vapor activity ($P_p = 9435$ Pa), 30 °C by gravimetric method [46] **h** 0.4 vapor activity ($P_p = 4348$ Pa), 22 °C by gravimetric method [47] **i** 0.5 vapor activity ($P_p = 6215$ Pa), 25 °C, 0% RH by static method – electronic microbalance [26] **j** 0.2 vapor activity ($P_p = 2486$ Pa), 25 °C, 0% RH by static method – electronic microbalance [26] **k** 0.9 vapor activity ($P_p = 11,187$ Pa), 25 °C, 0% RH by gravimetric method [45] **l** 0.5 vapor activity ($P_p = 58$ Pa), 25 °C, 0% RH by microgravimetric method, adapted from [48] **m** 0.3 vapor activity ($P_p = 34.8$ Pa), 25 °C, 0% RH by microgravimetric method, adapted from [48].

were δ_T (J/cm^3)^{1/2} corresponds to the overall Hildebrand solubility parameter and δ_D , δ_P and δ_H are the Hansen solubility parameters that represent contributions from the nonpolar interaction, polar interaction and hydrogen bonding, respectively [38].

When the distance $\Delta\delta = 0$ (Eq. (6)), the solvent and polymer are thermodynamically similar that the polymer will be highly soluble. As the distance gets greater, the solubility declines [39]. A good solubility level is assigned when distance $\Delta\delta$ is smaller than 5 (J/cm^3)^{1/2} [25].

$$\Delta\delta = \left[(\delta_{DP} - \delta_{DS})^2 + (\delta_{PP} - \delta_{PS})^2 + (\delta_{HP} - \delta_{HS})^2 \right]^{1/2} \quad (6)$$

δ_T and $\Delta\delta$ were calculated from literature values of δ_D , δ_P and δ_H . Results are given in Table 4.

So, a small distance was found between PLA and benzaldehyde, which confirmed the experimental results shown in Fig. 2. Moreover, this experimental result is in accordance with theoretical studies that reported that the obvious place to look for a rational plasticizer is in the aromatics compounds because PLA presents a high nonpolar interaction value δ_D [39].

Few papers in literature reported data on sorption of organic compounds in PLA. Fig. 3 represents a comparison of the solubility coefficients of aroma compounds in PLA and other polymers derived from literature. Obviously physical and chemical properties of a same kind of polymer like crystallinity, morphology, and chemical composition were not identical in these papers and could influence the value of *S* [40–42].

These data show that for a same couple polymer/solute a large discrepancy appears for the value of *S*. The main difference in the values of *S* comes from first on the methodology and the activity of the aroma compound used and secondly if *S* is measured directly from the polymer weight uptake or indirectly from the coefficient of permeability. For example, Colomines et al. [26] studied vapor phase sorption (% mass uptake) of ethyl acetate in PLA samples at different activities (0.2, 0.5 and 0.9) using a microbalance by 20 h.

Table 5

Masse uptake, glass transition temperature (T_g) and degree of crystallinity (χ) of PLA films using DSC before and after sorption of aroma compound.

Material	Conditioning	Aroma compound	P _b (Pa)	Masse uptake (μg/g)	T _g (°C)	χ
PLA Biomer L9000	Before	—	—	—	58.4 ± 0.3 ^a	2 ± 1 ^a
	After	Ethyl acetate	1243.0	7000	46.5 ± 1.6 ^b	20 ± 2 ^b
			2486.0	43,000	43.5 ± 5.4 ^b	37 ± 2 ^c
			6215.0	98,500	9.5 ± 0.9 ^c	39 ± 5 ^{c,d}
11187.0	178,000	0.9 ± 1.6 ^d	42 ± 2 ^d			
PLA Biomer L9000	Before	—	—	—	58.4 ± 0.3 ^a	2 ± 1 ^a
	After	Ethyl butanoate	207	2000	57.3 ± 1.1 ^{a,b}	14 ± 3 ^{b,c}
			414	3500	57.3 ± 0.3 ^{a,b}	12 ± 1 ^b
			1035	4000	56.9 ± 0.5 ^b	16 ± 2 ^c
1863	7000	28.7 ± 0.5 ^c	34 ± 1 ^d			
PLA Biomer L9000	Before	—	—	—	58.4 ± 0.3 ^a	2 ± 1 ^a
	After	Ethyl hexanoate	855	1000	57.3 ± 0.3 ^a	10 ± 1 ^b
PLA Biophan	Before	—	—	—	56.6 ± 1.7 ^a	12 ± 3 ^b
	After	Mixed aroma solution	Between 3.4 and 429	883 ± 78	57.7 ± 0.2 ^a	20.9 ± 0.1 ^a
PLA2002D	Before	—	—	—	54.8 ± 0.7 ^b	20.1 ± 0.2 ^b
	After	Mixed aroma solution	Between 3.4 and 429	685 ± 67	59.9 ± 0.1 ^a	1.3 ± 0.3 ^a
PLA4032D	Before	—	—	—	58.6 ± 0.3 ^b	2.6 ± 0.4 ^b
	After	Mixed aroma solution	Between 3.4 and 429	184 ± 18	64.3 ± 0.5 ^a	4.2 ± 1.0 ^a
					62.6 ± 0.1 ^b	2.4 ± 1.5 ^a

^{a, b, c, d} Different letters indicate significant differences at $p < 0.05$ (Duncan). Statistical analysis was carried out separately for each PLA type and its aroma compounds.

They showed that at an activity of 0.2, Biophan (30 μm in thickness) sorbed 700 μg of ethyl acetate per g of polymer whereas PLA Biomer L9000 (190 μm in thickness) sorbed only 190 μg of ethyl acetate per g of polymer. In our study, activities of ethyl acetate were 0.035 and 0.00024 and we found that PLA Biophan sorbed 91.8 and 16.17 μg per g of polymer, respectively. Our results for Biophan (between 12.3 and 17.0 × 10⁻³ kg m⁻³ Pa⁻¹) are thus one order of magnitude higher than the results of Colomines et al. [26]. They showed that at 25 °C the apparent solubility coefficient was 0.35 × 10⁻³ kg m⁻³ Pa⁻¹ at an activity of 0.2. The values of Colomines et al. [26] were therefore highly underestimated, because the sorption equilibrium was not reached as also mentioned by the authors.

Nevertheless, independently of the method, for a same couple polymer/solute when low activities were used and equilibrium was reached, solubility coefficients were close. That can be observed in the case of ethyl acetate sorbed in PLA, where S founded in this work is on the same order of magnitude than the results of Auras et al. [25] who studied PLA 98% L-isomers and presented a solubility coefficient of 6.17 × 10⁻³ kg m⁻³ Pa⁻¹ at 30 °C and an activity of 0.2. These results showed that at low activities, S was independent of partial pressure following Henry's law.

Fig. 3 also shows values for a same solute and different polymers, for example, the sorption of ethyl acetate in the PLA types studied at low activity in this work are similar to values reported for poly(ethylene terephthalate), low-density polyethylene (LDPE) and polypropylene (PP). In the case of ethyl hexanoate, its solubility coefficient in PLA is lower than in bi-axially oriented polypropylene (biOPP), PP and LDPE. Benzaldehyde presented a solubility coefficient in PLA higher than in PP. From the total solubility parameters calculated for PP and PE, 16.1 and 17.9, respectively, it could be predicted that ethyl hexanoate should have a slighter affinity for PP ($\Delta\delta = 6.7$) and PE ($\Delta\delta = 7.1$) compared with PLA ($\Delta\delta = 7.4$). In the case of benzaldehyde, its affinity for PLA ($\Delta\delta = 2.7$) is higher than for PP ($\Delta\delta = 9.7$) and PE ($\Delta\delta = 9.2$). So, experimental sorption values showed a good agreement with literature and theoretical affinity parameters.

3.3. Effect of aroma compounds sorption on PLA samples

Colomines et al. [26] and Courgneau et al. [27] showed that the sorption of ethyl acetate into PLA induced morphological changes

in the polymer structure. Both authors evidenced plasticizing and induced crystallization. However, the ethyl acetate activities used were high, 0.5 in Colomines's paper and 0.2 in Courgneau's paper. For example, Colomines et al. [26] found that T_g decreased from 50.9 ± 0.1 °C to 16.9 ± 1.9 °C, after 3 days of contact at 0.5 activity. Such high activities are at least one order of magnitude higher than expected activities upon application of PLA for example as food packaging film. In order to test the effect of aroma compound sorption at low activities (10⁻²) on the thermo-mechanical properties of PLA samples, they were tested before and after conditioning. The results are given in Table 5 and typical raw DSC data in Fig. 4 and Fig. 5.

For each PLA type and the aroma compounds sorbed, statistical analysis showed significant differences ($p < 0.05$) in T_g and X_c (Table 5).

From Table 5 and Fig. 4 it becomes clear that ethyl acetate has a high plasticizing effect on PLA and induces crystallization although the sorption equilibrium was not reached in the case of the presented experiment after 14 days of conditioning. The effect of ethyl acetate was already observed by Colomines et al. [26] and Courgneau et al. [27]. After contact with the two homologous molecules of the ethyl esters serie, DSC measurements were carried

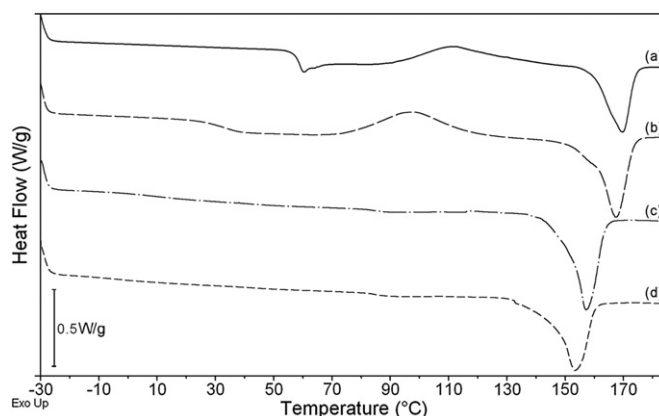


Fig. 4. DSC thermograms for PLA Biomer L9000 before conditioning (a) and after conditioning with ethyl acetate at a vapor activity of 0.2 (b) 0.5 (c) and 0.9 (d).

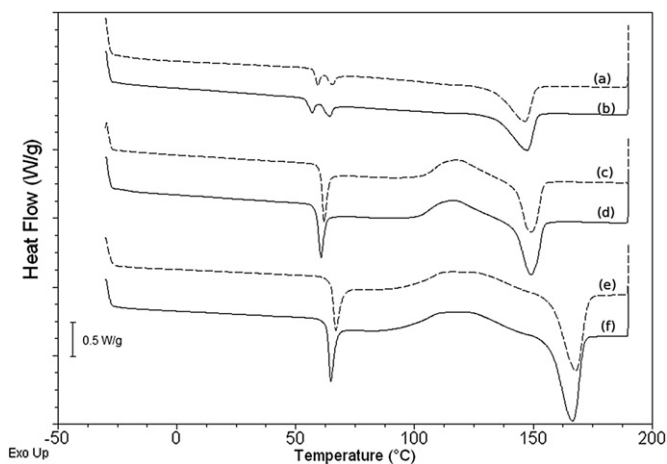


Fig. 5. DSC thermograms for PLA Biophan before conditioning (a) and after conditioning (b), for PLA2002D films before conditioning (c) and after conditioning (d) and PLA4032D films before conditioning (e) and after conditioning (f) in mixed aroma compound headspace at a partial pressure between 3.4 and 429 Pa.

out on the thick PLA samples. Comparison of DSC data after contact with ethyl acetate and with ethyl butanoate shows that the effect on the PLA microstructure was higher with ethyl butanoate as the decrease of T_g is larger. Ethyl hexanoate showed smaller effects, but the sorbed quantity was also very small. However, it was still able to induce significant crystallization of the polymer.

Furthermore, Table 5 shows that, when mass uptake increased, the glass transition temperatures of PLA Biomer L9000 clearly decreased and its crystallinity increased. However, for ethyl butanoate, a sorption of 7000 $\mu\text{g/g}$ was necessary to shift the T_g to 30 °C and to observe a crystallinity multiplied by 2. For the ethyl esters series, crystallinity gradually increased with the activity until to reach an average maximum of 35%.

What is even more interesting is that at very low activities of the six aroma compounds in mixture, such as 3.45×10^{-2} for the ethyl acetate (Table 3, Fig. 5) a slight decrease in T_g was observed in all types of PLA (Table 5, Fig. 5). Small plasticization of PLAs by aroma compounds at very low concentration (<200 $\mu\text{g/g}$) is thus found. However, at very low activities, no solvent induced crystallization of the samples was observed.

4. Conclusions

Sorption of aroma compound was determined by MHE and MHS-SPME at low vapour activities comparable to conditions which can be found in the headspace of packed foodstuff. The analysis of the polymer thermal properties after conditioning showed a slight decrease in T_g of PLA films, which means that a plasticization effect of aroma compounds occur already at vapor activities in the order of 10^{-2} . An effect of solvent induced crystallization was observed from 10^{-1} vapor activities. The results showed that PLA films studied have a high affinity for common aroma compounds and in particular for benzaldehyde, that could have a plasticizer effect.

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References

- [1] Sinclair RG. The case for polylactic acid as a commodity packaging plastic. *Journal of Macromolecular Science, Pure and Applied Chemistry* 1996;33: 585–97.
- [2] Auras R, Harte B, Selke S. An overview of polylactides as packaging materials. *Macromolecular Bioscience* 2004;4:835–64.
- [3] Lau O-W, Wong S-K. Contamination in food from packaging material. *Journal of Chromatography A* 2000;882:255–70.
- [4] Ducruet V, Fournier N, Saillard P, Feigenbaum A, Guichard E. Influence of packaging on the aroma stability of strawberry syrup during shelf life. *Journal of Agricultural and Food Chemistry* 2001;49:2290–7.
- [5] Ducruet V, Vitrac O, Saillard P, Guichard E, Feigenbaum A, Fournier N. Sorption of aroma compounds in PET and PVC during the storage of a strawberry syrup. *Food Additives and Contaminants Part A-Chemistry Analysis Control Exposure & Risk Assessment* 2007;24:1306–17.
- [6] Tawfik MS, Devlieghere F, Steurbaut W, Huyghebaert A. Chemical contamination potential of bottle materials. *Acta Alimentaria* 1997;26:219–33.
- [7] Togawa J, Kanno T, Horiuchi J, Kobayashi M. Gas permeability modification of polyolefin films induced by D-limonene swelling. *Journal of Membrane Science* 2001;188:39–48.
- [8] van Willige RWG, Linszen JPH, Meinders MBJ, van der Stege HJ, Voragen AGJ. Influence of flavour absorption on oxygen permeation through LDPE, PP, PC and PET plastics food packaging. *Food Additives and Contaminants Part A-Chemistry Analysis Control Exposure & Risk Assessment* 2002;19:303–13.
- [9] Hernandez-Munoz P, Gavara R, Hernandez RJ. Evaluation of solubility and diffusion coefficients in polymer film-vapor systems by sorption experiments. *Journal of Membrane Science* 1999;154:195–204.
- [10] Samus MA, Rossi G. Methanol absorption in ethylene-vinyl alcohol copolymers: relation between solvent diffusion and changes in glass transition temperature in glassy polymeric materials. *Macromolecules* 1996;29:2275–88.
- [11] Dury-Brun C, Lequin S, Chalier P, Sp Desobry, Ae Voilley. Tracer aroma compound transfer from a solid and complex-flavored food matrix packed in treated papers or plastic packaging film. *Journal of Agricultural and Food Chemistry* 2007;55:1411–7.
- [12] Nerin C, Albinana J, Philo MR, Castle L, Raffael B, Simoneau C. Evaluation of some screening methods for the analysis of contaminants in recycled polyethylene terephthalate flakes. *Food Additives and Contaminants* 2003;20: 668–77.
- [13] van Willige RWG, Linszen JPH, Legger-Huysman A, Voragen AGJ. Influence of flavour absorption by food-packaging materials (low-density polyethylene, polycarbonate and polyethylene terephthalate) on taste perception of a model solution and orange juice. *Food Additives and Contaminants* 2003;20:84–91.
- [14] Berline C, Ducruet V, Brillouet JM, Reynes M, Brat P. Evolution of aroma compounds from orange juice stored in polyethylene terephthalate (PET). *Food Additives and Contaminants Part A-Chemistry Analysis Control Exposure & Risk Assessment* 2005;22:185–95.
- [15] Toebe JM, Hoojjat H, Hernandez RJ, Giacini JR, Harte BR. Interaction of flavour components from an onion/garlic flavoured sour cream with high impact polystyrene. *Packaging Technology and Science* 1990;3:133–40.
- [16] Nielsen TJ, Giacini JR. The sorption of Limonene/Ethyl acetate binary vapour mixtures by a biaxially oriented polypropylene film. *Packaging Technology and Science* 1994;7:247–58.
- [17] Lebossé R, Ducruet V, Feigenbaum A. Interactions between reactive aroma compounds from model citrus juice with polypropylene packaging film. *Journal of Agricultural and Food Chemistry* 1997;45:2836–42.
- [18] Abrantes S. GC-MS Identification of styrene and oligomers in polystyrene plastic for milk packaging – headspace and solution injection technique. *HRC-Journal of High Resolution Chromatography* 1993;16:113–5.
- [19] Schellenberg J, Knoll S, Nord G, Leukefeld W. Effect of styrene oligomers on syndiospecific polymerization of styrene. *European Polymer Journal* 2003;39: 2351–7.
- [20] Kolb B. Multiple headspace extraction – a procedure for eliminating the influence of the sample matrix in quantitative headspace gas chromatography. *Chromatographia* 1982;15:587–94.
- [21] Tavss EA, Santalucia J, Robinson RS, Carroll DL. Analysis of flavor absorption into plastic packaging materials using multiple headspace extraction gas chromatography. *Journal of Chromatography* 1988;438:281–9.
- [22] Kolb B, Ettré LS. Theory and practice of multiple headspace extraction. *Chromatographia* 1991;32:505–13.
- [23] Ezquerro Ó, Pons B, Tena MT. Multiple headspace solid-phase microextraction for the quantitative determination of volatile organic compounds in multi-layer packagings. *Journal of Chromatography A* 2003;999:155–64.
- [24] Louch D, Motlagh S, Pawliszyn J. Dynamics of organic compound extraction from water using liquid-coated fused-silica fibers. *Analytical Chemistry* 1992; 64:1187–99.
- [25] Auras R, Harte B, Selke S. Sorption of ethyl acetate and d-limonene in poly(lactide) polymers. *Journal of the Science of Food and Agriculture* 2006;86:648–56.
- [26] Colomines G, Ducruet V, Courgneau C, Guinault A, Domenek S. Barrier properties of poly(lactic acid) and its morphological changes induced by aroma compound sorption. *Polymer International* 2010;59:818–26.
- [27] Courgneau C, Domenek S, Lebossé R, Guinault A, Avérous L, Ducruet V. Effect of crystallization on barrier properties of formulated polylactide. *Polymer International* 2012;61:180–9.

- [28] Mihai M, Huneault MA, Favis BD. Rheology and extrusion foaming of chain-branched poly(lactic acid). *Polymer Engineering & Science* 2010;50:629–42.
- [29] Mihai M, Huneault MA, Favis BD, Li H. Extrusion foaming of semi-crystalline PLA and PLA/thermoplastic starch blends. *Macromolecular Bioscience* 2007; 7:907–20.
- [30] Carrasco F, Pagès P, Gámez-Pérez J, Santana OO, Maspoch ML. Processing of poly(lactic acid): characterization of chemical structure, thermal stability and mechanical properties. *Polymer Degradation and Stability* 2010;95:116–25.
- [31] Ezquerro Ó, Pons B, Tena MT. Development of a headspace solid-phase microextraction-gas chromatography-mass spectrometry method for the identification of odour-causing volatile compounds in packaging materials. *Journal of Chromatography A* 2002;963:381–92.
- [32] Fischer EW, Sterzel HJ, Wegner G. Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. *Colloid & Polymer Science* 1973;251:980–90.
- [33] Wenzl T, Lankmayr EP. Reduction of adsorption phenomena of volatile aldehydes and aromatic compounds for static headspace analysis of cellulose based packaging materials. *Journal of Chromatography A* 2000;897:269–77.
- [34] Carrillo JD, Tena MT. Determination of volatile oak compounds in aged wines by multiple headspace solid-phase microextraction and gas chromatography-mass spectrometry (MHS-SPME-GC-MS). *Analytical and Bioanalytical Chemistry* 2006;385:937–43.
- [35] Pennarun PY, Dole P, Feigenbaum A. Functional barriers in PET recycled bottles. Part I. Determination of diffusion coefficients in bioriented PET with and without contact with food simulants. *Journal of Applied Polymer Science* 2004;92:2845–58.
- [36] Ducruet V, Domenek S, Guinault A, Courgneau C, Bernasconi M, Plessis C. Barrier properties of PLA towards oxygen and aroma compounds. In: *Italian Journal of Food Science, Special Issue Shelf-life international meeting 23–25 June 2010. Spain: Zaragoza*; 2011. p. 59–62.
- [37] Jin Z, Tian Y, Wang Y. Chemistry and thermodynamics properties of lactic acid and lactide and solvent miscibility. In: Auras RA, Lim LT, Selke SEM, Tsuji H, editors. *Poly(lactic acid): synthesis, structures, properties, processing, and applications*. John Wiley & Sons; 2010. p. 19–25.
- [38] Hansen CM. *Hansen solubility parameters: a user's handbook*. 2nd ed. Taylor & Francis Group; 2007.
- [39] Abbott S. Chemical compatibility of poly(lactic acid): a practical framework using Hansen solubility parameters. In: Auras R, Lim LT, Selke SEM, Tsuji H, editors. *Poly(lactic acid): synthesis, structures, properties, processing, and applications*. John Wiley & Son, Inc; 2010. p. 83–96.
- [40] Shimoda M, Matsui T, Osajima Y. Behavior of diffusion, permeation and sorption of flavor compounds in vapor-phase with polyethylene film. *Journal of Japanese Society for Food Science and Technology-Nippon Shokuhin Kagaku Kogaku Kaishi* 1987;34:402–6.
- [41] Landois-Garza J, Hotchkiss JH. Permeation of high-barrier films by ethyl esters. In: Hotchkiss JH, editor. *Food and packaging interactions*. Washington, DC: American Chemical Society; 1988. p. 42–58.
- [42] Nielsen TJ, Jagerstad IM, Oste RE, Wesslen BO. Comparative absorption of low-molecular aroma compounds into commonly used food packaging polymer films. *Journal of Food Science* 1992;57:490–2.
- [43] DeLassus PT. Sorption and diffusion of flavors in plastic packaging. In: McGorrian RJ, Leland JV, editors. *Flavor–food interactions*. Washington, DC: American Chemical Society; 1996. p. 152–61.
- [44] Dury-Brun C, Hirata Y, Guillard V, Ducruet V, Chalier P, Voilley A. Ethyl hexanoate transfer in paper and plastic food packaging by sorption and permeation experiments. *Journal of Food Engineering* 2008; 89:217–26.
- [45] Hirata Y, Ducruet V. Effect of temperature on the solubility of aroma compounds in polyethylene film. *Polymer Testing* 2006;25:690–6.
- [46] Hernandez RJ, Giacín JR, Shirakura A, Jayaraman K. Diffusion and sorption of organic vapors through oriented poly(ethylene terephthalate) films of varying thermomechanical history. *Antec*; 1990. pp. 557–559.
- [47] Barr CD, Giacín JR, Hernandez RJ. A determination of solubility coefficient values determined by gravimetric and isostatic permeability techniques. *Packaging Technology and Science* 2000;13:157–67.
- [48] Qin Y, Rubino M, Auras R, Lim L-T. Impact of polymer processing on sorption of benzaldehyde vapor in amorphous and semicrystalline polypropylene. *Journal of Applied Polymer Science* 2008;110:1509–14.