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Abiotic degradation and accelerated ageing of microplastics from biodegradable and recycled materials in artificial seawater

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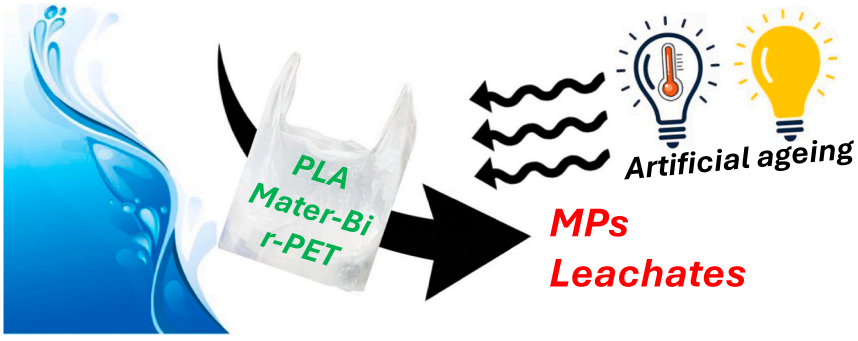
HIGHLIGHTS

- PLA, Mater-Bi®, and recycled PET were used to produce reference microplastics.
- Accelerated ageing of reference microplastics was conducted in artificial seawater.
- All polyesters exhibited hydrolysis.
- Monomers and oligomers from the polymers were detected and quantified in the leachates.

GRAPHICAL ABSTRACT



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ABSTRACT

Microplastics (MPs) are considered one of the most widespread pollutants in all ecosystems worldwide. In the environment, MPs can undergo hydrolysis and/or oxidation, resulting in the release of low-molecular weight degradation products, along with additives, and adsorbed organic pollutants. In this study, the morphological, chemical, and thermal changes of microplastics obtained from two biodegradable plastics, polylactic acid and Mater-Bi®, and a recycled plastic, recycled-polyethylene terephthalate, were examined after accelerated ageing under photo-oxidative conditions in synthetic seawater in a Solarbox system, and after thermal treatment in the dark. Thermal properties were studied by thermogravimetric analysis, differential scanning calorimetry, and evolved gas analysis-mass spectrometry. Compositions and changes of chemical components of the polymers were evaluated by attenuated total reflection-Fourier transform infrared spectroscopy and pyrolysis-gas chromatography–mass spectrometry. The leachable fractions and degradation products released in synthetic seawater by degraded MPs were characterized by gas chromatography–mass spectrometry. This study allowed us to identify hydrolysis as the main degradation pathway of the polymers under analysis, and to characterize not only the oligomers and degradation products released in the water as a consequence of degradation, but also additives

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used in plastic item formulations. This study improves our understanding of these polymers' behavior under accelerated ageing conditions.

1. Introduction

In 2022, global plastic production reached 400 million tons (exclusive of the additional nearly 90 million tons of synthetic fibers), with 58 million tons produced solely in Europe (Plastics Europe, 2023). Recently, different methods for recycling plastic materials have been developed. However, only 14 % of plastic worldwide is recycled (Wimberger et al., 2024). A significant fraction of plastic waste is still mismanaged, and most plastics are not easily degradable, making plastics pollution a worldwide environmental problem (Tian et al., 2023). Once in the environment, plastics undergo physical (morphological) degradation and mechanical fragmentation as a result of chemical degradation (hydrolysis, photo-oxidation) and biodegradation (Andrady, 2011), resulting in the formation of microscopic particles, so-called microplastics (MPs). The presence of MPs throughout the ecosystems has raised growing attention in the scientific community, with a rapidly increasing number of studies investigating the risks associated to microplastics pollution and the related harmfulness to the environment and human health.

To limit plastic production from fossil carbon sources and tackle the increasing pollution by the typically persistent commodity plastics, alternative polymeric materials, generally referred to as bioplastics, have been developed to reduce the environmental burden deriving from the plastics lifecycle. The definition of bioplastics includes both biodegradable and bio-based polymers (Ferrari et al., 2022). The latter definition refers to polymers totally or partially obtained from renewable materials (biomass), irrespective of their biodegradability (Ibrahim et al., 2021). Biodegradability, on the other hand, does not necessarily imply a bio-based origin, as a biodegradable polymer can be derived from fossil carbon sources as well. Biodegradability is a property referred to the capability of a polymer to undergo biological decomposition into carbon dioxide (CO_2), water (H_2O), and low molecular weight oxidized organic compounds (Council, 2019), the latter being generally considered useful as soil amendment. However, the fate of end-of-life biodegradable polymers in the environment is still poorly investigated, since they are designed to be sent to composting plants where they can be processed under controlled temperature and humidity. If released in the environment, biodegradable plastics may undergo chemical, biological, and physical degradation, resulting in bio-microplastics (bio-MPs) generation before complete degradation is reached (Brizga et al., 2020). The environmental degradation and potential toxicity of such bio-MPs, which could also involve the release of molecular fragments, are still poorly understood (Mastrolia et al., 2022). Preliminary studies based on the exposure of different organisms to polylactic acid (PLA) have shown neurotoxic effects and oxidative stress (Capolupo et al., 2023; Chagas et al., 2021).

The aim of this study was the analytical characterization of microplastics, and molecular degradation products generated by two biodegradable bioplastics, PLA and Mater-Bi® (brand name for a bioplastic blend developed and patented by Novamont S.p.A., Italy), and a recycled conventional plastic (r-PET, polyethylene terephthalate), upon thermal and photo-oxidative ageing in artificial seawater. Since bioplastic production grows year after year, PLA and Mater-Bi® were studied, as they are among the most widely produced and used biodegradable bioplastics annually (Bioplastics).

The experimental plan included: a) thermal ageing in the dark at 55 °C (average water temperature 40 °C); b) accelerated photo-oxidative ageing in a SolarBox system (average water temperature 40 °C); c) ageing in the dark at room temperature (control, procedural blank). The effects of the accelerated ageing on the three polymeric materials were investigated by thermoanalytical techniques as evolved gas analysis-mass spectrometry, differential scanning calorimetry, thermogravimetry, and pyrolysis-gas chromatography–mass spectrometry, while the fractions leached in seawater from the degraded MPs were characterized by gas chromatography–mass spectrometry.

2. Material and methods

2.1. Samples

Commercial tableware composed of PLA and Mater-Bi®, together with recycled r-PET cups (Gradisco, Italy) conforming to the standard EN 13432 (EN 13432:2002) were used as samples. Micro-powders of each material were prepared by cryomilling commercial items using a Retsch ZM 200 centrifugal mill operated for 15 s at 18000 rpm, and then sieved to generate MPs smaller than 500 μm.

Deuterated anthracene (anthracene-d_{10}, 99.5 % deuterated, Sigma-Aldrich, USA) was used as internal standard for analytical pyrolysis experiments. Tridecanoic acid (C13, 150 μg/g in acetone, Sigma-Aldrich) and hexadecane (150 μg/g in isooctane, Sigma-Aldrich, USA) were used in GC–MS experiments as derivatization and injection standards, respectively. *N*,*O*-Bis(trimethylsilyl)trifluoroacetamide with 1 % chlorotrimethylsilane (BSTFA +1 % TMCS, Sigma-Aldrich) was used as derivatizing agent. Synthetic seawater for the ageing experiments was prepared according to available guidelines (ASTM D 1141-98, 2021). Samples were weighed for all experiments using an XS3DU microanalytical balance (Mettler Toledo, USA) with seven digits and a precision of 1 μg. All the solvents used in this work were LC-MS grade (Sigma-Aldrich).

2.2. Ageing experiments

Five aliquots of about 100 mg of MPs for each polymer were placed into quartz vials with 5 mL of synthetic seawater. Three parallel ageing experiments were carried out as follows: i) 4 weeks in the dark at room temperature (Control 4 W); ii) 4 weeks in the dark at 55 °C (Dark 4 W); iii) ageing in a SolarBox system (CO.FO.ME.GRA. mod. 1500E RH) equipped with a Xenon lamp with a UV filter at 290 nm and a filter for external UV rays, operating at about 55 °C and with a radiation power of 550 W/m^2 for 1 week, 2 weeks, and 4 weeks (SB 1 W, SB 2 W, SB 4 W, respectively). The average temperature of the synthetic seawater during the ageing experiments both in the dark and in the Solarbox reached 40 °C.

After the treatments for all the aged MPs samples, the artificial seawater was filtered off with a porous septum (filter membrane disk Magna Nylon, 47 mm, 0.2 μm pore size, GVS SpA, Zola Predosa, Italy). Both fractions (seawater and MPs) were separately collected and stored at 4 °C to retain degraded products. The microplastics on the filters were washed with milli-Q water to remove residual salts, then the filters were collected in Petri dishes (60 × 15 mm) and dried in a desiccator until constant weight. For the analyses, the MPs were collected directly from the filters with stainless-steel tweezers and analyzed.

The same ageing setups and sample pretreatments were applied to the procedural blanks containing only artificial sea water to check and exclude possible contaminations.

2.3. Thermogravimetric analysis (TGA)

TGA of MPs before and after induced degradation was performed with a TGA Q500 v6.4 Build 193 analyzer under controlled heating from 30 °C to 700 °C at 10 °C/min under nitrogen flow (60 mL/min). About 3–5 mg of sample were weighed and analyzed in each experiment.

2.4. Evolved gas analysis-mass spectrometry (EGA-MS)

EGA-MS of MPs before and after degradation was performed with a micro-furnace pyrolyzer EGA/PY-3030D® (Frontier Laboratories Ltd., Japan) interfaced with a 6890 N gas chromatographer and coupled to a 5973 single quadrupole mass spectrometer (Agilent Technologies, USA). During each experiment, 100–150 μg of sample were weighted and inserted in the pyrolysis furnace, and the temperature was increased from 50 °C to 800 °C at 10 °C/min. The interface between the pyrolyzer and the GC–MS system was held at a temperature 100 °C higher than that of the furnace, up to a maximum of 300 °C. The GC injector operated in split mode (20:1 ratio) at 280 °C. The evolved desorption/pyrolysis products were directly sent to the mass spectrometer using a UADTM-2.5 N deactivated stainless-steel capillary tube (3 m × 0.15 mm, Frontier Lab.) held at 300 °C and using helium (1 mL/min) as the carrier gas. The temperature of the transfer line was 280 °C. The mass spectrometer was operated in electronic ionization (EI) positive mode (70 eV, *m/z* 36–600). The temperature of the ion source and quadrupole analyzer were 230 °C and 150 °C, respectively.

2.5. Pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS)

Py-GC–MS analysis of MPs was performed using a multi-shot pyrolyzer EGA/PY-3030D® (Frontier Lab.), and an 8890 gas chromatograph coupled with a 5977B mass spectrometer (Agilent). The gas chromatograph was equipped with a split/splitless injector and an HP-5MS capillary column (5 % diphenyl-95 % dimethylpolysiloxane, 30 m × 250 μm × 0.25 μm, Agilent). The mass spectrometer was operated in electronic ionization (EI) positive mode (70 eV, *m/z* 50–500). The temperature of the ion source was 230 °C and that of the quadrupole 150 °C.

Around 70 μg of the sample were weighted in each experiment. 5 μL of anthracene-d_{10} were added as an internal standard. Samples were pyrolyzed at 600 °C with a split ratio of 1:20 and interface at 280 °C. The pyrolysis products were eluted in constant flow (1 mL/min) of helium. The transfer line was maintained at 280 °C. The GC program temperature was 40 °C for 6 min, 20 °C/min to 310 °C for 40 min. The data were processed with Agilent MassHunter Qualitative Analysis 10.0 and NIST 20 mass spectra library.

2.6. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR)

Spectra of MPs were recorded with a Nicolet™ iS50 spectrometer equipped with Smart iTX ATR accessory (Thermo Fisher). Each sample was subjected to 32 scans with a resolution of 4 cm^{-1} in the spectral range 4000–650 cm^{-1}.

2.7. Gel permeation chromatography analysis (GPC)

Gel permeation chromatography of the unaged and aged polymers was performed with a Jasco instrument comprising a PU-2080 Plus four-channel pump with degasser, two PL gel MIXED-E Mesopore (Polymer Laboratories) columns in series placed in a Jasco CO-2063 column oven thermostated at 30 °C, a Jasco RI 2031 Plus refractive index detector, and a Jasco UV-2077 Plus multi-channel ultraviolet (UV) 120 spectrometer; the ChromNav Jasco software was used for data acquisition and analysis. The solution analyzed were prepared by dissolving polymers in trichloromethane (5 mL/min) and filtered with an Agilent filter with a porosity of 2 μm. The eluent was trichloromethane at 1 mL/min flow rate.

2.8. Extraction, derivatization, and GC–MS analysis of leached fraction

After the ageing experiments, the leached fraction in the artificial seawater was extracted with *n*-hexane (3 × 600 μL), acidified with 2 mL of 6 M HCl, and extracted again with diethyl ether (3 × 900 μL). Aliquots of the hexane and diethyl ether extracts were mixed and spiked with 5 μL of C13 derivatization standard, evaporated under a gentle stream of nitrogen, and derivatized with 20 μL of BSTFA-TMCS at 60 °C for 30 min. After derivatization, the samples were redissolved in 150 μL of isooctane and spiked with 10 μL of hexadecane injection standard before GC–MS analysis. The extraction method was operated also for the artificial seawater (blank) to evaluate possible contamination. Analyses were performed with a 6890 N GC instrument coupled with a 5975 mass spectrometer (Agilent). The chromatographic separation was performed with an HP-5MS capillary column (stationary phase 5 % diphenyl-95 % dimethylpolysiloxane, 30 m × 250 μm × 0.25 μm, Agilent), equipped with a deactivated fused silica guard column (2 m × 320 μm, Agilent). The samples were injected in splitless mode at 280 °C, and the injection volume was 2 μL. Chromatographic conditions were: helium flow 1 mL/min, 80 °C for 2 min, 10 °C/min to 310 °C for 20 min. The mass spectrometer was operated in electronic ionization (EI) positive mode (70 eV, *m/z* 50–600). The temperature of the ion source was 230 °C and that of the quadrupole 150 °C. The data were analyzed with Agilent MassHunter Qualitative Analysis 10.0 and NIST 20 mass spectra library.

3. Results

3.1. PLA

3.1.1. Polymer ageing

PLA MPs were first characterized by Py-GC–MS and EGA-MS analyses to assess their chemical composition, including the possible presence of additives. Both thermoanalytical measurements were performed at all stages of artificial ageing to evaluate modifications in the composition and thermal properties of the materials. The pyrolytic profile of PLA 0 W (Fig. 1) was characterized mainly by the presence of 2,3-pentanedione (7.1 min), acrylic acid (8.3 min), and the two lactides in *meso*- and *DL*- form (13.2 min and 13.6 min, respectively). The pyrolytic profiles and pyrolysis products of PLA MPs are presented in Fig. S3 and Table S2 of the Supporting information. No differences were observed by comparing the pyrograms of PLA MPs before and after artificial ageing, both in the Solarbox and in the dark.

TGA and EGA-MS results were compared by assessing the 5 % weight loss, onset, offset, and signal maximum temperatures for each profile ($T_{5\%}$, T_{onset}, T_{offset}, T_{max}). The thermal parameters and degradation temperatures determined by EGA-MS and TGA are listed in Table 1. EGA-MS analysis of PLA 0 W MPs showed a thermal degradation peak from 332 °C to 387 °C, with T_{max} at 368 °C (Fig. 2). The T_{max} of PLA Dark 4 W was 367 °C, higher than PLA SB 4 W (366 °C). Due to use of similar water temperatures in both the artificial ageing experiments, this difference was probably due to more effective degradation in the Solarbox system compared to the thermal ageing alone. Upon accelerated ageing in Solarbox, the thermal degradation temperature was found to decrease at T_{max} = 358 °C after 2 weeks, but then to increase again at T_{max} = 366 °C after 4 weeks of irradiation, suggesting the occurrence of mass loss involving peeling off of the most highly degraded surface layer of the particles (Gil-Castell et al., 2016). The analysis of the average mass spectra of the EGA-MS profiles allowed us to identify the presence of ions with *m/z* 44, 56, 100, 128, 200, and 272, which are characteristic of the fragmentation of cyclic PLA oligomers with different chain lengths (De Falco et al., 2023; Marchelli et al., 2024). The DSC analysis highlighted a modification of the crystalline percentages of PLA MPs due to the accelerated weathering (Table S7). The TGA analysis results were in agreement with those obtained by EGA-MS, showing a decrease in T_{max} and $T_{5\%}$ for all aged MPs. This result can be related to the decrease in average molecular weight due to hydrolysis promoted by the heating in artificial seawater (Budin and Jaafar, 2022; Spiridon et al., 2015).

The hydrolysis processes occurring in PLA MPs were further confirmed by GPC analysis, in which a decrease in both number ($\bar{M}_n$) and weight ($\bar{M}_W$) average molecular weights was observed. The

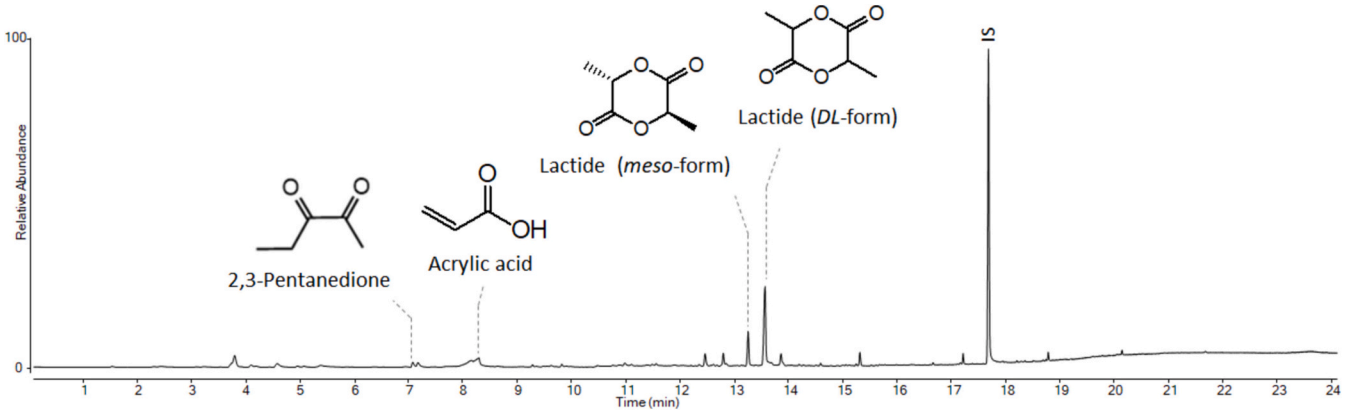

Fig. 1. Total ion chromatogram obtained from Py-GC–MS analysis of PLA 0W; IS is the internal standard anthracene-d_{10}.

Table 1
Thermal parameters from TGA and EGA-MS profiles of unaged (0W) and aged PLA MPs. The weight % of solid residue is also listed for TGA experiments. Control 4W: kept in the dark at 25 °C, for 4 weeks; Dark 4W: kept in the dark at 40 °C for 4 weeks; SB 1W: SolarBox ageing for 1 week; SB 2 W: SolarBox ageing for 2 weeks; SB 4 W: SolarBox ageing for 4 weeks.

Sample	TGA analysis			EGA-MS analysis		
	$T_{5\%}$ (°C)	T_{max} (°C)	Residue (%)	T_{onset} (°C)	T_{max} (°C)	T_{offset} (°C)
PLA 0W	333	376	1.2	332	368	387
PLA Control 4W	321	374	1.7	333	364	378
PLA Dark 4W	271	375	1.0	331	367	384
PLA SB 1W	331	375	2.1	332	366	380
PLA SB 2W	287	367	2.6	323	358	364
PLA SB 4W	302	372	1.4	323	366	385

complete results are presented in the Supporting information (Table S3). The process of PLA hydrolysis entails the diffusion of water within the amorphous region of the bioplastic, which results in the cleavage of ester bonds and the concomitant reduction in molecular weight. This phenomenon also leads to the release of lactic acid and its oligomers (Fig. S1a) (Lv et al., 2022).

ATR-FTIR was used to detect changes in the distribution of functional groups in the PLA MPs during ageing. The infrared spectra of the PLA MPs at the different ageing stages are shown in Fig. S4 in the Supporting information, and are in agreement with those available in the literature for this class of polymers (Meaurio et al., 2006). The comparison between the ATR-FTIR spectra obtained at different stages of artificial ageing showed an increase in the intensities of the peak at 920 cm^{-1} for PLA Dark 4 W, corresponding to the characteristic band of PLA α-crystalline phase. The increment of the peak at 920 cm^{-1} can be associated with possible modification of the crystalline phase of the polymer (Meaurio et al., 2006). No other significant differences were noticed between the spectra recorded before and after ageing.

The results obtained for the PLA MPs suggest that the polymer undergoes partial hydrolysis during artificial ageing in water, in agreement with what was highlighted by previous studies (Li et al., 2022), both in the UV-accelerated ageing and at 40 °C at the dark (Table S3).

3.1.2. *Leaching of degradation products*

As mentioned before, PLA in water can undergo acidic hydrolysis process (Lv et al., 2022), thus leading to the possible release of oligomers and monomers in the water (Fig. S1a). The analysis of the organic species leached from PLA during artificial ageing showed the presence of lactic acid and lactic acid dimer as the main polymer degradation compounds, along with 4-*tert*-butyl phenol (plasticizer), and butylated

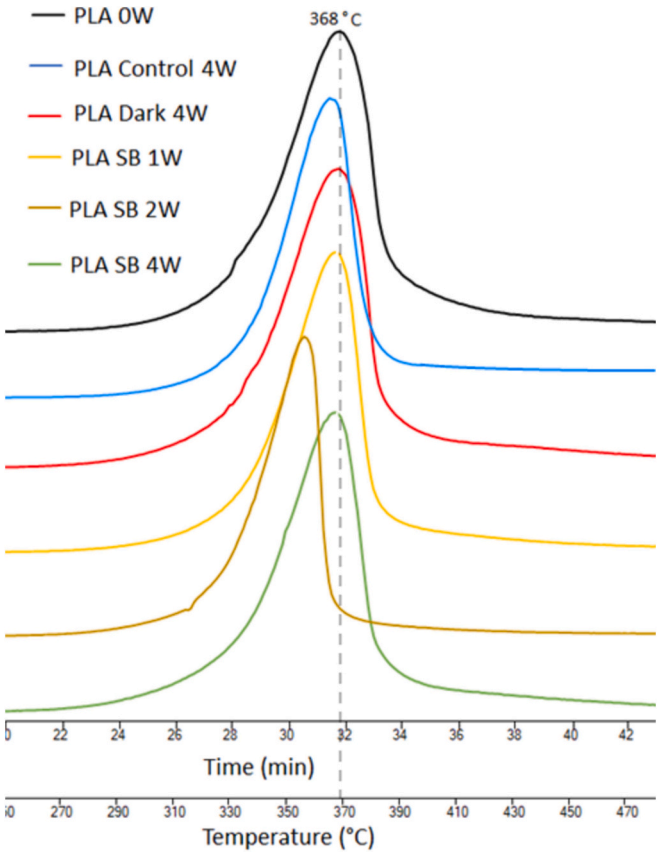

Fig. 2. Normalized EGA profiles of unaged (0W, black) and aged PLA MPs. Control 4W: kept in the dark at 25 °C for 4 weeks (blue); Dark 4W: kept in the dark at 40 °C for 4 weeks (red); SB 1W: SolarBox ageing for 1 week (yellow); SB 2W: SolarBox ageing for 2 weeks (brown); SB 4W: SolarBox ageing for 4 weeks (green).

hydroxytoluene (antioxidant), two polymer additives (Fig. 3a). The levels of these compounds were significantly higher compared to the blank levels (Fig. S2 in the Supporting Information) The presence of monomers and oligomers in the water, together with a decrease of the molecular weight of the polymer highlighted by the GPC analysis, confirmed the occurrence of hydrolysis. In detail, the concentrations of lactic acid and its dimer increased during the artificial ageing up to about 7.6 μg/g (Fig. 3b). On the other hand, the concentration of the leached oxidation products in water after 4 weeks of ageing in the dark was characterized by a concentration of lactic acid of 20 μg/g. The

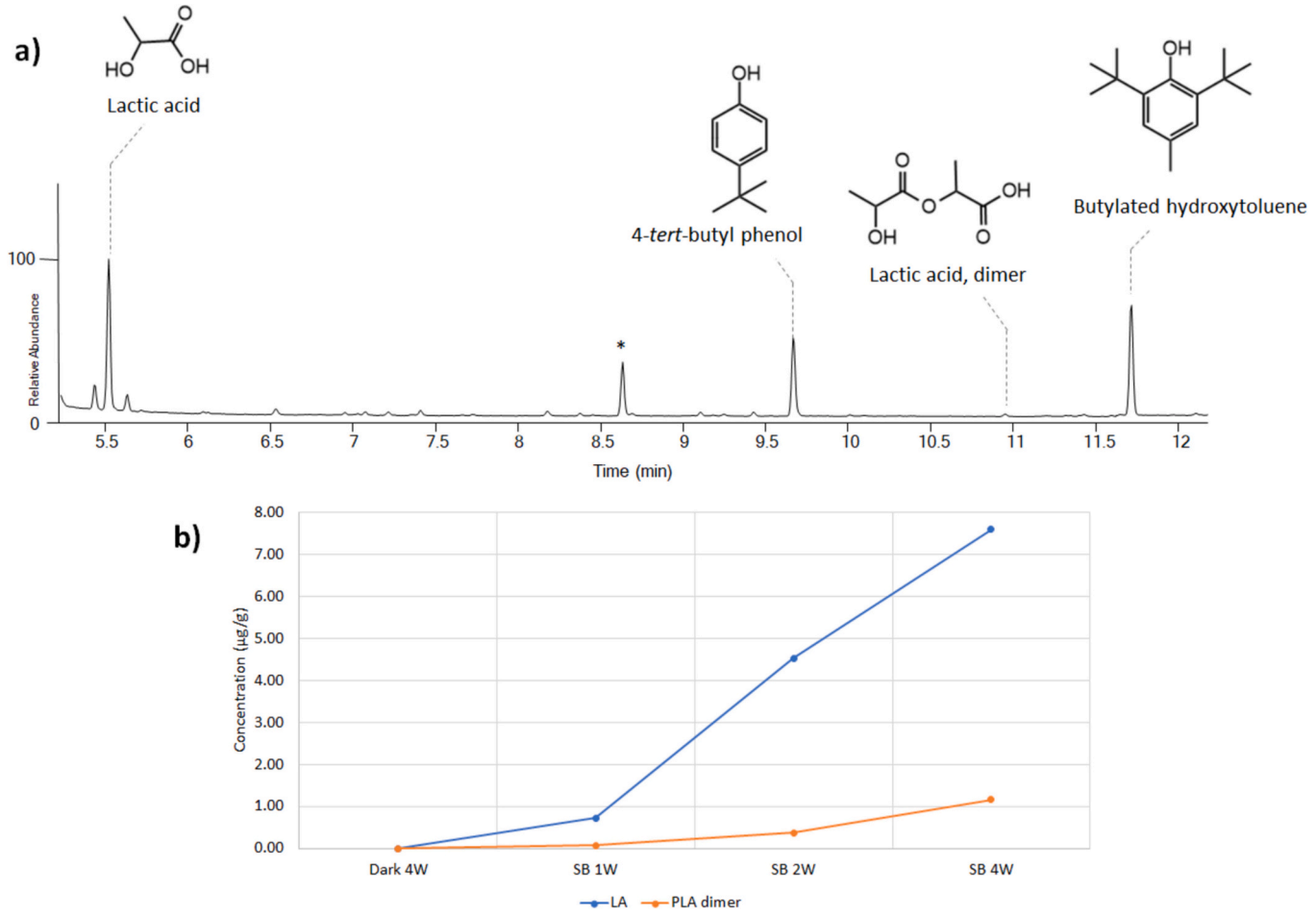

Fig. 3. a) Chromatogram obtained from the GC–MS analysis of the soluble fraction released by PLA SB 4W. b) Concentration of lactic acid (LA, blue profile) and PLA dimer (orange profile) in the soluble fraction released by PLA MPs. Control 4 W: kept in the dark at 25 °C, for 4 weeks; SB 1W: SolarBox ageing for 1 week; SB 2W: T = SolarBox ageing for 2 weeks; SB 4W: SolarBox ageing for 4 weeks. *: compound found in the blank.

presence of a significative concentration of this species in the water during thermal ageing at the dark suggested that the main degradation pathway of PLA can be ascribed to hydrolysis, while the effects of the UV-light were negligible or that the degradation products were partially degraded by the irradiation. Concerning the polymer additives, the concentrations of these species reached the highest relative abundances

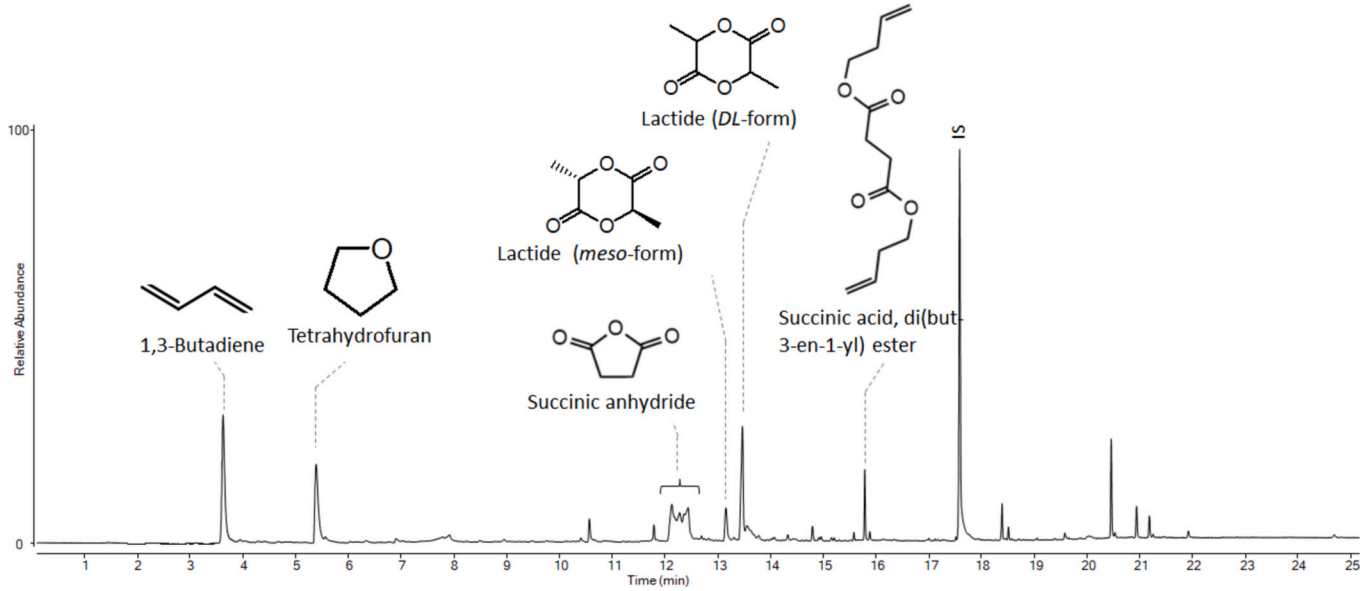

Fig. 4. Total ion chromatogram obtained from Py-GC–MS analysis of unaged MBi 0W MPs; IS is the internal standard anthracene-d_{10}.

after 2 weeks in SolarBox, suggesting a nearly exhaustive extraction from the PLA particles after 4 weeks of ageing.

3.2. Mater-Bi

The pyrolytic profile of the unaged Mater-Bi® microplastics (MBi MPs), displayed in Fig. 4, was characterized by the presence of the markers of PLA and poly(butylene succinate) (PBS): 2,3-pentanedione (6.9 min), acrylic acid (7.9 min) and lactide in *meso*- and *DL*- form (13.2 min and 13.5 min, respectively) deriving from PLA; succinic anhydride (12.0–12.5 min), and 1,6,11,16-tetraoxocycloicosan-2,5,12,15-tetraone (20.9 min) characteristic of the pyrolysis of PBS (De Falco et al., 2023; Shin et al., 2011). All the pyrolytic profiles and products of Mater-Bi® are reported in the Supporting information (Fig. S7 and Table S4). On the other hand, levoglucosane, the pyrolysis marker of starch (Shin et al., 2011), was not detected in the pyrolysis profile, even after derivatization with a trimethylsilyl (TMS) agent, suggesting that this Mater-Bi® sample contains little-to-no starch as a component of the polymer blend. Indeed, since its first introduction in the market in 1992, Mater-Bi® has progressively evolved into a brand name for a family of biodegradable polymer-based materials initially consisting of plasticized and/or blended starch derivatives, but evolved over time into a portfolio of products not always including starch as a component (Novamont, 2012).

3.2.1. Polymer ageing

By comparing the pyrograms of aged and unaged MBi MPs, the only significant modification of the pyrolysis profile was detected for the MBi Dark 4 W, which showed an increase in the relative intensities of tetrahydrofuran, and the *meso*- and *DL*- lactides.

EGA-MS analyses allowed us to obtain a more comprehensive view of the chemical composition of the MBi MPs (Fig. 5). The thermogram of the unaged MBi MPs showed the presence of two peaks belonging to PLA and PBS, respectively: the first peak from 255 °C to 329 °C, with T_{max} = 301 °C, was related to PLA, while the second peak from 350 °C to 420 °C, with T_{max} = 390 °C, was related to PBS. As in the case of Py-GC–MS, the presence of starch in the formulation could not be detected. For the samples aged in the SolarBox, there were no significant differences in the T_{max} of the PBS fraction. On the contrary, the T_{max} of PLA fraction decreased from 301 °C to 288 °C during the 4 weeks of artificial ageing. Mater-Bi® SB 4 W showed the highest decrease in the T_{max} of the PLA fraction. For both ageing conditions, the average mass spectrum assigned to the aged PLA fraction featured the presence of the ions with *m/z* 43, 45, 56, 100, and 144, characteristic of the two lactides and oligomers of PLA. For the PBS fraction, the average mass spectrum featured ions with *m/z* 71 and 101 from succinic acid, *m/z* 54 and 55 from butylene, and *m/z* 173 from the fragmentation of the 3-butenyl ester of succinic acid (De Falco et al., 2023).

TGA analyses were also performed on MBi MPs after ageing. As for the EGA-MS, the TGA profiles of MBi MPs showed the presence of two peaks corresponding to the highest degradation rate of the main degradation steps occurring between 280 and 330 °C (T_{max} 307 °C) and 375–430 °C (T_{max} 399 °C), related to the PLA and PBS fractions of the material, respectively (Georgousopoulou et al., 2016). Interestingly, the thermal degradation temperature of PLA in MBi MPs was significantly lower than that observed in PLA MPs. A possible explanation for such difference is the presence of inorganic fillers, which are commonly used in Mater-Bi® formulations. Some inorganics are known to act as catalysts during pyrolysis, favouring the thermal degradation of oxygenated polymers (Ishimura et al., 2021). This hypothesis is consistent with the

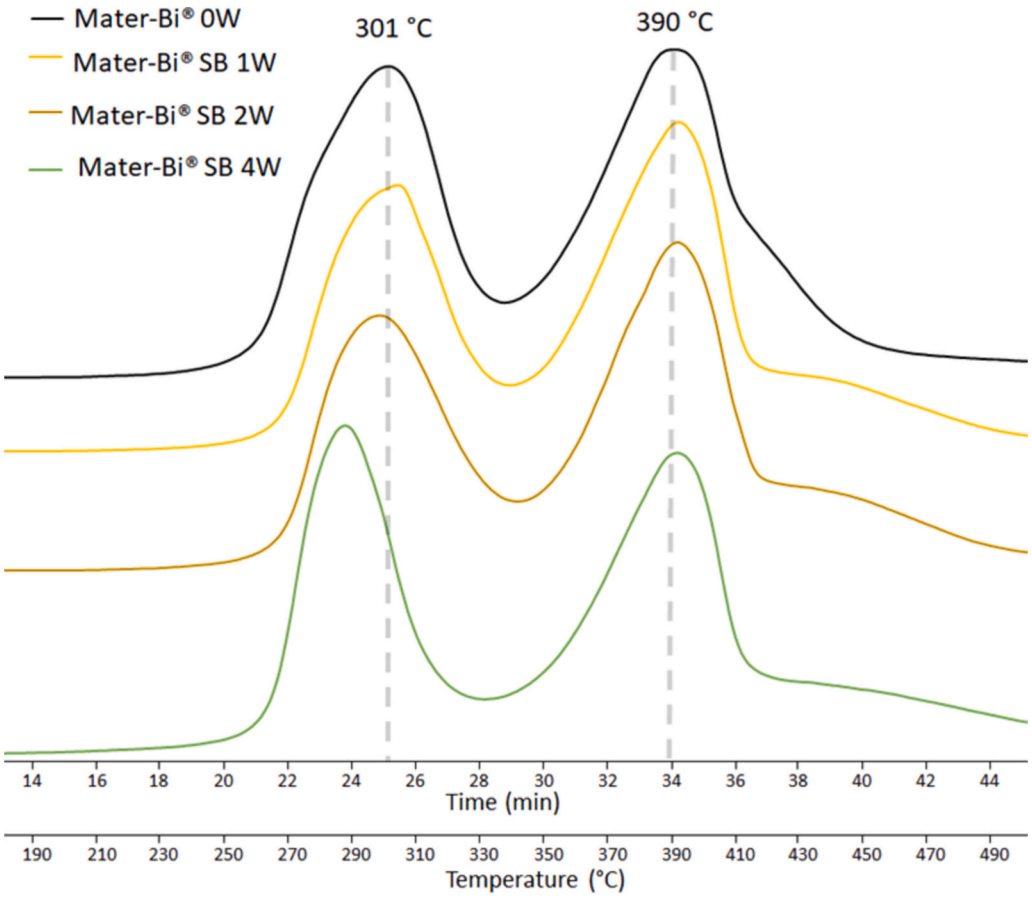

Fig. 5. Normalized EGA-MS profiles of unaged (0W, black) and aged in SolarBox MBi MPs. SB 1W = SolarBox ageing for 1 week (yellow); SB 2W: SolarBox ageing for 2 weeks (brown); SB 4W: SolarBox ageing for 4 weeks (green).

high percentage of solid residue (24 %) obtained after TGA of MBi MPs. On the other hand, the different crystallinity of PLA MPs and the PLA fraction in MBi MPs (De Falco et al., 2023) can hardly be associated with the different thermal stability of the two polymers, since DSC analyses showed a higher percentage of crystallinity for the PLA in Mater-Bi® than in PLA MPs, which would result in a higher rather than lower stability of the former (Table S7). The TGA profiles of aged samples were in agreement with EGA-MS profiles, showing a reduction of the thermal degradation temperature mainly ascribable to the PLA fraction, with a higher variation due to the ageing in SolarBox. X-ray fluorescence spectroscopy analysis performed on the residues showed the presence of calcium, titanium, and iron (data available in (Marchelli et al., 2024)). Titanium was probably in the form of TiO_2, used as a white pigment, calcium could be related to the presence of chalk (Ca_2SO_4) while iron was attributable to catalyst residues used in the production of the bioplastic. The complete list of thermal degradation temperatures obtained for both TGA and EGA-MS is reported in Table 2.

As for PLA, the DSC analyses performed on the polymer at different stages of ageing showed a negligible modification of the crystalline domain of the PLA fraction in Mater-Bi®, while no modification could be detected for the PBS fraction. The results are available in the Supporting information (Section 3.2.1).

The ATR-FTIR spectra of MBi MPs (Fig. S8 in the Supporting information) showed peaks at 1756 and 1714 cm^{-1} from the carbonyl stretching vibrations of the ester group of both PLA and PBS, respectively, in the range 1450–1310 cm^{-1} from symmetrical and asymmetrical bending vibrations of -CH_3 and -CH_2 (Barletta and Pizzi, 2021), and at 954 and 919 cm^{-1} due to skeletal vibrations of the C—O bond of PLA (Meaurio et al., 2006). The peaks at 3676, 1010, and 690 cm^{-1} correspond to the vibrational modes of O—H stretching, Si—O stretching, and Si-O-Si stretching, respectively, indicating the presence of talc ($Mg_3Si_4O_{10}(OH)_2$) in the formulation of Mater-Bi® as inorganic filler (Bracciale et al., 2024). No significant differences were noticed between the spectra recorded before and after ageing. Similar to what observed for PLA, the GPC analysis highlighted a decreasing in the $\bar{M}_n$ and $\bar{M}_W$ of the polymer around 20 % (Table S5), confirming the occurrence of the hydrolysis.

3.2.2. Leaching of degradation products

As mentioned for PLA, also MBi could undergo hydrolysis leading to the release in water of monomers and oligomers from both the PLA and PBS fractions (Kanemura et al., 2012) (Fig. S1a, b). The GC–MS analysis of the soluble fraction released by aged MBi MPs showed the presence of monomers and oligomers from both PLA and PBS (Fig. 6a). In detail, lactic acid and its oligomers (up to the tetramer), 1,4-butanediol, succinic acid, and PBS oligomers variously terminated by 1,4-butanediol or succinic acid co-units could be identified. All these hydrolysis products, together with a decrease in the molecular weight of the polymer highlighted by the GPC analysis, are in agreement with a hydrolysis process involved during the ageing process.

In the samples after 4 weeks of ageing in the Solarbox, it was also possible to detect monocarboxylic acids such as levulinic acid, 3-hydroxypropionic acid, 2-oxoacetic acid, 4-oxohexanoic acid, 5-oxohexanoic acid, 7-oxononanoic acid, 3-hydroxyoctanoic acid, 7-hydroxynonanoic acid, 9-hydroxydecanoic acid, 2-hydroxyheptanoic acid and 11-hydroxyundecanoic acid. In addition, the extracts leachates showed the presence of dicarboxylic acids such as pentanedioic acid, hexanedioic acid, suberic acid, azelaic acid, and sebacic acid as the most abundant ones. These compounds probably derive from hydrolysis and free radical reactions occurring in the polymer chain or the additives present in the MPs, fully extracted by the synthetic seawater. Semi-quantitative analysis was performed to evaluate the trends in the leached degradation products concentration over time. For this purpose, the intensity of the peaks of the chemical species from Mater-Bi® PLA (PLA oligomers) and PBS fractions (dicarboxylic acids) were related to the peaks of lactic acid and azelaic acid, respectively.

The concentrations of the different classes of compounds are shown in Fig. 6b. The analysis showed an increase of all chemical species that was directly proportional to the irradiation time. Specifically, the concentration of degradation products resulting from PLA (ΣPLA oligomers, yellow profile) was generally lower compared to the one from PBS degradation products (ΣPBS oligomers, light blue profile). As for the hydrolysis products, the analysis highlighted a gradual increase in the concentration of dicarboxylic acids derived from the oxidative radical reactions. Azelaic acid is shown in Fig. 6b as representative of this class of compounds.

The concentration of lactic acid leached in water from Mater-Bi® Dark 4 W was about four times higher than Mater-Bi® SB 4 W, while the oxidized species such as the dicarboxylic acids were almost absent. These results suggest that hydrolysis is indeed the main degradation pathway of Mater-Bi®, but that the effects of UV irradiation may also have influenced the ageing process.

3.3. Recycled polyethylene terephthalate (r-PET)

3.3.1. Polymer degradation

The main pyrolytic products of r-PET 0 W detected by Py-GC–MS and EGA-MS (Fig. 7) analysis were: vinyl benzoate (13.2 min), benzoic acid (13.6 min), divinyl terephthalate (16.1 min), ethylene dibenzoate (19.1 min), 2-(benzoyloxy)ethyl vinyl terephthalate (21.1 min), ethan-1,2-diyl divinyl diterephthalate (24.1 min). A similar pool of pyrolysis products was observed for virgin PET (Shin et al., 2011). The pyrolytic profiles and a complete list of the pyrolysis products are available in the Supporting information (Fig. S11 and Table S6).

The Py-GC–MS profile of r-PET Dark 4 W showed an increase in the relative abundance of vinyl benzoate, benzoic acid, biphenyl, ethylene dibenzoate and 2-(benzoyloxy)ethyl vinyl terephthalate, and a decrease in ethan-1,2-diyl-divinyl terephthalate. No differences between the pyrograms of r-PET 0 W and SB 4 W MPs were noted.

The EGA-MS profile of r-PET 0 W showed a single thermal degradation peak from 383 °C to 510 °C, with T_{max} at 441 °C. The T_{max} of r-PET SB 4 W decreased from 441 °C to 437 °C, suggesting initial photo-induced degradation. The average mass spectrum of r-PET samples presented the characteristic ion peaks with m/z 44, 77, 105, 122, 149, 297 from the thermal degradation products of PET: vinyl benzoate, benzoic acid, divinyl terephthalate, and 2-(benzoyloxy) ethyl vinyl terephthalate (Biale et al., 2021). The TGA results agree with those obtained by EGA-MS. The complete list of thermal degradation

Table 2
Characteristic values of TGA thermograms, and degradation temperatures (T_{onset}, T_{offset}, T_{max}) obtained from the EGA profiles of Mater-Bi® MPs unaged (0W) and aged in SolarBox: SB 1W = 1 week; SB 2W = 2 weeks; SB 4W = 4 weeks.

Sample	TGA analysis					EGA-MS analysis					
	PLA fraction		PBS fraction		Residue (%)	PLA fraction			PBS fraction		
	$T_{5\%}$ (°C)	T_{max} (°C)	$T_{5\%}$ (°C)	T_{max} (°C)		T_{onset} (°C)	T_{max} (°C)	T_{offset} (°C)	T_{onset} (°C)	T_{max} (°C)	T_{offset} (°C)
Mater-Bi® 0W	280	307	375	399	24	255	301	329	350	390	420
Mater-Bi® SB 1W	285	308	380	405	24	267	301	332	350	390	416
Mater-Bi® SB 2W	285	304	378	404	24	268	298	335	352	391	419
Mater-Bi® SB 4W	280	298	375	405	24	265	288	316	350	391	416

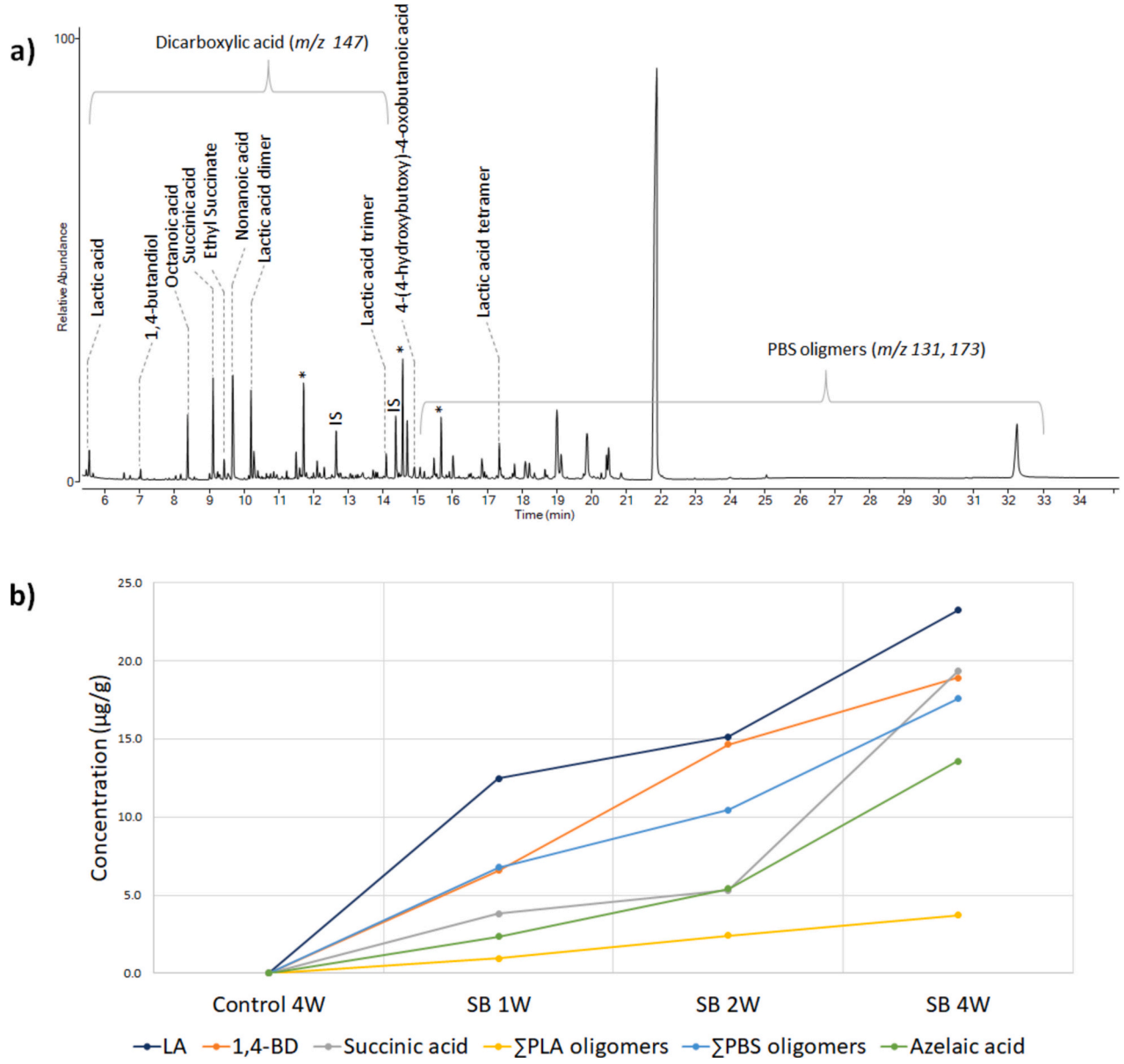

Fig. 6. a) Chromatogram obtained from the GC–MS analysis of the soluble fraction released by Mater-Bi® MPs SB 4W; b) concentration of lactic acid (LA, blue profile), 1,4-butanediol (1,4-BD, orange profile), succinic acid (grey profile), PLA oligomers (ΣPLA oligomers, yellow profile), PBS oligomers (ΣPBS oligomers, light blue profile), and azelaic acid (green profile) in the soluble fraction released by Mater-Bi® MPs after ageing in SolarBox. Control 4W: kept in the dark at 25 °C, for 4 weeks; SB 1W: SolarBox ageing for 1 week; SB 2W: SolarBox ageing for 2 weeks; SB 4W: SolarBox ageing for 4 weeks. *: compounds found in the blank.

temperatures obtained from EGA-MS and TGA is given in Table 3. DSC analysis did not show any modification in the thermal properties of the r-PET-MPs during the ageing. The full results obtained with the DSC analysis on the r-PET MPs are available in the Supporting information (Section 3.3.1).

The ATR-FTIR spectrum of r-PET (Fig. S12) did not show any peculiarity with respect to that of virgin PET, with the characteristic carbonyl absorption at 1712 cm^{-1} (Chen et al., 2012), two broad and intense C-O-C(=O) stretching absorptions bands of the ester groups at 1240 and 1091 cm^{-1}.The spectra were also characterized by the presence of two narrow peaks at 1577 and 1505 cm^{-1} derived from the stretching modes of aromatic carbons, and two intense peaks at 872 and 722 cm^{-1} from aromatic C—H and carbon ring deformation modes. No differences were observed in the spectra of the aged samples. As for the infrared spectroscopy, the GPC analysis did not show a significant result.

3.3.2. *Leaching of degradation products*

The GC–MS profile of the r-PET extract after 4 weeks of artificial ageing in Solarbox (Fig. 8a) showed peaks ascribable to terephthalic acid, 4-((2-hydroxyethoxy)carbonyl)benzoic acid (MHET), and bis(2-hydroxyethyl) terephthalate (BHET). All these species can be associated with the hydrolysis of r-PET (Fig. S1c). The same degradation products were detected in the seawater-soluble fraction obtained from the degradation of r-PET Dark 4 W.

The concentrations of the detected species increased as the UV irradiation time increased, as shown in Fig. 8b. At the end of the 4 weeks of artificial ageing in SolarBox, the concentration of the terephthalic acid was around 16 µg/g, while the total concentration of oligomers was 7.5 µg/g. The concentration of these species after the artificial ageing at the dark showed lower values with a concentration of the acid of 5.0 µg/g, and a concentration of the oligomers lower than 1.0 µg/g, suggesting a partial effect of the UV-light irradiation on the MPs during the ageing.

As for what was highlighted for PLA and Mater-Bi®, the analysis of

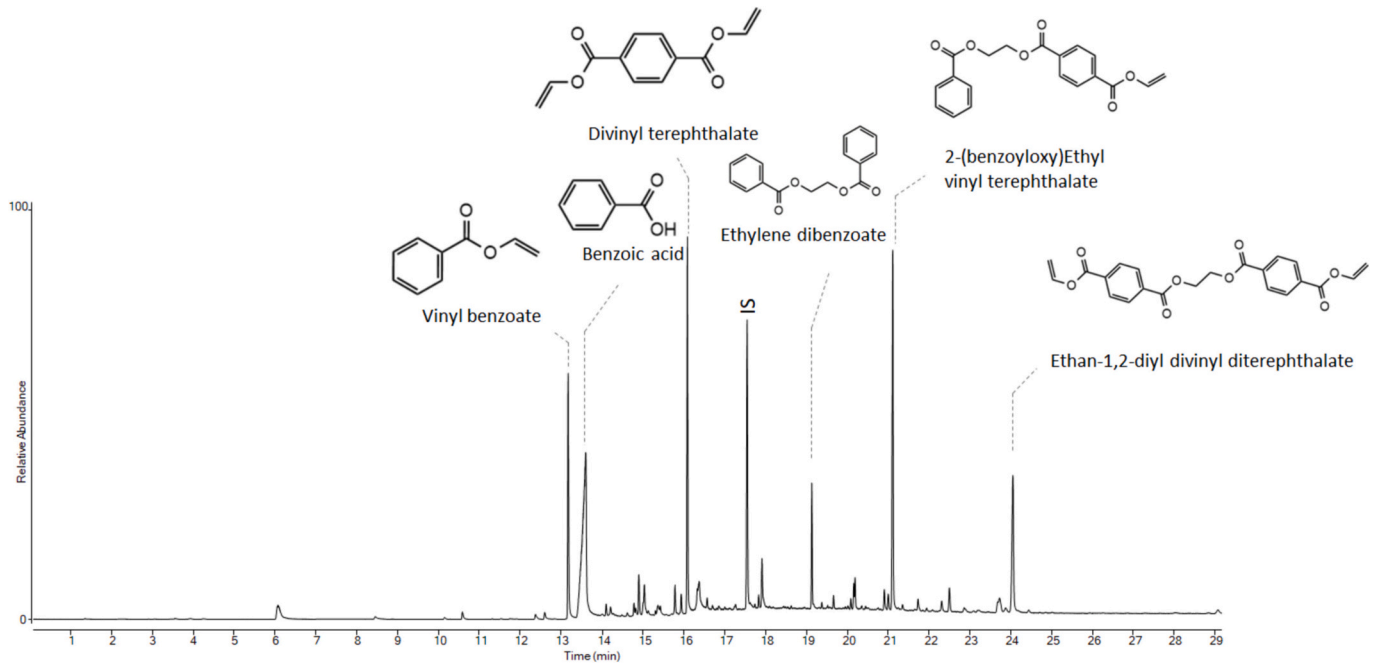

Fig. 7. Total ion chromatogram obtained from Py-GC–MS analysis of r-PET 0W; IS is the internal standard, anthracene-d_{10}.

Table 3
Characteristic values of TGA thermograms, and degradation temperatures (T_{onset}, T_{offset}, T_{max}) obtained from the EGA profiles of r-PET MPs unaged (0W) and aged. SB 4W: SolarBox ageing for 4 weeks.

Sample	TGA analysis			EGA-MS analysis		
	$T_{5\%}$ (°C)	T_{max} (°C)	Residue (%)	T_{onset} (°C)	T_{max} (°C)	T_{offest} (°C)
r-PET 0W	408	447	11.1	383	441	510
r-PET SB 4W	404	434	17.4	399	437	495

the water-soluble fraction suggested the occurrence of hydrolysis, a common degradation pathway of polyester polymers. Since the bulk and superficial analysis performed on r-PET were not conclusive, we can hypothesize that the hydrolysis occurred on the superficial layer of the MPs, and that the most degraded layer of the MPs was peeled off during the ageing.

4. Discussion

The multianalytical approach applied to PLA and MBi MPs showed that during artificial ageing, both in the dark and in the Solarbox system at 40 °C, the polymers underwent hydrolysis processes (highlighted by GPC and GC–MS analyses) and changed their thermal properties (through TGA, EGA-MS, and DSC analyses).

The GC–MS analysis results obtained for the water extracts of PLA MPs are consistent with these degradation processes, showing the leaching of lactic acid and its oligomers from the polymer with concentrations up to 20 μg/g. Similarly, the analysis of the water extracts obtained from the artificial ageing of MBi MPs showed the presence of monomers involved in the production of this material. Moreover, the analysis also highlighted the presence of a series of mono- and dicarboxylic acids with different functional groups bonded on the alkyl chain and different chain-lengths deriving from possible oxidative radical reactions involved in the photo-oxidative ageing of the biopolymer. The monomers and oligomers of lactic acid, 1,4-butanediol, and succinic acid resulting from PLA and PBS released in the seawater were quantified with concentrations up to 23 μg/g.

Although none of the monomers released in the seawater due to the hydrolysis processes from PLA and Mater-Bi® can be considered harmful, the possible effects of the oligomers are still unknown. As oligomers and ageing oxidated by-products are released into seawater, they may become bioavailable; therefore, further studies are needed to assess the potential harmfulness and toxicity of these species in water environments.

The artificial ageing in seawater performed on r-PET MPs induced the leaching of monomers and linear oligomers. In particular, the analysis highlighted the formation of phthalate derivatives that are known to be harmful to the human reproductive system (He et al., 2015).

For PET oligomers, data on the harmfulness of these compounds could not be found in the scientific literature, which prevents any assessment of their potential toxicity and environmental effects.

All the analyses of the leachates released in seawater from the aged MPs, showed the presence of additives as 4-*tert*-butylphenol and butylated hydroxytoluene, a plasticizer and an antioxidant, respectively, at different concentrations depending on the ageing conditions. 4-*tert*-Butylphenol is considered a noxious aquatic pollutant for its chronic toxicity, estrogenic activity, and high persistence in the environment (Wang et al., 2023). Butylated hydroxytoluene is one of the most widely used antioxidants, leading to global attention due to its toxicity in aquatic environments (Achar et al., 2020).

5. Conclusions

PLA, Mater-Bi®, and recycled polymers are used and considered as alternatives to more commonly used traditional polymers, however there is still lack of information on their behavior in the long term especially when dispersed in open environments.

To evaluate their possible behaviors in the environment, the assessment of the main structural changes induced by different types of ageing was complemented by the characterization of the main species leached in water, such as small oligomers, molecular degradation products, and additives.

Hydrolytic chain scission was confirmed to be the main degradation pathway of PLA; on the other hand, photo-oxidative processes did not seem to contribute significantly to the overall degradation pattern

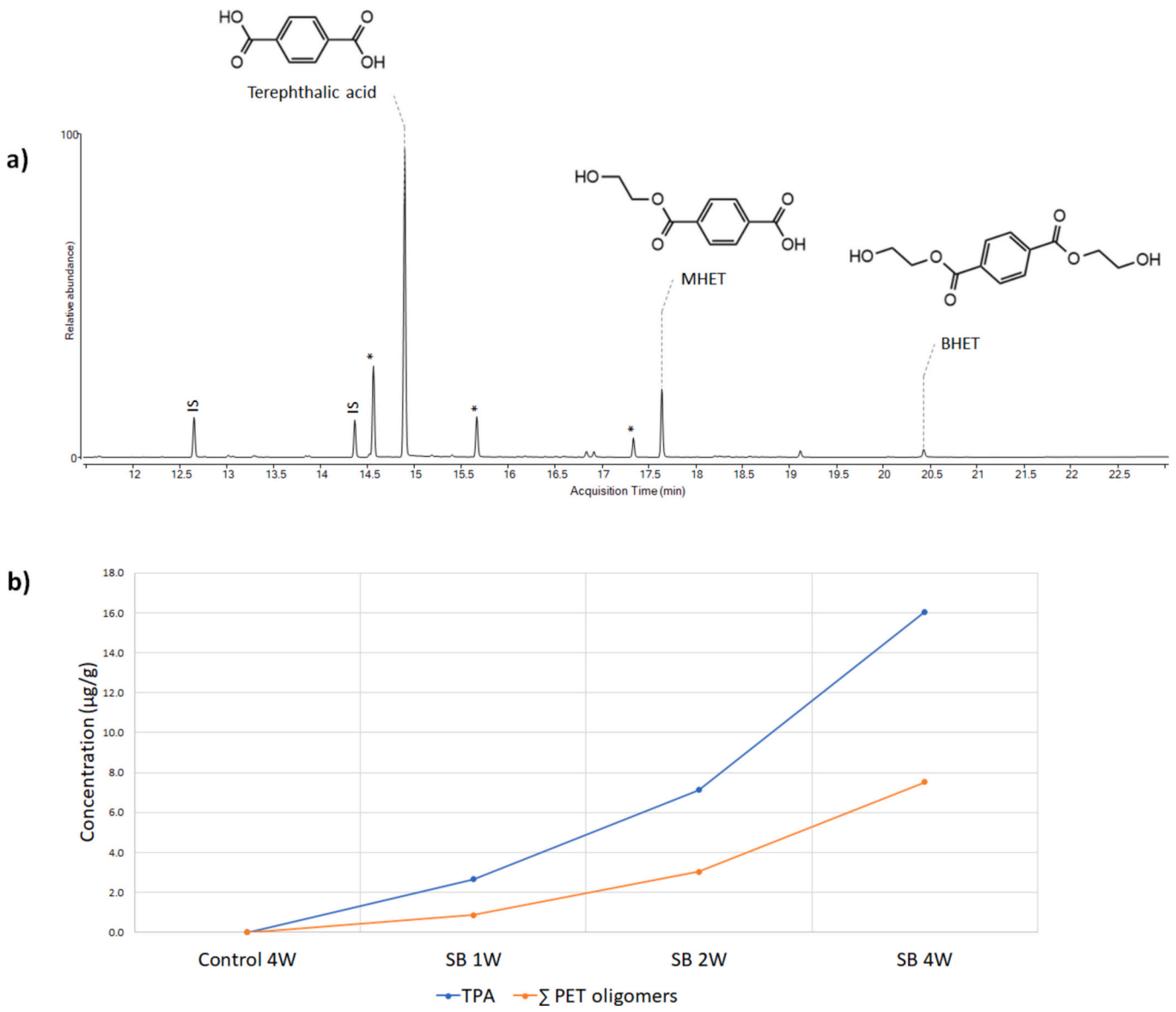

Fig. 8. a) Chromatogram obtained from the GC–MS analysis of the soluble fraction released by r-PET SB 4W; b) concentration of terephthalic acid (TPA, light blue profile) and PET oligomers (orange profile) in the soluble fraction released by r-PET MPs after ageing in SolarBox. Control 4W: kept in the dark at 25 °C for 4 weeks; SB 1W: SolarBox ageing for 1 week; SB 2W: SolarBox ageing for 2 weeks; SB 4W: SolarBox ageing for 4 weeks. MHET: 4-((2-hydroxyethoxy)carbonyl)benzoic acid; BHET: bis(2-hydroxyethyl) terephthalate. *: compounds found in the blank.

within the timeframe of the adopted ageing conditions. The GC–MS analysis of the leachates highlighted the presence of lactic acid and its dimers, along with some polymer additives 4-*tert*-butyl phenol, and butylated hydroxytoluene, known to be toxic in water environments.

Mater-Bi®, a blend of PLA and PBS, showed degradation processes analogous to those for PLA, with a prevalence of hydrolysis mechanisms. As for degradation products released in water, the analysis highlighted the presence of oligomers of both PLA and PBS, along with different oxidation products such as mono- and dicarboxylic acids, with an increase in the concentration of these species with ageing time with UV irradiation. The presence of these species in water raises concerns about these biodegradable materials if not correctly disposed of and released in water environments since there are no studies on their toxicity in the literature.

The chemical composition and r-PET thermal features upon artificial ageing did not differ from the ones associated to the non-recycled polymer, with PET oligomers and terephthalic acid as the most abundant species detected in the water-soluble fraction.

While this was a preliminary study, it did allow us to evaluate the behavior of these biodegradable and sustainable materials under different degradation conditions, and to characterize the different classes of compounds released in water. The obtained results could contribute to raise awareness about the urgent necessity to comprehensively evaluate the composition and possible toxicity and effects of these species released in the environment.

CRediT authorship contribution statement

Leonardo Barlucchi: Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **Greta Biale:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **Jacopo La Nasa:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Marco Mattonai:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Stefano Pezzini:** Writing – review & editing,

Investigation, Formal analysis, Data curation. **Andrea Corti:** Methodology, Conceptualization. **Valter Castelvetro:** Writing – review & editing, Supervision, Data curation, Conceptualization. **Francesca Modugno:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.176832.

Data availability

Data will be made available on request.

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