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Quantitative determination of volatile organic compounds formed during Polylactide processing by MHS-SPME

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ABSTRACT

Polylactide (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.

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 Fig. 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;

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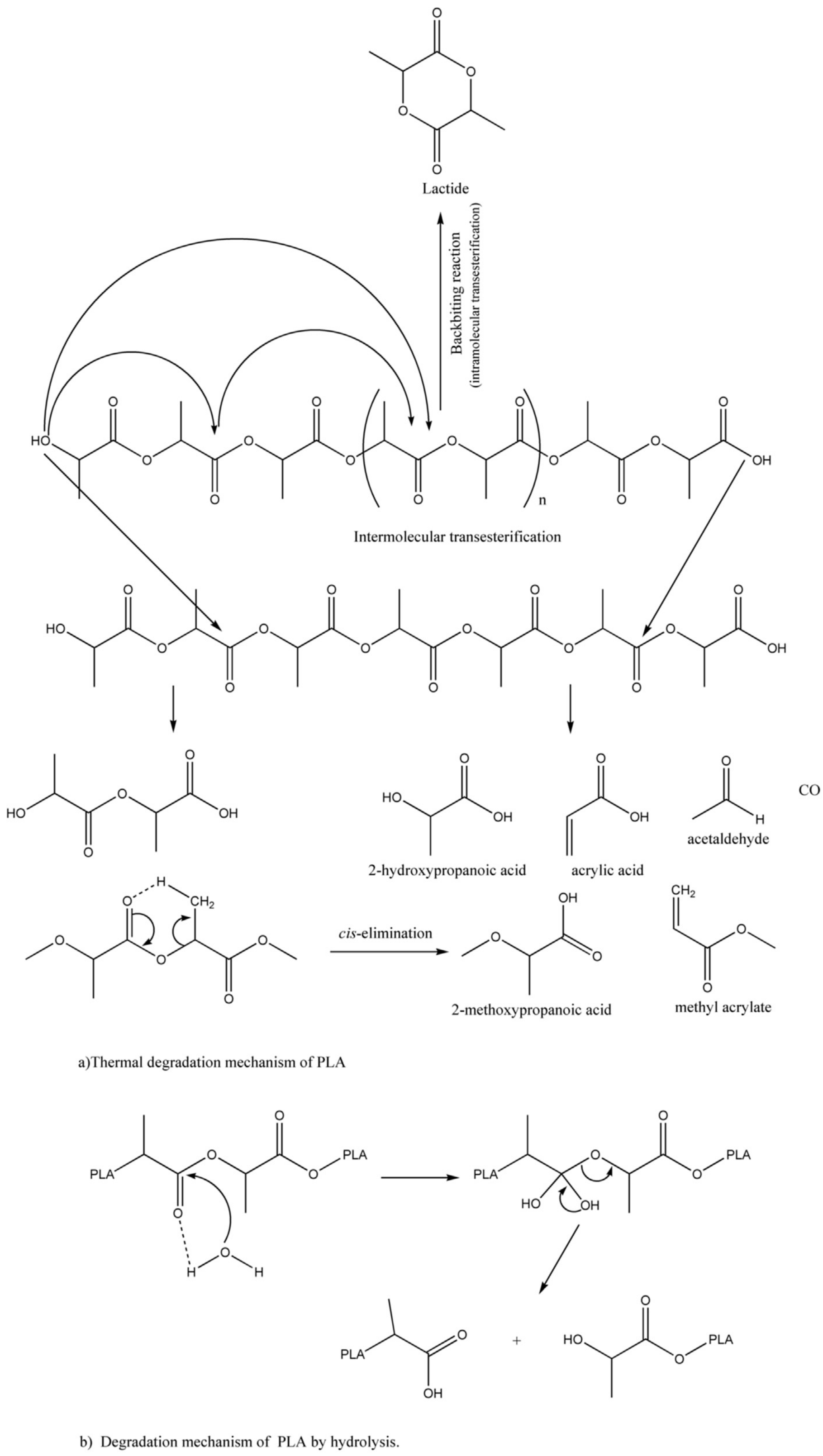

Fig. 1. Main degradation mechanisms of PLA: a) Thermal degradation mechanism of PLA; b) Degradation mechanism of PLA by hydrolysis. Adapted from Nishida, 2010 [18] and Oliveira et al., 2016 [44].

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;