



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

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### ABSTRACT

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<sub>g</sub>) 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.

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### 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]

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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 <sub>vs</sub> 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<sub>vs</sub>: saturated vapour pressure at 25 °C; log P: octanol-water partition coefficient.

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