

Deterioration of bioplastics in the soil environment: A thermoanalytical insight into the composition and degradation of commercial biodegradable polymers

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ARTICLE INFO

Keywords:

Py-GC-MS, Poly(lactic acid)
Starch-based bioplastics
Soil
Aging
VOCs

ABSTRACT

Bioplastics are increasingly promoted as more sustainable alternatives to conventional plastics, yet their environmental fate and degradation pathways remain poorly understood. This study presents a comprehensive thermoanalytical investigation of commercial biodegradable plastic products aged in agricultural soil for 100 days. Polylactic acid (PLA) and starch-based bioplastics (SB) were characterized before and after soil exposure by Py-GC-MS, EGA-MS, TGA, and HS-SPME/GC-MS to assess polymer composition, thermal behavior, aging-related changes, and additive content. The analyses revealed that these materials have chemically complex formulations containing multiple polymeric components, volatile and semi-volatile degradation products, oligomeric species, and additives. Py-GC-MS and EGA-MS enabled the identification of key polymer markers and degradation signatures, whereas HS-SPME/GC-MS was particularly effective in detecting volatile compounds and formulation-related additives. The results demonstrate the chemical variability of commercial bioplastics, which may contain multiple polymeric components, copolymers, and additives capable of influencing their thermal properties and response to environmental aging. This work highlights the utility of combined thermoanalytical techniques, particularly Py-GC-MS, in providing a detailed understanding of the composition and environmental aging of bioplastics.

1. Introduction

Bioplastics are receiving increasing global attention and gradually entering the market as sustainable alternatives to conventional plastics, aiming to address challenges associated with plastic production and end-of-life management. However, the replacement of traditional plastics with bioplastics — defined as bioderived and/or biodegradable materials — does not necessarily resolve the problems of resource depletion and plastic waste accumulation. Increasing concerns have been raised regarding the overall environmental benefits of bioplastics. These include their limited biodegradability, since not all biodegradable plastics degrade under natural conditions and biodegradation is highly dependent on the specific environmental compartment; thus, a material may biodegrade in one environment while persisting in another, and

several products still require industrial composting conditions that are not widely available [1]; end-of-life management challenges, which underscore the need for effective disposal strategies for all bioplastics regardless of their biodegradability [2,3], competition with food production, as many bio-based plastics derive from crops like corn, sugarcane, or potatoes, competing with food supply [4]; poor knowledge of the secondary products of bioplastic degradation [5,6]; and the formation of microbioplastics prior to complete degradation [7,8]. Recent reviews have further emphasized that the environmental performance of bioplastics is strongly context-dependent and cannot be generalized solely on the basis of their bio-based origin or compostability claims [9].

In general, the long polymer chains of biodegradable plastics are initially broken down through chain scission induced by environmental factors such as water, sunlight, temperature and other abiotic stressors,

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<https://doi.org/10.1016/j.jaap.2026.107997>

Received 11 May 2026; Received in revised form 7 July 2026; Accepted 21 July 2026

Available online 23 July 2026

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leading to shorter units of oligomers, dimers, and monomers. These low-molecular-weight compounds can pass through the semi-permeable outer membranes of microorganisms, making them available as substrates for microbial metabolism [10]. Moreover, when bioplastics are exposed to environmental conditions, water-soluble additives and adsorbed chemicals can leach out and migrate into soils where they may be imbibed by seeds or be taken up by seedling roots. Consequently, assessing the environmental impacts of bioplastics requires a full comprehension of the potential environmental risks associated with these materials. In this respect, recent literature has highlighted that biodegradable plastics in soil may undergo incomplete degradation and generate intermediate products, including oligomers, monomers, and micro(nano)plastic fragments, whose long-term environmental effects remain insufficiently understood [6,8].

A key point to consider is that bioplastics fall into three distinct categories: bio-based and biodegradable, fossil-based and biodegradable, bio-based and non-biodegradable. Biodegradable plastics are often viewed as advantageous because they can be collected along with the organic fraction of municipal solid waste and processed through biological treatments — both aerobic and anaerobic — for material and energy recovery. However, information on the exact chemical composition of commercial biodegradable plastics is typically not available, complicating the assessment of their degradation behavior. Recent studies on commercial biodegradable products have also underlined the limited transparency of producers with respect to exact formulation and additive content, as well as the need to test real commercial items rather than only neat polymers or model materials [11]. Therefore, accurate evaluation of degradation processes requires detailed characterization of the chemical composition, including both polymeric structures and additives, using reliable analytical methods. Various analytical techniques are used to characterize polymers, including Fourier transform infrared spectroscopy (FTIR), FTIR-focal plane array (FTIR-FPA), Raman spectroscopy, scanning electron microscopy (SEM), and thermo-analytical methods. FTIR and Raman spectroscopy allow rapid identification of functional groups and polymeric structures, whereas SEM provides information on surface morphology and physical deterioration. However, these techniques may be less effective in detecting minor additives, blend components, or low-abundance degradation products in complex commercial materials. By contrast, thermoanalytical techniques, especially when coupled with MS or GC-MS, are particularly powerful for the analysis of biopolymers because they allow the detection of low-abundance degradation products and offer greater discrimination of complex mixtures than spectroscopic methods [12]. Accordingly, EGA-MS, HS-SPME/GC-MS, and Py-GC-MS are especially well suited to investigate the composition of multicomponent biodegradable plastics and the changes induced by environmental aging.

This study employed a systematic analytical approach combining Py-GC-MS, evolved gas analysis-MS (EGA-MS), thermogravimetric analysis (TGA), and headspace solid-phase microextraction (HS-SPME)/GC-MS to investigate commercial biodegradable plastics. Thermal degradation profiles, pyrolysis markers, and compounds released at different temperatures were identified for biodegradable polymers. The obtained information was then used to evaluate how soil exposure modifies the volatile fraction, thermal behavior, and detectable compositional features of these materials, thus providing insight into the early transformation processes that may influence their environmental fate in soil. In this context, recent analytical pyrolysis work has also shown that even small amounts of non-biodegradable polymers such as polyethylene may be present in biodegradable plastic formulations, further emphasizing the need for accurate thermoanalytical characterization of commercial products [13].

PLA plates and starch-based (SB) film bags were selected as representative commercial bioplastics due to their significant market penetration. In fact, PLA is the most technologically established and abundantly produced bioplastic, representing 37.1% of global bioplastics production in 2024, followed by starch-based bioplastics, which

represented 5.7% of the total output [14]. The precise chemical composition of SB film bags is not publicly disclosed. Among starch-based biopolymers, one of the most widely used commercial formulations is Mater-Bi®, produced by the Italian company Novamont. Mater-Bi® is marketed as a family of biodegradable and compostable bioplastics intended for a wide range of applications, including shopping and waste collection bags, disposable tableware, food packaging films, and agricultural mulching films. The composition of SB bioplastics varies [15], but it typically includes starch (from corn, potatoes, or other plants), poly(butylene adipate-co-terephthalate) (PBAT), polylactic acid (PLA), and additives (plasticizers, inorganic fillers) [16–18]. Furthermore, biodegradable polymers are often blended with non-biodegradable ones, mainly polyethylene (PE), to improve their properties and reduce production costs [13,19]. This chemical variability of co-polymers together with the presence of additives of different natures affects the material crystallinity, the thermal behavior and ultimately the biodegradability of this bioplastic category [20,21]. Therefore, the biodegradability of starch-blend bioplastics can vary significantly among different products of this bioplastic category, and the specific composition of each formulation should be correlated with its ability to degrade under different environmental conditions and the timescale for complete degradation. As regards biodegradable bags, there is currently not only a lack of information on their exact chemical composition, but also evidence suggesting that, during degradation, these materials may release additives that are potentially toxic to organisms [6,17,22].

The present study investigates the chemical composition of these biodegradable products and assesses the effects of soil-induced aging on their chemical structure, thermal behavior, and volatile release. The aim of the study was not to assess the certified compostability of these products under industrial composting conditions, which represent their intended end-of-life pathway, but rather to determine whether exposure to agricultural soil under outdoor conditions could induce detectable changes during the early stages of environmental weathering. This approach was considered environmentally relevant because compostable bioplastics may also enter soil environments through mismanaged disposal, littering, agricultural use, compost application, or incomplete collection and treatment. Under such non-ideal conditions, these materials are not necessarily expected to undergo rapid or complete biodegradation, but they may still experience partial aging and release volatile compounds, additives, or degradation products. Accordingly, the first objective was to identify thermal degradation profiles, pyrolysis markers, and compounds released at different temperatures from commercial biodegradable plastics using a systematic analytical approach combining Py-GC-MS, EGA-MS, TGA, and HS-SPME/GC-MS. Notably, this study reports, for the first time, the combined application of Py-GC-MS and HS-SPME/GC-MS to investigate the chemical characteristics of commercial biodegradable products and aged biodegradable plastic samples obtained from a laboratory-scale soil incubation experiment. The complementarity of these techniques enabled the characterization of both the volatile/semi-volatile fraction and the polymeric matrix, providing a more comprehensive molecular description of the investigated materials. Particular attention was devoted to the effects of soil aging, in order to determine whether environmental exposure in agricultural soil modifies the detectable composition of the bioplastics, the release of volatile compounds, and their thermal degradation behavior. From an environmental perspective, these aspects are relevant because they provide information not only on the persistence of the polymeric matrix, but also on the possible transformation of formulation-dependent compounds during the early stages of degradation.

2. Materials and methods

2.1. Experimental design and sample collection

The deterioration condition of the bioplastic in soil was simulated in

sterile cell culture flasks with ventilated caps (250 mL, Thermo Scientific). In particular, about 40 g of agricultural soil was introduced into cell culture flasks, followed by the addition of 1 wt% and 5 wt% of SB and PLA after the materials were cut into small pieces of $0.1\text{--}0.5 \times 0.1\text{--}0.5$ cm size. All treatments were set up with three replicates. The prepared flasks were placed outdoors at the Tecnopolo of Rimini, University of Bologna, from February to May 2022 under natural environmental exposure. During this period, the average daily temperature was 10.5°C in March (maximum 15.7°C , minimum 4.5°C), 12.8°C in April (maximum 17.2°C , minimum 7.2°C), and 19.8°C in May (maximum 24.4°C , minimum 14.7°C). However, direct exposure to rainfall was prevented by the experimental setup. Aged bioplastic samples were collected after 30 and 100 days in order to examine two stages of early soil aging, namely an initial short-term exposure and a longer incubation period, and to evaluate whether detectable changes in composition, thermal behavior, and volatile release occurred within 100 days under the adopted outdoor conditions. At the end of the exposure period, the bioplastics were removed from the soil, rinsed with deionized water to remove adhering soil particles, and dried before analysis. Furthermore, to verify the effect of the cleaning treatment on bioplastics, the same procedure was tested on unaged samples, and analyses were also carried out on samples that were not subjected to cleaning prior to analysis. An agricultural clay soil [23] from the "Ganazzoli Filippo Mezzani" farm, Parma, Emilia-Romagna, Italy, was sampled from the top 20 cm of soil and used in this experiment. The chemical properties of the soil are reported in Table SM1.

Regarding the tested material, the experiment was conducted using SB and PLA products that are commercially available in Italian supermarkets. Two items classified as bio-based biodegradable plastics were selected, differing in polymer type and product form, i.e., plates in PLA and starch-based film bags in SB. All selected bioplastic products were labelled as compostable according to the Italian regulation UNI EN 13432:2002.

2.2. Methods

2.2.1. Evolved gas analysis – mass spectrometry (EGA-MS)

EGA-MS analyses of bioplastics were performed using an EGA/Py-3030D micro-furnace pyrolyser (Frontier Laboratories Ltd., Fukushima, Japan) coupled with a 7890B Agilent HP gas chromatograph (GC) connected to a 5977B Agilent HP quadrupole mass spectrometer (MS) (Agilent Technologies, Palo Alto, USA). The injection port was connected to the MS through a deactivated metal capillary tube (Ultra ALLLOY®, $3\text{ m} \times 0.15\text{ mm}$, Frontier Laboratories Ltd.) installed in the GC oven. $50\text{--}80\text{ }\mu\text{g}$ of bioplastic was weighed in a clean stainless-steel cup and inserted into the microfurnace. The microfurnace was heated from 50°C to 600°C at $10^\circ\text{C min}^{-1}$ and the interface temperature was set at 300°C . The GC injector was operated in split mode with a 30:1 ratio at 300°C . The oven was kept at 300°C during the whole analysis. The analyses were performed in constant flow mode at 1.0 mL min^{-1} using helium as carrier gas. The MS was operated in electron ionization (EI) mode at 70 eV in positive mode (scanning $29\text{--}600\text{ m/z}$) with transfer line temperature 250°C , ion source temperature 230°C and quadrupole temperature 150°C . The collected mass spectrometry data were processed using Agilent MassHunter software (version 10.0, Agilent Technologies). Each sample was analysed in triplicate to evaluate the reproducibility of the peak area (A_p) and peak temperature (T_p). The A_p was calculated by dividing the area integrated from the total ion thermogram (TIT) by the sample weight, while the T_p was determined as the temperature corresponding to the maximum of the TIT. The reproducibility of the TIT-derived A_p , expressed as relative standard deviation (RSD), was lower than 9%, whereas the reproducibility of T_p , expressed as standard deviation, was within 2°C .

2.2.2. Pyrolysis-GC-MS

Py-GC-MS analyses were performed using the same instrumentation

described above for EGA-MS. Approximately $60\text{ }\mu\text{g}$ of each bioplastic sample was weighed in a clean stainless-steel cup and introduced into the microfurnace. Based on the EGA-MS results and previous studies on the Py-GC-MS analysis of biopolymers [12,19], single-shot flash pyrolysis was carried out at 600°C for 1 min. The interface temperature was maintained at 280°C , and helium was used as the carrier gas at a constant flow rate of 1.0 mL min^{-1} . The GC injector was operated in split mode (30:1) at 280°C and equipped with an ultra-inert liner packed with deactivated glass wool (Agilent Technologies, part no. 5190-2295). Pyrolysis products were separated by an HP-5MS fused silica capillary column (stationary phase poly[5% diphenyl/95% dimethyl]siloxane, $30\text{ m} \times 0.25\text{ mm i.d.}$, $0.25\text{ }\mu\text{m}$ film thickness, Agilent Technologies, USA) with the following temperature program: 45°C to 300°C at $10^\circ\text{C min}^{-1}$, then a hold for 5 min at 300°C , using helium as carrier gas (1 mL min^{-1}). The MS was operated in EI positive mode (70 eV, scanning $29\text{--}600\text{ m/z}$) with transfer line temperature 250°C , ion source temperature 230°C and quadrupole temperature 150°C .

2.2.3. Headspace solid-phase microextraction-GC-MS

Headspace solid-phase microextraction (HS-SPME) analysis was employed to characterize volatile substances released from unaged and aged bioplastics. The analysis was performed as previously described for the identification of volatile organic compounds released from plastic [24,25] with some modifications. Briefly, samples weighing ca. 10 mg were placed into 20 mL headspace vials and then sealed with silicone/PTFE septa and aluminum caps (Thermo Fisher Scientific, Waltham, MA, U.S.A.). HS-SPME was carried out at three separate extraction temperatures (50 , 100 , and 150°C). In each analysis, a $75\text{ }\mu\text{m}$ carboxen/polydimethylsiloxane (CAR/PDMS) fused silica fiber (SUPELCO, Bellefonte, PA, United States) was exposed for 15 min to the headspace of a sealed vial, with the bottom of the vial heated on a hot plate at the selected temperature, before insertion of the fiber into the GC injector, fitted with an Agilent Ultra Inert liner for SPME (Agilent Technologies, part no. 5190-4048), and the analytes were thermally desorbed at 280°C for 10 min in splitless mode. Analyses were carried out on an Agilent 7820 A gas chromatograph coupled with an Agilent 5977 MSD (Agilent Technologies, USA). Separation was conducted with a HP-5MS fused silica capillary column (stationary phase poly[5% diphenyl/95% dimethyl]siloxane, $30\text{ m} \times 0.25\text{ mm i.d.}$, $0.25\text{ }\mu\text{m}$ film thickness, Agilent Technologies, USA), using helium as the carrier gas at a flow rate of 1 mL min^{-1} . The following thermal program of the capillary column was used: from 35°C (hold time 2 min) to 280°C at $10^\circ\text{C min}^{-1}$, then a hold for 5 min at 280°C . The corresponding mass spectrum of each peak was obtained using an Agilent 5977 MSD operating under electron impact ionization at a voltage of 70 eV, and data acquisition was in full scan mode over a range of m/z $10\text{--}450$ with transfer line temperature 250°C , ion source temperature 230°C and quadrupole temperature 150°C . Each sample was analyzed in triplicate. Before each analytical sequence, blank tests were conducted using the SPME fiber alone and sealed vials with empty headspace to ensure the absence of contaminants.

2.2.4. Thermogravimetric analyses

Thermogravimetric analysis (TGA) of bioplastic samples before and after soil aging was conducted using an Eltra Thermotest thermogravimetric analyzer (Eltra GmbH, Haan, Germany). About 20 mg of each sample was placed in an alumina crucible and heated from 50 to 700°C at a rate of $10^\circ\text{C min}^{-1}$ under a nitrogen flow of 40 mL min^{-1} . The mass loss (TG) and derivative curves (DTG) of the samples were represented as a function of temperature. The main information provided by the TGA results, particularly by the DTG curves, concerns the characteristic temperatures of the thermal degradation events of the bioplastic components and the relative contribution of thermally distinguishable fractions. The characteristic temperatures of the thermal reactions were defined as T_{onset} , T_{endset} and T_{peak} and correspond to the initial, final, and maximum degradation temperatures, respectively.

3. Results and discussion

The differences in the chemical characteristics between the bioplastics introduced into agricultural soil at 1 and 5 wt% were negligible. Therefore, the results reported below refer to both concentrations without distinguishing between them.

3.1. EGA-MS

The TITs and corresponding average mass spectra obtained for unaged and aged SB and PLA bioplastic are shown in Figs. 1a and 2a, respectively. TITs obtained from all unaged and aged bioplastic samples are reported in Figs. SM1 and SM2 of the [Supplementary Material](#). The EGA-MS profiles of both unaged and aged SB bioplastic samples exhibited three distinct degradation peaks, each differing in relative abundance. The first peak, with lower intensity, shows a maximum at $T_{P1} = 325\text{ }^{\circ}\text{C}$ and features in the associated average mass spectrum ions at m/z 43, 44, 56 and 69, suggesting the presence of PLA and polysaccharide in the sample. The second peak is a major thermal degradation region with $T_{P2} = 404\text{ }^{\circ}\text{C}$ and shows in the associated average mass spectrum the typical m/z ions of PBAT (m/z 55, 129, 149, 203) [26]. The third peak at $560\text{ }^{\circ}\text{C}$ presents m/z 78, 105 and 149 as main ions in its average mass spectrum, featuring ions typical of aromatic species as reported in De Falco et al. [12].

SB represents a family of biodegradable and compostable bioplastics, initially consisting of plasticized and/or blended starch derivatives, and developed over twenty-five years of research in a product line not always including starch as a component [27]. The chemical composition of SB bags is reported in the literature as blends of

starch/polycaprolactone, starch/PBAT and PLA/PBS [12,19,28].

EGA-MS analysis provided detailed insight into the chemical composition of the SB samples, revealing the co-presence of PLA and PBAT (Fig. 1b). This interpretation was further supported by the Py-GC-MS results, which did not reveal any unequivocal starch-derived compounds. Accordingly, although the sample was commercially classified as a starch-based bioplastic, its analytical profile under the adopted conditions was dominated by polyester-related compounds, indicating that the detectable composition of the material was predominantly polyester-based.

However, this finding may also reflect analytical limitations, as starch-derived products may have overlapped with polyester-derived pyrolysis products under the single-shot Py-GC-MS conditions employed. Therefore, the absence of starch markers cannot be considered definitive evidence of the complete absence of starch in the material. In this respect, further analyses based on more selective thermal separation approaches, such as double-shot Py-GC-MS, may improve the resolution of the different fractions and allow a more reliable assessment of the possible presence of starch.

The first peak from $240\text{ }^{\circ}\text{C}$ to $340\text{ }^{\circ}\text{C}$ was related to PLA, whereas the second peak from $350\text{ }^{\circ}\text{C}$ to $440\text{ }^{\circ}\text{C}$ was associated with PBAT. The TITs (Fig. 1a) and the Extract Ion Thermograms (EITs) of ions at m/z 129 and 149 (Fig. SM1) highlight the same T_p from unaged and aged SB and greater A_p of PBAT from unaged SB bioplastic. In fact, the EITs of ions at m/z 129 (assigned to $^+\text{O}=\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$, PBAT) and 149 (assigned to $^+\text{O}=\text{C}-\text{Ph}-\text{COOH}$, PBAT) present a T_p of $390\text{ }^{\circ}\text{C}$ and $408\text{ }^{\circ}\text{C}$, respectively, and evolve at temperatures around the TP of the TIT ($390\text{ }^{\circ}\text{C}$) peak for unaged and aged SB. Instead, the TITs and EITs of ions at m/z 129 and 149 show higher A_p values for unaged SB ($>23\%$) than for

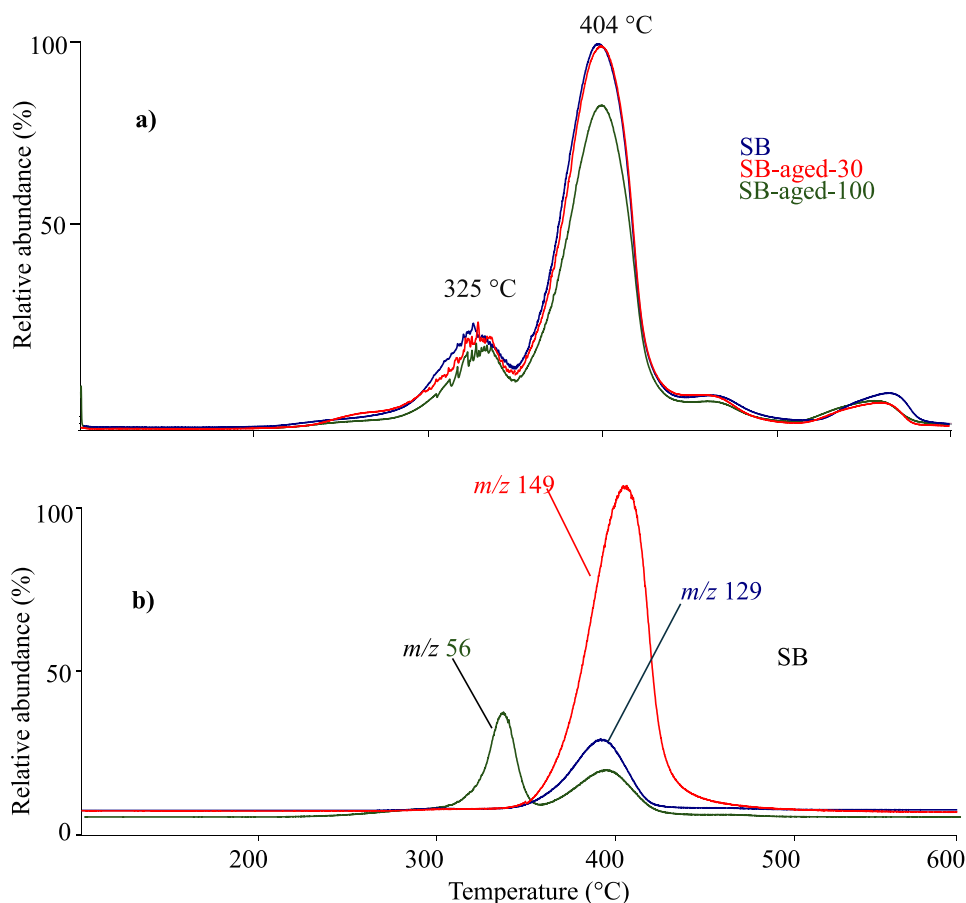


Fig. 1. EGA-MS thermograms obtained from unaged (SB) and aged starch-based (SB-aged) bioplastic. a) Total ion thermograms (TITs) obtained by EGA-MS analysis of 60 μg unaged and aged SB bioplastics; b) Extracted ion thermograms (EITs) of ions at m/z 56 (meso-lactide and D,L-lactide, black, PLA), 129 ($^+\text{O}=\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$, blue, PBAT), and 149 ($^+\text{O}=\text{C}-\text{Ph}-\text{COOH}$, red, PBAT) of unaged SB bioplastic.

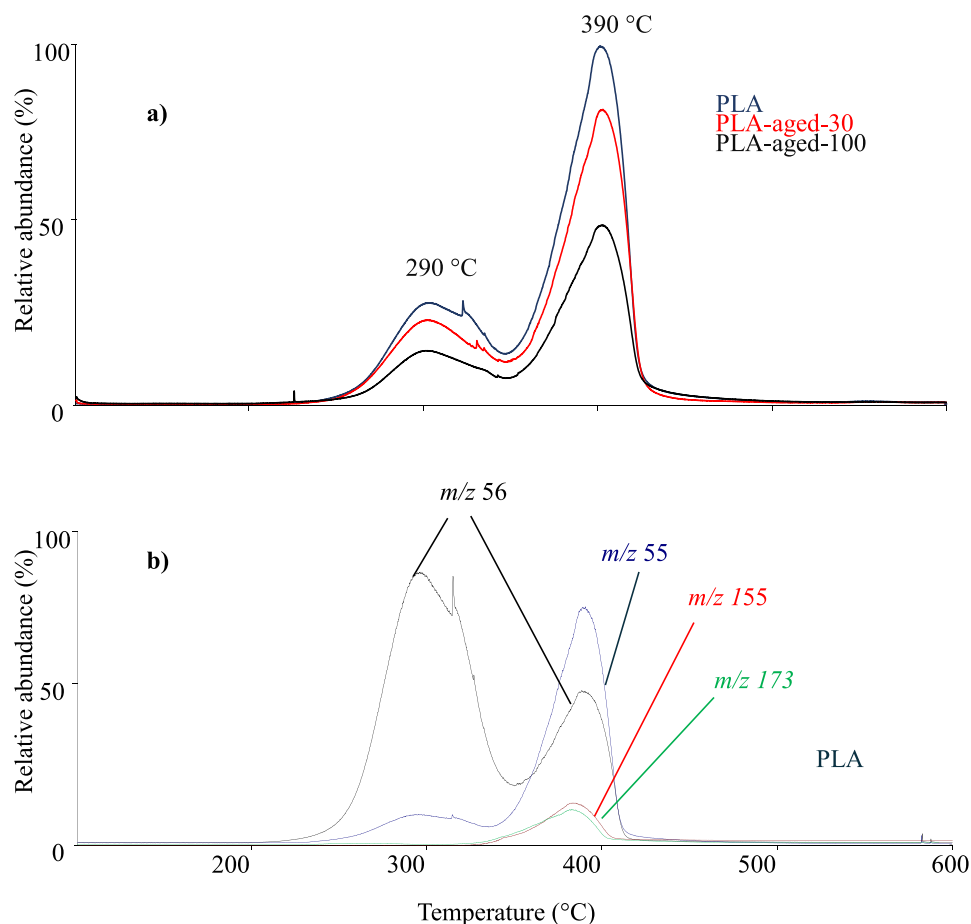


Fig. 2. EGA-MS thermograms obtained from unaged (PLA) and aged PLA (PLA-aged) bioplastic. a) TITs obtained by EGA-MS analysis of 60 μg of unaged and aged PLA bioplastics; b) EITs of ions at m/z 55 (butylene, blue, PLA), 56 (*meso*-lactide and *D,L*-lactide, black, PLA), 155 (succinic acid, di(3-butenyl) ester, red, PBS), and 173 (succinic acid, di(3-butenyl) ester), green, PBS) of unaged PLA bioplastics.

aged SB (Table SM3), suggesting that incorporation of bioplastics into soil for 100 days alters the thermal behavior and chemical characteristics of SB. These changes may reflect the combined action of abiotic and biotic aging processes during soil exposure. In particular, hydrolytic chain scission of ester-containing polymer fractions may have affected the molecular architecture of the material, with consequent effects on the amount and distribution of thermally evolved products detected by EGA-MS. At the same time, the reduction in signal intensity may also be associated with the preferential alteration or depletion of more labile formulation-dependent components, including low-molecular-weight compounds and oligomeric fractions. In such a multicomponent material, these processes may affect the different polymer fractions to different extents, resulting in changes in relative peak intensity without necessarily generating new thermally distinguishable degradation regions. Details on the pyrolysis products derived from the adipate and terephthalate sequences, characterized by the fragment ions at m/z 129 and 149, respectively, are provided in the Supplementary Materials.

The EGA-MS profiles of unaged and aged PLA bioplastic show a main degradation peak at 390 °C, with a shoulder peak at lower temperatures (Fig. 2a). The main m/z signals correspond to the thermal degradation products of PLA and PBS (Fig. 2b). In fact, both peaks showed intense signals at m/z 43, 45, 56 and 144, characteristic of *meso*- and *D,L*-lactides [12]. The major thermal degradation region with $TP_2 = 390$ °C shows in the associated average mass spectrum the typical m/z ions of PBS (m/z 71, 101, 155, 173). The average mass spectrum is dominated by signals at m/z 71, 101, associated with succinic acid, and 173, associated with the fragmentation of 3-butenyl ester of succinic acid [29]. No variations in T_p were observed by comparing the

chromatograms of PLA samples before and after aging. EGA-MS results instead highlight clear changes in A_p after 100 days in soil. A reduction of approximately 25% in the intensity of all m/z signals associated with both PLA and PBS was detected after 100 days of soil exposure (Table SM5), indicating that the PLA/PBS blend underwent detectable changes in its EGA-MS profile during soil aging. Such variations may reflect early degradation-related phenomena, including hydrolytic chain scission of ester-containing fractions and the preferential alteration of low-molecular-weight or thermally labile components, which may modify the relative abundance of the evolved products without necessarily implying extensive bulk degradation of the material.

3.2. Volatile organic compounds

HS-SPME/GC-MS analysis of unaged and aged SB and PLA bioplastics, performed at three extraction temperatures (50, 100, and 150 °C), enabled the detection of volatile and semi-volatile organic compounds. In particular, extraction at 150 °C allowed the detection of 23 and 21 VOCs in SB and PLA samples, respectively. Examples of TIC chromatograms related to analyses performed at 50, 100 and 150 °C on the unaged PLA and SB samples are shown in Figs. 3 and 4, respectively, along with the peak identification in Table 1. The corresponding HS-SPME/GC-MS chromatograms of unaged and aged bioplastics obtained at all extraction temperatures are reported in Supplementary Material Figs. SM3–8.

The VOC profile at 50 °C of SB (Fig. SM3) was characterized by the presence of ethyl acetate (2.1 min), tetrahydrofuran (2.2 min), octanal (8.2 min) and 1,6-dioxacyclododecane-7,12-dione (16.1 min). The

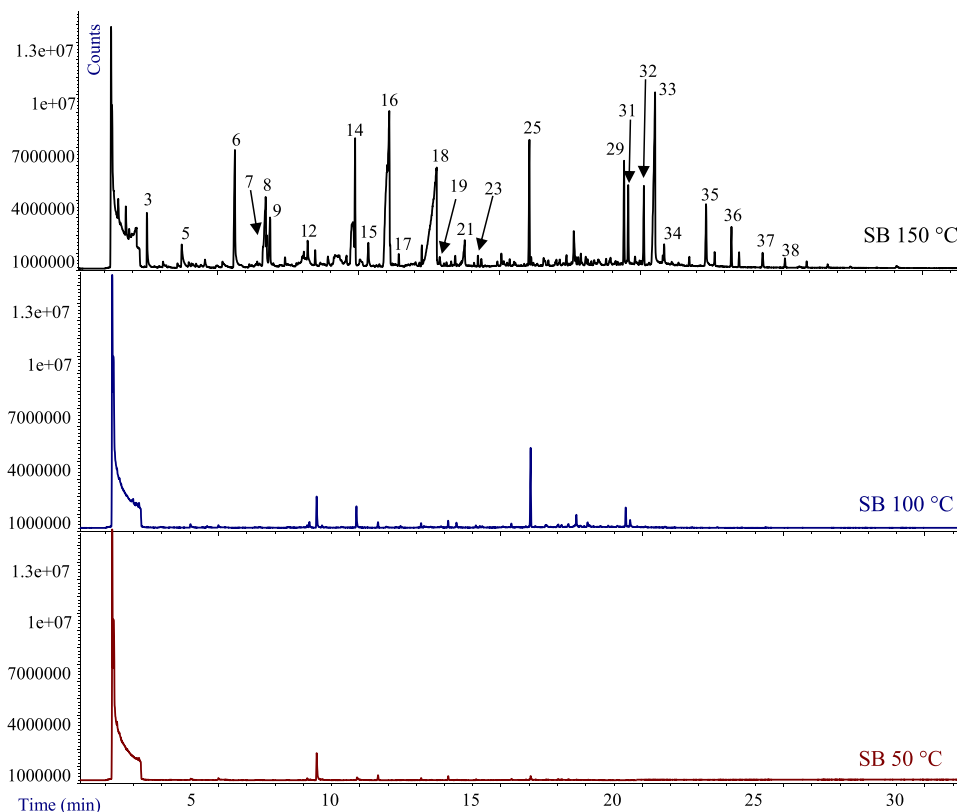


Fig. 3. Total ion chromatograms of volatile organic compounds from unaged starch-based (SB) bioplastics obtained by HS-SPME/GC-MS. Peak numbers refer to compounds listed in [Table 1](#).

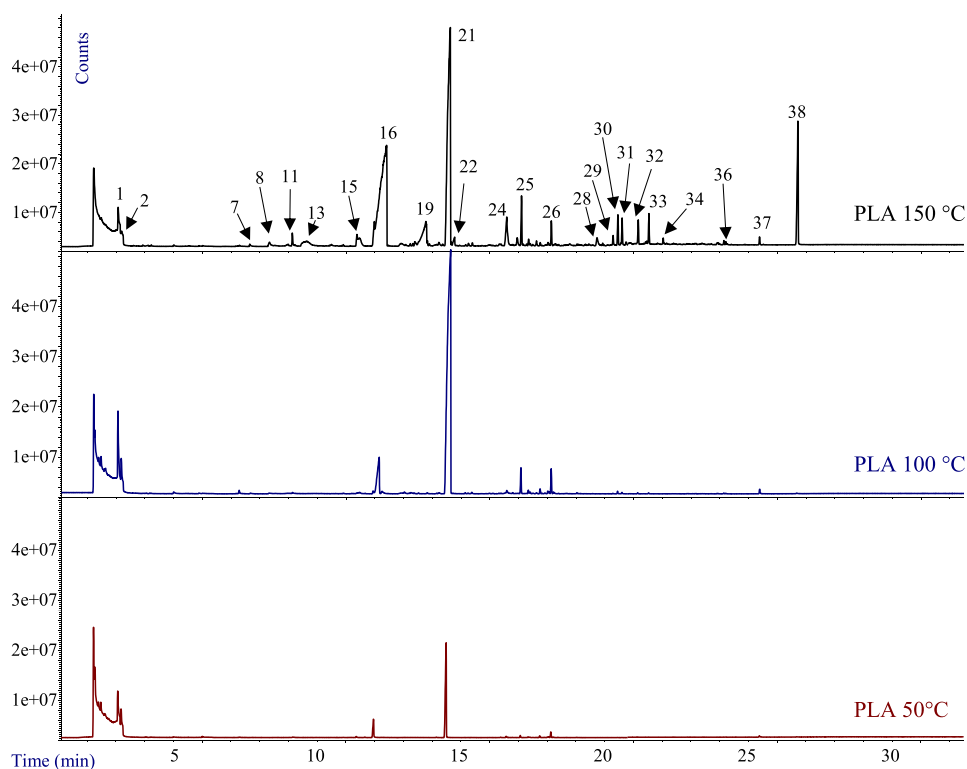


Fig. 4. Total ion chromatograms of volatile organic compounds from unaged PLA obtained by HS-SPME/GC-MS. Peak numbers refer to compounds listed in [Table 1](#).

profile of HS-SPME/GC-MS analyses performed at 100 °C on aged and unaged SB (Fig. SM4) was characterized by the presence of the markers of PLA and PBAT: lactide in *DL*-form (11.2 min) deriving from PLA; 1,6-

dioxacyclododecane-7,12-dione (16.1 min) characteristic of the thermal degradation of PBAT. Moreover, 7,9-di-*tert*-butyl-1-oxaspiro(4,5) deca-6-9-diene-2,8-dione was detected in SB samples, indicating the

Table 1

HS-SPME/GC-MS data and structural assignments of compounds obtained from unaged and aged PLA and SB samples. Chromatograms are shown in Figs. 3 and 4.

# Peak ^a	RT (min)	Compound	Main ions (m/z) ^b	Polymer
1	2.07	ethyl acetate	43, 45, 61, 88	PBAT, PBS
2	2.18	tetrahydrofuran	41, 42, 71, 72	
3	2.53	hydroxyacetone	43, 31, 74	
4	3.31	acrylic acid	45, 56, 72	PLA
5	3.74	1-penten-3-one	27, 29, 55, 84	PLA
6	5.66	2-furanmethanol	39, 41, 42, 98	
7	6.65	butyrolactone	41, 42, 56, 86	
8	6.71	cyclopentanone	41, 42, 55, 56, 84	PBAT
9	6.93	2-cyclopenten-1-one, 2-hydroxy-	41, 42, 55, 69, 98	PBS
10	7.33	1,4-butanediol	41, 42, 44, 57, 71	
11	8.13	cyclohexane, isocyanato-	41, 54, 67, 82, 97	
12	8.23	octanal	41, 43, 56, 57	PBS
13	8.62	succinic anhydride	42, 44, 55, 56, 100	
14	9.93	nonanal	41, 43, 56, 57	
15	10.48	3,6-dimethyl-1,4-dioxane-2,5-dione (<i>meso</i> form)	43, 45, 56, 144	PLA
16	11.16	3,6-dimethyl-1,4-dioxane-2,5-dione (<i>DL</i> form)	43, 45, 56, 144	PLA
17	11.47	decanal	41, 42, 43, 55, 57	PBS
18	12.73	nonanoic acid	41, 55, 57, 60, 73	
19	12.92	undecanal	41, 43, 55, 57, 82	
20	13.33	decanoic acid	41, 43, 57, 60, 73	PBS
21	13.54	unknown	42, 54, 73, 87, 101, 142	
22	13.61	succinic acid, di(3-butenyl) ester	39, 54, 55, 80, 101, 155	
23	14.28	dodecanal	41, 43, 55, 57, 82	PLA, PBAT
24	15.59	1,6-diisocyanato-hexane	41, 43, 56, 69, 85, 99, 126	
25	16.11	1,6-dioxacyclododecane-7,12-dione	55, 84, 100, 129, 172	
26	17.14	unknown	41, 67, 79, 91	

Table 1 (continued)

# Peak ^a	RT (min)	Compound	Main ions (m/z) ^b	Polymer
27	17.34	ethylcitrate	43, 115, 157, 203	additive
28	18.73	unknown	45, 55, 56, 90, 83, 118	PBS
29	19.28	3-butenyl 4-hydroxybutyl succinate	55, 73, 89, 101, 155, 173	
30	19.46	azelaic acid	41, 45, 55, 60, 83, 152	
31	19.60	dibutyl phthalate	41, 76, 150, 149	PBAT
32	20.17	7,9-di-tert-butyl-1-oxaspiro (4,5) deca-6-9-diene-2,8-dione	55, 57, 175, 205	antioxidants
33	20.54	palmitic acid	41, 43, 57, 60, 73, 256	antioxidants
34	21.03	3,5-di-tert-butyl-4-hydroxyphenylpropionic acid	57, 263, 264, 278	
35	22.34	stearic acid	41, 43, 57, 60, 73, 284	
36	23.26	tributyl acetylcitrate	43, 129, 185, 259, 329	additive
37	24.38	unknown	55, 71, 87, 101, 129, 155	PBS
38	25.69	1,6,11,16-tetraoxacycloicosane-2,5,12,15-tetraone	55, 73, 101, 155, 173, 227	PBS

NOTES:

^a Peak referred to GC peak labels in Figs. 3 and 4.

^b m/z of characteristic ions (bold base peak).

presence of the commercial antioxidant Irganox® 1010 [30,31]. Differences were observed by comparing the chromatograms of SB obtained at 50 and 100 °C before and after soil aging, with volatile compounds markedly reduced after 100 days of soil aging. These modifications are consistent with early-stage weathering processes affecting the more labile fractions of the material [8,32]. In particular, the decrease in the relative intensity of volatile and semi-volatile compounds may indicate the preferential loss, transformation, or depletion of low-molecular-weight constituents, residual monomers, oligomers, and additives during aging in soil [8]. Such changes may arise from hydrolytic processes and/or surface-level microbial activity acting on the formulation under outdoor exposure conditions [33].

The VOC profile at 150 °C of SB (Fig. 3) was characterized by a wide range of compounds derived from the thermal degradation of PBAT (e.g., cyclopentanone, 1,6-dioxacyclododecane-7,12-dione), PBS (e.g., succinic anhydride, succinic acid, di(3-butenyl) ester) and PLA (e.g., acrylic acid, 3,6-dimethyl-1,4-dioxane-2,5-dione (*meso*- and *DL*-form)). In addition, 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6-9-diene-2,8-dione and 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid were detected, likely originating from commercial antioxidant Irganox® 1010 [30,31], Rianox® 1010 and Irganox® 1076 [34], respectively.

The VOC profiles of SB obtained at 150 °C (Fig. SM5) did not show

any appreciable effect of soil aging on the GC–MS patterns of the volatile compounds released from the bioplastic, indicating that the overall composition of thermally released volatiles remained substantially unchanged over the 100-day soil exposure period.

The VOC analysis at 50 and 100 °C of unaged and aged PLA samples (Figs. SM6 and SM7) shows peaks related to the PLA and PBAT: lactide in *DL*- form (11.2 min) arising from PLA; 1,6-dioxacyclododecane–7,12-dione (16.1 min) characteristic of the thermal degradation of PBAT.

The VOC emission profiles of HS-SPME/GC-MS analyses conducted at 150 °C (Fig. 4) show peaks related to the butylene succinate moiety such as succinic anhydride (8.6 min), di(3-butenyl) ester of succinic acid (13.6 min), 3-butenyl 4-hydroxybutyl succinate (19.3 min), 1,6,11,16-tetraoxacycloicosane–2,5,12,15-tetraone (25.7 min). However, the results of analysis performed at 150 °C are also characterized by the presence of the markers of PLA such as butyrolactone (6.7 min) and lactide in *meso*- and *DL*- form (10.5 min and 11.2 min, respectively). The chromatogram (Fig. 4) moreover highlights products typical of PBAT, namely the cyclopentanone (6.7 min), 1,6-diisocyanato-hexane (15.6 min) and 1,6-dioxacyclododecane–7,12-dione (16.1 min), along with additives such as 7,9-di-*tert*-butyl–1-oxaspiro (4,5) deca–6–9-diene–2,8-dione (20.2 min) and tributyl acetyl citrate (23.3 min). Although the presence of nitrogen is inconsistent with the PBAT structure, the detection of 1,6-diisocyanato-hexane may be attributed to a polymer additive, as previously reported [12,26]. Comparison of the chromatograms of unaged and aged PLA samples revealed clear changes in the VOC profiles after soil exposure. Specifically, a decrease in the relative intensities of butylene succinate products, *meso*- and *DL*- lactides and additive-related peaks was observed (Fig. SM8). These changes are consistent with early alterations of the more labile fractions of the formulation during soil exposure [35]. Because HS-SPME/GC-MS is

particularly sensitive to readily releasable compounds, the observed decrease in signal intensity likely reflects the preferential transformation, depletion, or release of low-molecular-weight constituents and additives before major modifications become evident in the bulk polymeric matrix.

The HS-SPME/GC-MS technique has already been successfully applied to polymer characterization and the identification of VOCs emitted from expanded PS [36]. This study reports for the first time the application of HS-SPME/GC-MS analysis to bioplastic samples obtained from a controlled soil incubation experiment, providing insights into the effects of soil weathering on their chemical characteristics. Furthermore, the results suggest that, even at 50 °C, there is a potential for the migration of volatile substances from PLA-based bioplastics into foodstuffs.

3.3. Py-GC-MS

Py-GC-MS has previously been applied to characterize and monitor the degradation mechanism of PLA and SB bioplastics [12,19]. In general, in the pyrolysis of PLA acetaldehyde, acrylic acid, two lactide isomers and cyclic oligomers, up to pentamer, are generated as thermal decomposition products [37]. Py-GC-MS analysis of SB is characterized by the presence of the markers of PLA and PBS: 2,3-pentanedione, acrylic acid and lactide in *meso*- and *DL*- form deriving from PLA; succinic anhydride and 1,6,11,16-tetraoxacycloicosan–2,5,12,15-tetraone characteristic of the pyrolysis of PBS [19].

Examples of TIC pyrograms related to the unaged and aged bioplastics obtained at 600 °C are depicted in Figs. 5 and 6, with the peak identification provided in Table 2.

The pyrograms of SB samples were characterized by a series of

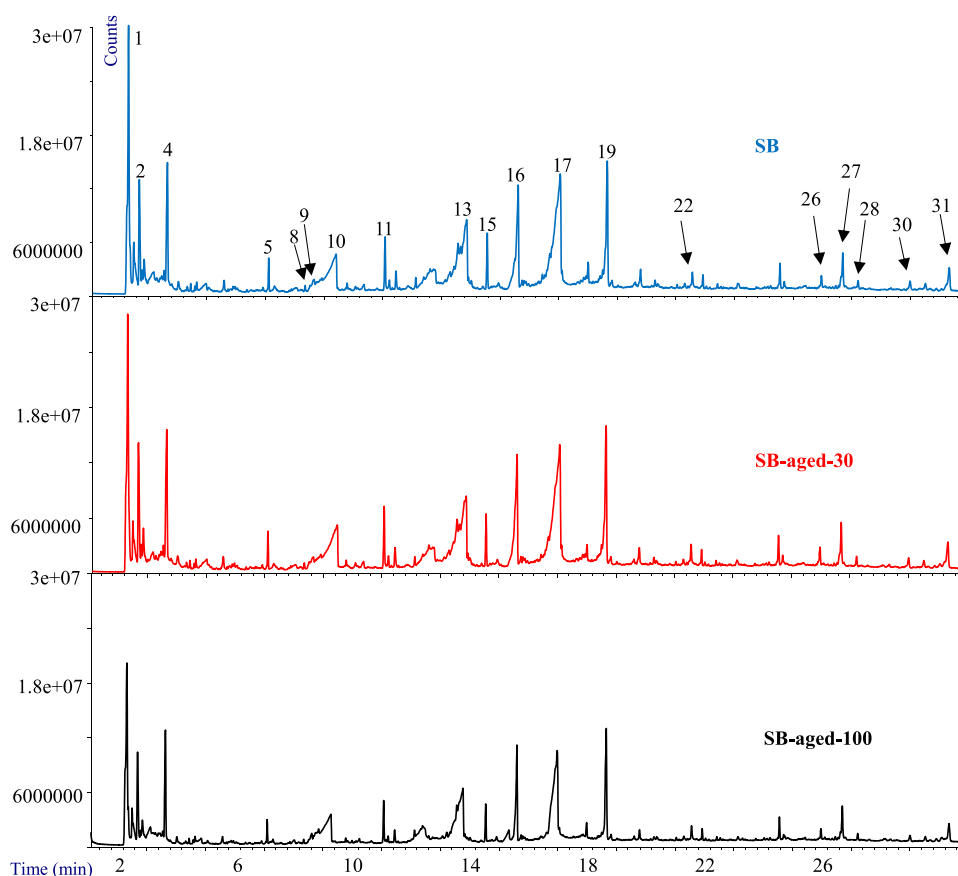


Fig. 5. TIC pyrograms obtained by Py-GC-MS at 600 °C of unaged starch-based (SB) and aged starch-based (SB-aged) samples. Peak numbers refer to compounds listed in Table 2.

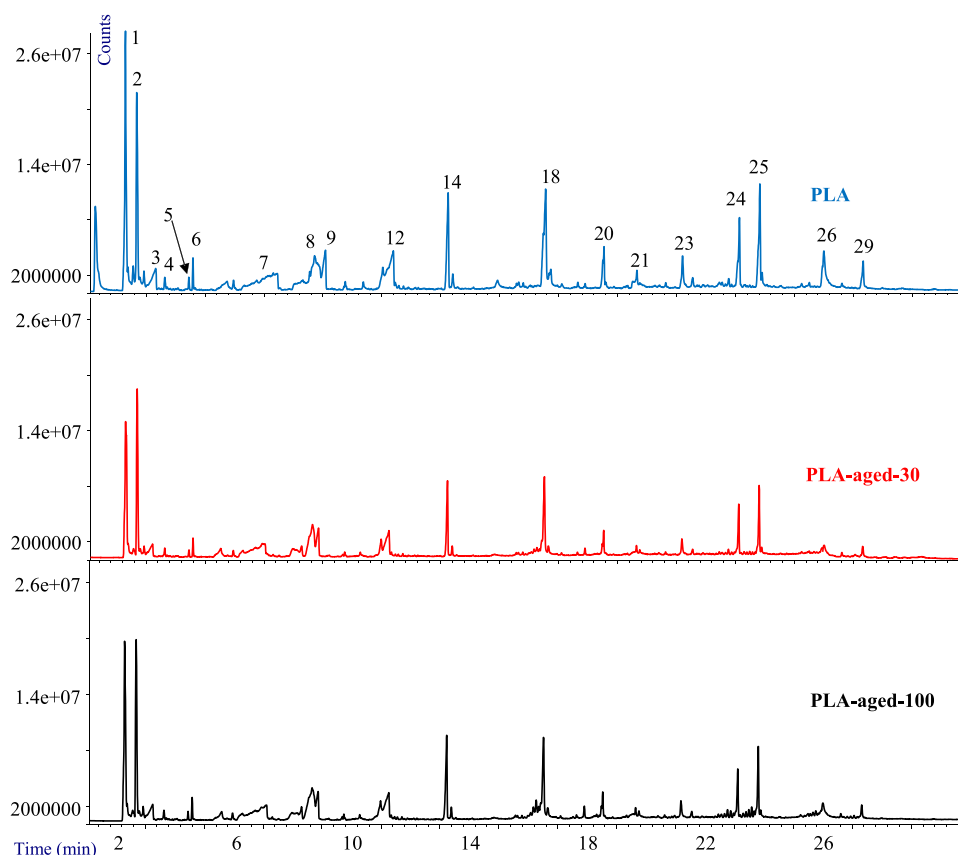


Fig. 6. TIC pyrograms obtained by Py-GC-MS at 600 °C of unaged PLA and aged PLA (PLA-aged) samples. Peak numbers refer to compounds listed in Table 2.

compounds, including 1,3-butadiene (1.3 min), tetrahydrofuran (1.7 min), cyclopentanone (2.7 min), pentanoic acid, 3-butenyl ester (3.8 min), *meso*- and *DL*- lactides (7.2 and 7.7 min), benzoic acid (8.3 min), 2-(formyloxy)-1-phenyl- ethanone (10.1 min), adipic acid, 3-butenyl ester (12.9 min), benzophenone (13.6 min), adipic acid, di(3-butenyl) ester (14.6 min), but-3-en-1-yl hydrogen terephthalate (15.9 min), di (but-3-en-1-yl) terephthalate (17.6 min), but-3-en-1-yl, 4-hydroxybut-1-yl terephthalate (20.6 min), 1,6,11,16-tetraoxacycloicosane-2,5,12,15-tetraone (25.0 min), 6-(4-((6-(but-3-en-1-yloxy)-6-oxohexanoyl)oxy)butoxy)-6-oxohexanoic acid (25.7 min), 4-(benzoyloxy)butyl but-3-enyl terephthalate (26.2 min), cyclic dibutylene adipate terephthalate (28.0 min) and but-3-en-1-yl 4-((6-(but-3-en-1-yloxy)-6-oxohexanoyl)oxy)butyl terephthalate (29.3 min). In summary, the main pyrolysis products of SB included succinic anhydride from PBS and several PBAT-derived compounds, such as 1,3-butadiene and di(3-butenyl) esters of adipic and terephthalic acids. Smaller peaks corresponding to *meso*- and *D,L*-lactides were also detected, indicating the presence of PLA in the polymer blend. Compound # 31 was identified, based on the interpretation of its mass spectrum, as but-3-en-1-yl 4-((6-(but-3-en-1-yloxy)-6-oxohexanoyl)oxy)butyl terephthalate. This pyrolysis product was proposed by Coralli et al. [26] as a specific pyrolysis marker of PBAT.

In contrast to previous Py-GC-MS studies of SB [19], the present analysis revealed several additional PBAT-related pyrolysis products. PBAT is widely used in packaging applications, often blended with other polyesters and starch-based materials to enhance mechanical properties and reduce production costs while maintaining biodegradability [38]. De Falco et al. [12] reported the same compounds and similar distributions in pyrograms from unaged SB bioplastics, along with additional starch-derived compounds (pyruvic aldehyde, 1,4:3,6-dianhydro- α -D-glucopyranose). However, in this study, the results of SB bioplastic Py-GC-MS analysis showed that levoglucosan, the typical pyrolysis marker of starch, was not detected in the pyrolysis profile, also in some analyses performed with

derivatization by a trimethylsilyl (TMS) agent. These findings, consistent with those reported by Barlucchi et al. [18], suggest that the SB samples analyzed contained only trace or negligible amounts of starch as a component of the polymer blend.

The main pyrolytic products of PLA detected by Py-GC-MS (Fig. 6) analysis were: 1,3-butadiene (1.3 min) and tetrahydrofuran (1.7 min) products typical of PBAT; *meso*- and *DL*- lactides (7.2 and 7.7 min) deriving from PLA; succinic acid, di(3-butenyl) ester (13.2 min), 3-butenyl 4-hydroxybutyl succinate (16.5 min), 3-butenyl 4-hydroxybutyl adipate (18.5 min), 1,6,11,16-tetraoxacycloicosane-2,5,12,15-tetraone (23.2 min), dibut-3-enyl-butane-1,4-diyl disuccinate (23.8 min), 1,6,11,16-tetraoxacycloicosane-2,5,12,15-tetraone (25.0) and 3-butenyl 4-(4-(3-butenyloxy)-4-oxobutanoyloxy) butyl adipate (26.9 min) characteristic of the pyrolysis of PBS.

Therefore, the main PLA pyrolysis products were lactide enantiomers and monomer units from the major PLA fraction and succinic acid anhydride from the PBS fraction. The lactide isomers may undergo cis-elimination and fragmentation reactions, generating acrylic acid (2.9 min) and acetaldehyde, respectively [12]. Unlike previous studies [37,39,40], which reported the presence of higher cyclic oligomers in PLA pyrograms, the chromatograms obtained in this study did not exhibit peaks beyond the 7.7 min retention time of the two lactide isomers. In accordance with the findings of De Falco et al. [12], the absence of oligomeric species may reasonably be ascribed to the higher pyrolysis temperature used here, which likely favored the fragmentation of PLA oligomers. PBS is widely employed in PLA-based formulations owing to its high strength and moderate plasticity, allowing the material to preserve high flow stress while markedly improving elongation [41,42].

Previous researchers have characterized PBS/PLA blends, either alone or with varying amounts of additives within the polymer matrix, using Py-GC-MS [43,44]. However, in this study, the results obtained from the Py-GC-MS of PLA analysis revealed a significantly higher

Table 2

Main pyrolysis products detected in the pyrograms of PLA and starch-based samples.

# Peak ^a	RT (min)	Compound	Main ions (m/z) ^b	Polymer
1	1.33	1,3-butadiene	39, 50, 51, 53, 54	PBAT
2	1.67	tetrahydrofuran	41, 42 , 71, 72	PBAT, PBS
3	2.91	acrylic acid	45, 56, 72	PLA
4	2.65	cyclopentanone	41, 55 , 84	PBAT
5	3.82	pentanoic acid, 3-butenyl ester	54, 55, 57, 85 , 115	PBAT
6	3.97	3-butenyl propionate	29, 54, 57	
7	6.70	succinic anhydride	42, 44, 55, 56 , 100	PBS
8	7.22	3,6-dimethyl-1,4-dioxane-2,5-dione (<i>meso</i> form)	43, 45, 56 , 144	PLA
9	7.66	3,6-dimethyl-1,4-dioxane-2,5-dione (<i>DL</i> form)	43, 45, 56 , 144	PLA
10	8.33	benzoic acid	39, 51, 77, 105, 122	PBAT
11	10.11	2-(formyloxy)-1-phenyl- ethanone	54, 77, 105, 135	PBAT
12	11.13	unknown	45, 55, 73, 87, 101	PBS
13	12.89	adipic acid, 3-butenyl ester	54, 55, 83, 101, 111, 129	PBAT
14	13.24	succinic acid, di(3-butenyl) ester	39, 54, 55, 80, 101, 155	PBS
15	13.57	benzophenone	39, 51, 77, 105 , 152, 182	PBAT
16	14.62	adipic acid, di(3-butenyl) ester	39, 55, 83, 101, 111, 129, 183	PBAT
17	15.92	but-3-en-1-yl hydrogen terephthalate	54, 65, 121, 149	PBAT
18	16.51	3-butenyl 4-hydroxybutyl succinate	55 , 73, 89, 101, 155, 173	PBS
19	17.66	di(but-3-en-1-yl) terephthalate	54, 104, 149, 203	PBAT
20	18.54	3-butenyl 4-hydroxybutyl adipate	55 , 71, 87, 101, 129, 155, 183	PBS
21	19.45	bis(4-hydroxybutyl) succinate	55 , 73, 101, 119, 142, 160	PBS
22	20.56	but-3-en-1-yl, 4-hydroxybut-1-yl terephthalate	54, 71, 104, 149, 203, 221	PBAT
23	21.17	unknown	55 , 71, 87, 101, 129, 155	PBS
24	23.16	1,6,11,16-tetraoxacycloicosane-2,5,12,15-tetraone	55 , 71, 101, 128, 173, 226	PBS
25	23.80	dibut-3-enyl-butane-1,4-diyl disuccinate	55 , 73, 101,	PBS

Table 2 (continued)

# Peak ^a	RT (min)	Compound	Main ions (m/z) ^b	Polymer
26	25.02	1,6,11,16-tetraoxacycloicosane-2,5,12,15-tetraone	155, 173, 227, 55 , 71, 101, 128, 173, 226	PBS
27	25.70	6-(4-((6-(but-3-en-1-yloxy)-6-oxohexanoyl)oxy)butoxy)-6-oxohexanoic acid	54 , 55 , 111, 129, 183, 255	PBAT
28	26.22	4-(benzoyloxy)butyl but-3-enyl terephthalate	54, 77, 105 , 149, 203, 325	PBAT
29	26.92	3-butenyl 4-(4-(3-butenyloxy)-4-oxobutanoyloxy)butyl adipate	55 , 71, 101, 129, 155, 173, 227	PBS
30	28.00	cyclic dibutylene adipate terephthalate	54, 55, 71, 104, 132, 149 , 211, 289	PBAT
31	29.33	but-3-en-1-yl 4-((6-(but-3-en-1-yloxy)-6-oxohexanoyl)oxy)butyl terephthalate	54, 55, 111, 149, 203 , 221, 275	PBAT

NOTES:

^a Peak referred to GC peak labels in Figs. 5 and 6.^b m/z of characteristic ions (bold base peak).

abundance of PBS pyrolysis markers compared to those reported in previous studies with 5% of PBS [43,44].

No noticeable differences were observed by comparing the pyrograms of PLA and SB before and after soil aging. The pyrolytic patterns of the unaged and aged bioplastics were similar in terms of the identified compounds, indicating that soil exposure for 100 days did not produce substantial changes in the detectable Py-GC-MS profiles of the investigated materials. These findings suggest that any compositional modifications remained limited or below the detection capability of the applied analytical approach, and that some bioplastic components were not selectively degraded during soil exposure.

3.4. Thermal characterisation by TGA

To evaluate thermal stability of selected bioplastic materials, experiments of thermogravimetry (TGA) combined with differential thermogravimetry (DTG) were carried out.

The TG and DTG curves obtained from unaged and aged bioplastics are shown in Fig. 7 and Figs. SM9–11, while the corresponding values of T_{onset} , T_{endset} and T_{peak} for SB and PLA bioplastics are reported in Table SM6.

For SB bioplastics, it is possible to observe an increase in these parameters, already after 30 days of soil aging, indicative of a degradation process. After 100 days, data reveal that T_{onset} increases from 232 to 305 °C, likely caused by an effective change in the polymeric structure of this material [45]. Moreover, a substantial increase in the main peak temperature (T_{peak}) at the end of soil period is noticeable, shifting from 355 °C to approximately 380 °C. This temperature shift can be regarded as an indicator of degradation progress [46]. Regarding final degradation temperatures, slight differences were observed in the T_{endset} of the unaged and aged SB bioplastic.

The TGA results for SB bioplastics were consistent with those obtained from EGA-MS, suggesting a PLA/PBAT blend. Previous TGA

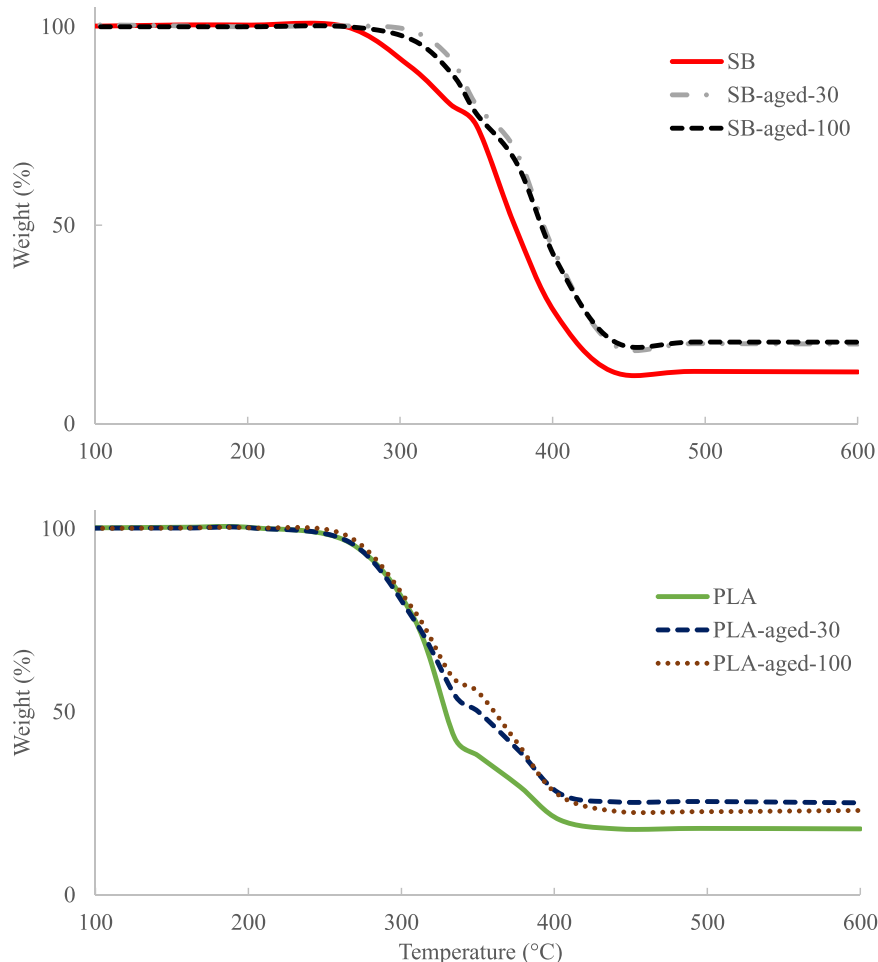


Fig. 7. TG curves obtained from unaged and aged starch-based (SB) and PLA samples.

studies on biopolymer blends have reported graphs for SB blends with the peculiar shoulder of PBAT in a temperature range from 390°C to 400°C, depending on the equipment and heating rate used [45,47].

As reported above, the EGA-MS profile of the unaged and aged SB bioplastic showed three degradation peaks with different relative abundance: the first peak, at lower intensity, with maximum at $TP_1 = 325^\circ\text{C}$; the second peak with major thermal degradation region at $TP_2 = 404^\circ\text{C}$; the third peak at 560°C . In contrast, TGA analyses highlighted two peaks of thermal degradation with a substantial increase in the main peak temperature (T_{peak}) from 355°C to around 380°C at the end of soil period. Furthermore, the EGA-MS results showed for major thermal degradation region a marked reduction of A_p for SB bioplastics after 100 days of soil aging. In agreement with the EGA-MS results, for the peak related to PBAT, the TGA analysis results show a slight decrease in the peak area at the end of soil period.

The results obtained from the TGA analysis of PLA did not show appreciable differences in the values of T_{onset} and T_{peak} , while there was a slight difference in T_{endset} between unaged and PLA after 100 days of soil aging. Unaged PLA exhibited a main degradation peak at 308°C with a minor shoulder at higher temperature. By contrast, EGA-MS profiles of both unaged and aged PLA showed a main degradation peak at 380°C and a lower-temperature shoulder, attributable to the PLA and PBS fractions. In addition, the TGA peak of unaged PLA was sharper and more intense, whereas aged PLA showed a broader and less intense peak, suggesting a more gradual degradation behavior after soil exposure. Moreover, the EGA-MS profile of aged PLA did not exhibit evident shoulders or secondary peaks, indicating that no additional thermally distinguishable degradation events were observed under the

adopted analytical conditions. These observations are consistent with partial aging of the formulation rather than extensive degradation of the bulk polymer matrix. In particular, the broadening and attenuation of the TGA peak after soil exposure may reflect changes in the molecular weight distribution and in the relative contribution of thermally labile fractions, plausibly associated with hydrolytic chain scission and the selective alteration or depletion of formulation-dependent components during soil aging.

4. Conclusions

Two commercially relevant biodegradable plastic products, PLA and SB, were analyzed by Py-GC-MS, EGA-MS, TGA, and HS-SPME/GC-MS to investigate their thermal degradation profiles, pyrolysis markers, and compounds released at different temperatures. While previous studies have reported on the thermochemical characterization of biodegradable polymers, this study represents the first comprehensive thermoanalytical investigation of both unaged and aged commercial biodegradable products by combining these complementary techniques.

HS-SPME/GC-MS analysis revealed that the thermal degradation products of SB bioplastics are characterized by a wide array of compounds originating from PBAT (e.g., cyclopentanone, 1,6-dioxacyclododecane-7,12-dione), PBS (e.g., succinic anhydride, succinic acid, di(3-butenyl) ester) and PLA (e.g., acrylic acid, 3,6-dimethyl-1,4-dioxane-2,5-dione (*meso*- and *DL*-form)). The same polymers in commercial SB were also identified by Py-GC-MS and EGA-MS.

Py-GC-MS and EGA-MS analyses of PLA highlighted peaks related to PLA and PBS, whereas HS-SPME/GC-MS additionally revealed the

presence of PBAT (e.g., 1,6-dioxacyclododecane–7,12-dione). The HS-SPME/GC-MS results also showed that, in the case of PLA plates, volatile compounds could be detected already at 50 °C under the adopted analytical conditions.

EGA-MS and TGA analyses further allowed differentiation between aged and unaged commercial bioplastics, indicating that incorporation into soil for 100 days modified their thermal behavior. HS-SPME/GC-MS was particularly informative in revealing aging-related changes in the volatile fraction, especially for PLA, whereas no substantial variations between aged and unaged materials were observed by Py-GC-MS. Taken together, these results suggest that, over the investigated time scale, soil exposure primarily affected the more labile and thermally releasable components of the formulations rather than producing major changes in the bulk pyrolytic profiles. From an environmental standpoint, this finding is relevant because it indicates that early aging in soil may alter the release of volatile compounds and formulation-dependent constituents even before extensive modifications of the polymeric matrix become evident. The soil incubation experiment was not intended to reproduce industrial composting conditions or to demonstrate complete biodegradation of the selected products under their intended end-of-life pathway. Rather, it was conceived as a laboratory-scale soil aging test to investigate the early transformation of commercial biodegradable plastics under environmentally relevant, non-ideal conditions.

From this perspective, the results indicate that even limited exposure to soil may alter the volatile fraction and thermally distinguishable behavior of commercial biodegradable plastics before extensive changes in the main polymeric matrix become evident. Overall, these findings underline the value of a comprehensive thermoanalytical approach for linking formulation complexity with the early environmental aging behavior of commercial bioplastics.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jaap.2026.107997](https://doi.org/10.1016/j.jaap.2026.107997).

References

- [1] A. Folino, D. Pangallo, P.S. Calabrò, Assessing bioplastics biodegradability by standard and research methods: Current trends and open issues, *J. Environ. Chem. Eng.* 11 (2023) 109424, <https://doi.org/10.1016/j.jece.2023.109424>.
- [2] G. Fredi, A. Dorigato, Recycling of bioplastic waste: A review, *Adv. Ind. Eng. Polym. Res.* 4 (2021) 159–177, <https://doi.org/10.1016/j.aiepr.2021.06.006>.
- [3] F. Marchelli, L. Fiori, The growing problem of waste bioplastics disposal, and a way to tackle it, *Waste Manag.* 201 (2025) 114786, <https://doi.org/10.1016/j.wasman.2025.114786>.
- [4] S. Nanda, B.R. Patra, R. Patel, J. Bakos, A.K. Dalai, Innovations in applications and prospects of bioplastics and biopolymers: a review, *Environ. Chem. Lett.* 20 (2022) 379–395, <https://doi.org/10.1007/s10311-021-01334-4>.
- [5] A. Nandakumar, J.-A. Chuah, K. Sudesh, Bioplastics: A boon or bane? *Renew. Sustain. Energy Rev.* 147 (2021) 111237 <https://doi.org/10.1016/j.rser.2021.111237>.
- [6] L. Hu, Y. Zhang, M. Zhang, Q. Chen, Y. Zhou, J. Fu, D. Zhang, X. Pan, A review on the release and environmental effects of biodegradable plastic degradation products, *Environ. Sci. Eur.* 37 (2025) 157, <https://doi.org/10.1186/s12302-025-01140-7>.
- [7] J. Brizga, K. Hubacek, K. Feng, The Unintended Side Effects of Bioplastics: Carbon, Land, and Water Footprints, *One Earth* 3 (2020) 45–53, <https://doi.org/10.1016/j.oneear.2020.06.016>.
- [8] P.A. Withana, X. Yuan, D. Im, Y. Choi, M.S. Bank, C.S.K. Lin, S.Y. Hwang, Y.S. Ok, Biodegradable plastics in soils: sources, degradation, and effects, *Environ. Sci. Process. Impacts* 27 (2025) 3321–3343, <https://doi.org/10.1039/D4EM00754A>.
- [9] S. Huang, Q. Dong, S. Che, R. Li, K.H.D. Tang, Bioplastics and biodegradable plastics: A review of recent advances, feasibility and cleaner production, *Sci. Total. Environ.* 969 (2025) 178911, <https://doi.org/10.1016/j.scitotenv.2025.178911>.
- [10] A.A. Shah, F. Hasan, A. Hameed, S. Ahmed, Biological degradation of plastics: A comprehensive review, *Biotechnol. Adv.* 26 (2008) 246–265, <https://doi.org/10.1016/j.biotechadv.2007.12.005>.
- [11] S.V. Afshar, A. Boldrin, T.H. Christensen, F. Corami, A.E. Dagaard, B. Rosso, N. B. Hartmann, Disintegration of commercial biodegradable plastic products under simulated industrial composting conditions, *Sci. Rep.* 15 (2025) 8569, <https://doi.org/10.1038/s41598-025-91647-z>.
- [12] F. De Falco, T. Nacci, L. Durnell, R.C. Thompson, I. Degano, F. Modugno, A thermoanalytical insight into the composition of biodegradable polymers and commercial products by EGA-MS and Py-GC-MS, *J. Anal. Appl. Pyrolysis* 171 (2023) 105937, <https://doi.org/10.1016/j.jaap.2023.105937>.
- [13] M. Mattonai, F. Nardella, M. Filomena, S. Gesti, G. Medaglia, E. Ribechini, Quantification of polyethylene in biodegradable plastics by analytical pyrolysis-based methods with GC split modulation, *J. Anal. Appl. Pyrolysis* 191 (2025) 107172, <https://doi.org/10.1016/j.jaap.2025.107172>.
- [14] European Bioplastics. Bioplastics market development update 2024, Nova-Institute. <https://www.european-bioplastics.org/market/>, 2024 (accessed 6 November 2025).
- [15] K. Elfehri Borchani, C. Carrot, M. Jaziri, Biocomposites of Alfa fibers dispersed in the Mater-Bi® type bioplastic: Morphology, mechanical and thermal properties, *Composites Part A Applied Science Manufacturing* 78 (2015) 371–379, <https://doi.org/10.1016/j.compositesa.2015.08.023>.
- [16] M. Aldas, J.M. Ferri, J. Lopez-Martinez, M.D. Samper, M.P. Arrieta, Effect of pine resin derivatives on the structural, thermal, and mechanical properties of Mater-Bi type bioplastic, *J. Appl. Polym. Sci.* 137 (2020) 48236, <https://doi.org/10.1002/app.48236>.
- [17] A. Crema, E. Dinelli, E. Fabbri, P. Galletti, N. Greggio, V. Lastella, A. Parodi, A. Pasteris, M. Pedrizzi, C. Samorì, Additives in bioplastics: Chemical characterization, migration in water and effects on photosynthetic organisms, *Sci. Total. Environ.* 955 (2024) 177205, <https://doi.org/10.1016/j.scitotenv.2024.177205>.
- [18] L. Barlucchi, G. Biale, J. La Nasa, M. Mattonai, S. Pezzini, A. Corti, V. Castelvetro, F. Modugno, Abiotic degradation and accelerated ageing of microplastics from biodegradable and recycled materials in artificial seawater, *Sci. Total. Environ.* 954 (2024) 176832, <https://doi.org/10.1016/j.scitotenv.2024.176832>.
- [19] B.M. Tselana, S. Muniyasamy, V.O. Ojijo, W. Mhike, Melt Processible Biodegradable Blends of Polyethylene Glycol Plasticized Cellulose Diacetate with Poly(lactic Acid) and Polybutylene Adipate-Co-Terephthalate, *J. Polym. Environ.* 31 (2023) 4891–4908, <https://doi.org/10.1007/s10924-023-02925-8>.
- [20] X. Quecholac-Piña, M.D.C. Hernández-Berriel, M.D.C. Mañón-Salas, R.M. Espinosa-Valdemar, A. Vázquez-Morillas, Degradation of Plastics under Anaerobic Conditions: A Short Review, *Polymers* 12 (2020) 109, <https://doi.org/10.3390/polym12010109>.
- [21] S. Agarwal, Biodegradable Polymers: Present Opportunities and Challenges in Providing a Microplastic-Free Environment, *Macro Chem. & Phys.* 221 (2020) 2000017, <https://doi.org/10.1002/macp.202000017>.
- [22] S. Bejgarn, M. MacLeod, C. Bogdal, M. Breitholtz, Toxicity of leachate from weathering plastics: An exploratory screening study with *Nitocra spinipes*, *Chemosphere* 132 (2015) 114–119, <https://doi.org/10.1016/j.chemosphere.2015.03.010>.
- [23] USDA, Natural Resources Conservation Service. National Soil Survey Handbook. U. S.D.A., U. S. Dep. Agric. (2005).
- [24] U. Sünata, P. Trebše, M.B. Kralj, Simply Applicable Method for Microplastics Determination in Environmental Samples, *Molecules* 26 (2021) 1840, <https://doi.org/10.3390/molecules26071840>.
- [25] P. Kusch, G. Knupp, Headspace-SPME-GC-MS Identification of Volatile Organic Compounds Released from Expanded Polystyrene, *J. Polym. Environ.* 12 (2004) 83–87, <https://doi.org/10.1023/B:JOEE.0000010053.20382.d7>.
- [26] I. Coralli, A.G. Rombolà, D. Fabbri, Analytical pyrolysis of the bioplastic PBAT poly (butylene adipate-co-terephthalate), *J. Anal. Appl. Pyrolysis* 181 (2024) 106577, <https://doi.org/10.1016/j.jaap.2024.106577>.
- [27] Novamont - Company Profile. <https://www.novamont.com/eng/company-profile> (accessed 6 November 2025).
- [28] M. Menossi, M. Cisneros, V.A. Alvarez, C. Casalongué, Current and emerging biodegradable mulch films based on polysaccharide bio-composites. A review, *Agron. Sustain. Dev.* 41 (2021) 53, <https://doi.org/10.1007/s13593-021-00685-0>.
- [29] F. Marchelli, M. Mattonai, R. Ferrentino, J. La Nasa, N. Pecorelli, F. Modugno, G. Andreottola, E. Ribechini, L. Fiori, Fostering Bioplastics Circularity through Hydrothermal Treatments: Degradation Behavior and Products, *ACS Sustain. Chem. Eng.* 12 (2024) 9257–9267, <https://doi.org/10.1021/acscuschemeng.4c02174>.
- [30] B.P. Singh, A.L. Cowie, R.J. Smernik, Biochar Carbon Stability in a Clayey Soil As a Function of Feedstock and Pyrolysis Temperature, *Environ. Sci. Technol.* 46 (2012) 11770–11778, <https://doi.org/10.1021/es302545b>.
- [31] C. Kalweit, S. Berger, A. Kämpfe, T. Rapp, Quantification and stability assessment of 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione leaching from cross-linked polyethylene pipes using gas and liquid chromatography, *Water Res.* 243 (2023) 120306, <https://doi.org/10.1016/j.watres.2023.120306>.
- [32] M.M. Abe, M.C. Branciforti, M. Brienza, Biodegradation of hemicellulose-cellulose-starch-based bioplastics and microbial polyesters, *Recycling* 6 (2021) 22, <https://doi.org/10.3390/recycling6010022>.
- [33] S. Bandopadhyay, L. Martin-Closas, A.M. Pelacho, J.M. DeBruyn, Biodegradable plastic mulch films: Impacts on soil microbial communities and ecosystem functions, *Front. Microbiol.* 9 (2018) 819, <https://doi.org/10.3389/fmicb.2018.00819>.

- [34] R. Khan, B.A. Perez, H.E. Toraman, Comparative analysis of additive decomposition using one-dimensional and two-dimensional gas chromatography: Part I - Irganox 1010, Irganox 1076, and BHT, *J. Chromatogr. A* 1732 (2024) 465243, <https://doi.org/10.1016/j.chroma.2024.465243>.
- [35] M. Karamanlioglu, R. Preziosi, G.D. Robson, Abiotic and biotic environmental degradation of the bioplastic polymer poly(lactic acid): A review, *Polym. Degrad. Stab.* 137 (2017) 122–130, <https://doi.org/10.1016/j.polymdegradstab.2017.01.009>.
- [36] X.-C. Song, M. Wrona, C. Nerin, Q.-B. Lin, H.-N. Zhong, Volatile non-intentionally added substances (NIAS) identified in recycled expanded polystyrene containers and their migration into food simulants, *Food Packag. Shelf Life* 20 (2019) 100318, <https://doi.org/10.1016/j.fpsl.2019.100318>.
- [37] F. Khabbaz, S. Karlsson, A.-C. Albertsson, PY-GC/MS an effective technique to characterizing of degradation mechanism of poly (L-lactide) in the different environment, *J. Appl. Polym. Sci.* 78 (2000) 2369–2378, [https://doi.org/10.1002/1097-4628\(20001220\)78:13<2369::AID-APP140>3.0.CO;2-N](https://doi.org/10.1002/1097-4628(20001220)78:13<2369::AID-APP140>3.0.CO;2-N).
- [38] J. Jian, Z. Xiangbin, H. Xianbo, An overview on synthesis, properties and applications of poly(butylene-adipate-co-terephthalate)–PBAT, *Adv. Ind. Eng. Polym. Res.* 3 (2020) 19–26, <https://doi.org/10.1016/j.aiepr.2020.01.001>.
- [39] C. Westphal, C. Perrot, S. Karlsson, Py-GC/MS as a means to predict degree of degradation by giving microstructural changes modelled on LDPE and PLA, *Polym. Degrad. Stab.* 73 (2001) 281–287, [https://doi.org/10.1016/S0141-3910\(01\)00089-1](https://doi.org/10.1016/S0141-3910(01)00089-1).
- [40] M.P. Arrieta, F. Parres, J. López, A. Jiménez, Development of a novel pyrolysis-gas chromatography/mass spectrometry method for the analysis of poly(lactic acid) thermal degradation products, *J. Anal. Appl. Pyrolysis* 101 (2013) 150–155, <https://doi.org/10.1016/j.jaap.2013.01.017>.
- [41] B. Imre, B. Pukánszky, Compatibilization in bio-based and biodegradable polymer blends, *Eur. Polym. J.* 49 (2013) 1215–1233, <https://doi.org/10.1016/j.eurpolymj.2013.01.019>.
- [42] Y. Deng, N.L. Thomas, Blending poly(butylene succinate) with poly(lactic acid): Ductility and phase inversion effects, *Eur. Polym. J.* 71 (2015) 534–546, <https://doi.org/10.1016/j.eurpolymj.2015.08.029>.
- [43] M. Llana-Ruiz-Cabello, S. Pichardo, N.T. Jiménez-Morillo, P. Abad, E. Guillamón, F.J. González-Vila, A.M. Cameán, J.A. González-Pérez, Characterisation of a bio-based packaging containing a natural additive from *Allium* spp. using analytical pyrolysis and carbon stable isotopes, *J. Anal. Appl. Pyrolysis* 120 (2016) 334–340, <https://doi.org/10.1016/j.jaap.2016.05.021>.
- [44] M. Llana-Ruiz-Cabello, S. Pichardo, N.T. Jiménez-Morillo, F.J. González-Vila, E. Guillamón, J.M. Bermúdez, S. Aucejo, A.M. Camean, J.A. González-Pérez, Pyrolysis-gas chromatography–isotope ratio mass spectrometry for monitoring natural additives in polylactic acid active food packages, *J. Chromatogr. A* 1525 (2017) 145–151, <https://doi.org/10.1016/j.chroma.2017.10.023>.
- [45] F. Ruggero, E. Carretti, R. Gori, T. Lotti, C. Lubello, Monitoring of degradation of starch-based biopolymer film under different composting conditions, using TGA, FTIR and SEM analysis, *Chemosphere* 246 (2020) 125770, <https://doi.org/10.1016/j.chemosphere.2019.125770>.
- [46] F. Luzzi, E. Fortunati, D. Puglia, R. Petrucci, J.M. Kenny, L. Torre, Study of disintegrability in compost and enzymatic degradation of PLA and PLA nanocomposites reinforced with cellulose nanocrystals extracted from *Posidonia oceanica*, *Polym. Degrad. Stab.* 121 (2015) 105–115, <https://doi.org/10.1016/j.polymdegradstab.2015.08.016>.
- [47] Z.N. Correa-Pacheco, J.D. Black-Solís, P. Ortega-Gudiño, M.A. Sabino-Gutiérrez, J. Benítez-Jiménez, A. Barajas-Cervantes, S. Bautista-Baños, L.B. Hurtado-Colmenares, Preparation and Characterization of Bio-Based PLA/PBAT and Cinnamon Essential Oil Polymer Fibers and Life-Cycle Assessment from Hydrolytic Degradation, *Polymers* 12 (2019) 38, <https://doi.org/10.3390/polym12010038>.