Polymer Degradation and Stability 241 (2025) 111539

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.journals.elsevier.com/polymer-degradation-and-stability

The fate of biodegradable polyesters in the marine environment

Thomas Viel [a,b,c,†], Immacolata Liotta [a,d,†], Roberto Avolio [a], Maria Emanuela Errico [a], Loredana Manfra [b,e], Giovanni Libralato [b,c], Valerio Zupo [f,‡], Maria Costantini [b,‡], Mariacristina Cocca [a,*]

[a] Institute of Polymers, Composites and Biomaterials, National Research Council of Italy, Via Campi Flegrei 34, 80078 Pozzuoli, Napoli, Italy
[b] Department of Ecosustainable Marine Biotechnology, Stazione Zoologica Anton Dohrn, Villa Comunale, 80121 Napoli, Italy
[c] Department of Biology, University of Naples Federico II, Via Cinthia 26, 80126 Napoli, Italy
[d] Department of Chemical and Materials Engineering and Industrial Production, University of Naples Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy
[e] Institute for Environmental Protection and Research (ISPRA), Via Vitaliano Brancati 48, 00144 Rome, Italy
[f] Department of Ecosustainable Marine Biotechnology, Stazione Zoologica Anton Dohrn, Ischia Marine Centre, Via Buonocore, Ischia (NA) Italy

ARTICLE INFO

Keywords:
Biodegradable polymers
Degradation
Fragmentation
Marine environment
Plastic pollution

ABSTRACT

The fate of polymeric materials depends on the chemical structure of the polymer and on environmental conditions. To mitigate environmental issues associated with plastic mismanagement at the end of life, great attention has been addressed to compostable and biodegradable polymers. Some of these polymers, even if biodegradable, are found in the form of microplastics in the environment. In this work, the degradation behavior of five biodegradable polymers, poly(butylene succinate), PBS, poly(butylene succinate-*co*-butylene adipate), PBSA, poly(ε-caprolactone), PCL, polyhydroxy butyrate, PHB, and poly (lactic acid), PLA, was evaluated using *ad hoc* set mesocosms simulating their presence in marine environment at different water depths for 363 days. Higher mass loss during aging was recorded for PCL and PHB. Cracks, grooves and holes were detected on all the samples at the end of the test. Exposure into seawater induces hydrolytic degradation of the polyesters confirmed by Fourier transform infrared and NMR spectroscopies. The identification of the polymer phase in the sand suggests the occurrence of fragmentation phenomena of some samples, particularly PCL, during ageing. Remarkably, not all biodegradable polyesters are biodegraded in the sea, thus their mismanagement at the end of life is likely to induce progressive accumulation in the environment.

1. Introduction

Plastics are widely used in almost all major manufacturing sectors due to their versatility and good performance. In fact, properties such as low cost, lightness, stability and good mechanical performance have made these materials unique and irreplaceable [1]. Global plastic production has grown rapidly over the past two decades up to ca. 400 million tons (Mt) per year in 2023, 8.4 % of which derive from recycled plastics and 0.7 % from bio-based plastics [2]. Due to the mismanagement of plastic waste, part of them ends up in the environment. Consequently, between 10 and 20 Mt of plastics end up in the oceans each year and it was estimated [3] that the amount of plastics might exceed the world fish stocks by 2050 [4]. As a consequence, plastic waste is presently wide diffused on land and in aquatic environments, impacting inland and coastal ecosystems [5,6]. Indeed, they are a source of secondary microplastics, as larger plastic wastes are broken down and fragmented through a combination of photochemical, biological, mechanical and chemical degradation, depending on the environmental conditions to which they are exposed [7,8]. In fact, exposure of plastic waste to various environmental factors, such as UV radiation, wind, waves, sea water and bacteria, can lead to cracking, surface erosion, abrasion and disintegration into mesoplastics (approximately 5–20 mm), large microplastics (~1–5 mm), small microplastics (~20–999 μm) and nanoplastics (<1 μm) [9,10]. These particles appear to be ubiquitous and have a great impact on the environment [11]. Consequently, their ingestion by marine organisms can take place and can cause damage to the stomach and negatively affect digestion. Moreover, through the passage from one trophic level to the next, microplastics can

* Corresponding author.
E-mail address: mariacristina.cocca@cnr.it (M. Cocca).
† These authors share first authorship.
‡ These authors contributed equally to this work.

https://doi.org/10.1016/j.polymdegradstab.2025.111539
Received 11 April 2025; Received in revised form 6 July 2025; Accepted 8 July 2025
Available online 9 July 2025

cause contamination of the food chain [11–14]. Microplastics have already been found in various human foods, beverages and in drinking water [15]. In response to this problem, EU strategies have been set to reduce the release of plastics into the oceans, such as promoting recycling, reuse of plastics and the use of biodegradable plastics [16]. Biodegradable plastics include bio-based plastics synthesized from renewable resources, such as poly (lactic acid), PLA, and poly(hydroxyalkanoate)s, PHA, or plastics made from fossil resources, including poly (ε-caprolactone), PCL, or both as in the case of some aliphatic polyesters, such as poly(butylene succinate), PBS, and poly(butylene succinate--*co*-butylene adipate), PBSA. Degradation mechanisms of these polymers depend on the chemical structure of the polymer backbone and environmental conditions, they could undergo hydrolysis, oxidation or follow other degradation pathways. These mechanisms can lead to the formation of polar oligomers, which are finally mineralized by microorganisms forming carbon dioxide, methane, water and biomass [17,18]. In recent years, a growing attention has been addressed to compostable and biodegradable polymers in order to reduce plastic pollution. In fact, the use of biodegradable plastics instead of conventional ones, in organic waste and agriculture, is likely to reduce the effects associated with plastic usage and improper waste disposal [19]. Given the increased usage of biodegradable polymers in various items and considering their potential release into the environment, it is necessary to understand their fate under a range of environmental conditions. Understanding their degradation during their experimental aging tests in simulating marine environments could support their applicability to reduce marine plastic pollution in case these materials end-up in the marine environment unintentionally. Several studies have examined degradation or toxicity behavior of different biodegradable polymers, focusing mainly on terrestrial ecosystems where in addition to an apparent degradation of the polymeric films, during burial tests, the release of microplastics was also reported [20]. In addition, the identification of biodegradation occurring at the interfaces during soil burial tests suggests that biodegradable plastics do not generate persistent microplastics, because as erosion increases the surface area, this in turn increases the rate of biodegradation [21].

The study of the biodegradation of biodegradable plastics in marine environments has increased during the last 10 years since some of these polymers have been found in the form of microplastics in various marine environments, such as fragments of PCL found in the Mediterranean Sea [22].

Different studies on degradation of biodegradable polymer in marine environment at real, mesocosm or lab scale have been conducted to evaluate their fate, and to develop standard test methods to support the determination of degradation of polymers in marine environments. Several paper reports the identification and the isolation of microbial communities involved in the biodegradation of biodegradable polymers in seawater [16,23,24]. Microbial decomposition study of PHA, PLA and polysaccharide esters performed exposing polymeric films at diverse deep-sea sites indicate that some biodegradable plastics can be degraded by the action of microorganisms on the deep-sea floor, but with much less efficiency than in coastal area [25]. Moreover, the effects of PLA and PP fragments obtained by commercial products and their leachates on seven marine species showed toxic effects on some consumer species, especially on the later life stages of *A. franciscana*, but no toxicity for decomposers or primary producers [26]. Degradation of plastic bags was followed in different simulated marine zones such as supralittoral, eulittoral, sublittoral benthic, deep-sea benthic, pelagic, buried in the sediments. Results highlighted total disintegration of Mater-Bi in <9 months when buried in wet sand, and a rate of 69 % of biodegradation when located at the sediment/sea water interface [27]. Feijoo et al. (2025) investigated biotic and abiotic degradation of conventional (Polyamide PA, Polypropylene PP and Polyethylene PE) and biodegradable polymers (PLA and PHBV) subjected to a real-scale marine environment for one year, revealing that only PHBV showed significant biodegradation, while PLA and conventional polymers (PP, PA, PE) remained unaltered [28]. The findings highlighted the need for careful interpretation of marine biodegradability labels and the potential influence of specific environmental factors on material degradation capabilities. The degradation behavior of some biodegradable polyesters buried in sandy beaches indicated that some of the analyzed materials might remain as beach litter if released into the environment as a consequence of an uncontrolled disposal [29]. A slowly biodegradation rate of different biodegradable polyesters exposed to marine environment along the coast of Korea was evaluated, with the following trend poly(butylene succinate-*co*-carbonate) > poly(butylene adipate-*co*-furanoate) ≫ poly(butylene succinate) > poly(butylene adipate-*co*-terephthalate) ≫ poly(L-lactic acid) [30]. Recently gaps of the standard test methods developed to determine the biodegradation of polymers in marine habitats, such as ISO 18830, ISO 19679, ISO 22404, ASTM D5988, and the ISO 23977 [31–35] have been reported as well as suggestion for the refinement of the proposed test method to improve reliability and reproducibility [36]. In such scenario, the degradation behavior of five biodegradable polymers PBS, PBSA, PCL, polyhydroxy butyrate, PHB and PLA was investigated in *ad hoc* mesocosms, mimiking the conditions in which the polymers can be found in the marine environment at different depths of the water column with the aim to effectively address the potential marine pollution risks posed by biodegradable polymers. The fate of the selected biodegradable polyesters in the marine environment was assessed by evaluating the physico-chemical and morphological properties of the tested materials.

2. Materials and methods

2.1. Materials

PBS (grade FZ91PM, Mn of 48·103 g/mol and Mw 150·103 g/mol [37]) and PBSA (grade FD92PM, Mn 54·103 g/mol and Mw 134·103 g/mol [38]), were kindly supplied by PTT MCC Biochem Company Limited, Bangkok, Thailand; PCL (CAPA 6506, Mw = 50,000 g/mol), was purchased from Solvay; PHB, (Biomer T19, Mw = 223·103 g/mol, Mw/Mn = 1.23), was supplied by Biomer (Germany) and PLA (Ingeo 4032D; <2 mol % of D stereoisomer, Mw = 183·103 g/mol), was purchased from Nature Works. All the polymers were dried in oven at 40 °C under vacuum for 24 h before usage.

2.2. Film preparations

Films were obtained by compression molding using a Dr Collin P200E heating press (Ebersberg, Germany). The materials were heated at specified temperature (120 °C PBS and PBSA, 100 °C PCL, 180 °C PHB and 175 °C PLA) and subjected to a pressure gradient. Initially, they were held at zero pressure for 5 min, then the pressure was raised to 50 bar for 2 min, followed by 100 bar for an additional 3 min, and finally, to 200 bar for 1 min. Then, the films were quickly cooled to room temperature using cold water. The resulting films were characterized by a thickness of ~300 μm.

2.3. Degradation tests

Mesocosms were used to model some marine environments at lab scale [39,40]. Three mesocosms were used for each polymer type in order to improve reproducibility of the experiments [41]. In Fig. 1 the three different exposure conditions at which the biodegradable polymers were exposed are shown.

The mesocosms were represented by 60 L glass tanks filled with 50 L of seawater and containing 10 kg of calcareous sand on the bottom, to produce a gravel of ca. 10 cm height. A Micra 400 centrifugal pump (400 L/h, SICCE, Italy) promoted the circulation of the seawater into a lateral filtration compartment (15 L) filled with perlon wool and ceramic rings. A SHG Activce Drops bacterial activator (Super High Group, Ovada, Italy) was added to each tank at the start of the experiment, according to

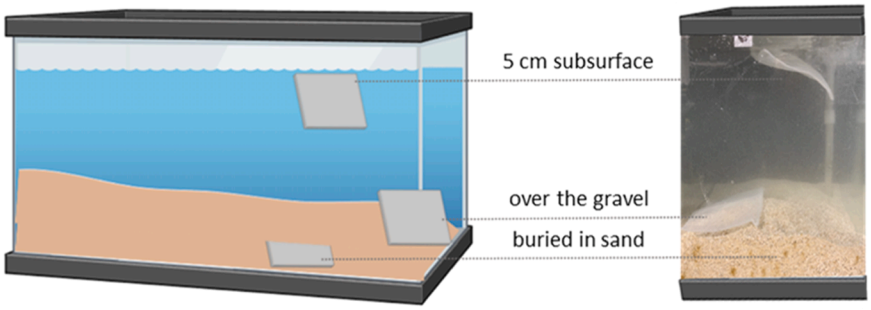

Fig. 1. Left draw and right picture of the experiment set up indicating the three different exposure conditions at which the biodegradable polymers were exposed 1) 5 cm subsurface, 2) over the gravel, 3) buried in sand.

the manufacturer's instructions, to prime the biological filtration and to promote the maturation of a natural environment. Polymeric films with dimensions of 13 cm x 6 cm were enclosed in nylon nets and positioned into three different exposure conditions: 1) 5 cm subsurface; 2) over the gravel; 3) buried in the sand.

The films were kept one year in the mesocosms and sampled at 113, 147, 224, 303, 363 days to study the behavior of biodegradable polymers in the marine environment, and also, to carry out analyses on the pieces of film.

2.4. Analytical techniques

At each sampling, films were characterized with different approaches to determine the degradation behavior of the polymers.

2.4.1. Gravimetric determination

The degradation of the tested polymers was monitored by gravimetric methods determining the weight loss (WL) of the samples, averaged over three samples of each polymer type and for each sampling time, using Eq. (1):

$$WL(\%) = 100 * (Wt_{ti}/Wt_{t0}) \quad (1)$$

where Wt_{ti} is the weight of the sample after a certain exposition time and Wt_{t0} is the weight before the exposition.

The average degradation rate (R) under the three exposure conditions for the tested polymers was calculated using the Eq. (2):

$$R(mg * day - 1 * cm - 2) = \Delta m / (t * A) \quad (2)$$

where Δm is the degraded mass (mg), t is the time interval (day) and A is the surface area (cm^2).

2.4.2. Thermal properties

Thermal properties of the samples were analysed by differential scanning calorimeter (DSC) and thermogravimetric analyser (TGA). DSC measurements were performed on film samples using a Mettler DSC 822e calorimeter, Mettler-Toledo, Inc. (Columbus, OH, USA), equipped with a liquid nitrogen accessory for fast cooling. The calorimeter was calibrated in temperature and energy using indium. Dry nitrogen was used as purge gas at a rate of 30 mL/min during the measurement. About 5 mg of the samples were sealed in standard aluminum 40 μL pans. The measurements on PBS, PBSA, PHB and PLA were carried out heating samples from −70 to 150 °C at 10 °C/min while measurements on PCL were carried out from −90 to 80 °C at 10 °C/min. DSC curves were analyzed using the STARe Software 8.1, Mettler-Toledo GmbH (Columbus, OH, USA). The crystallinity of the samples was calculated by dividing the sample melting enthalpy by the melting enthalpy of the fully crystalline polymer that was 93.6 J/g for PLA [42], 139.5 J/g for PCL [43], 142.0 J/g for PBSA [44], 145.0 J/g for PHB [45] and 195.0 J/g for PBS [46].

TGA measurements were carried out using a Perkin Elmer Pyris 1 analyzer. About 5 mg of each sample were placed in a platinum open pan and heated from 50 to 700 °C at 10 °C/min. High purity nitrogen was fluxed through the furnace at a flow rate of 40 mL/min. The temperature at the maximum weight-loss rate (T_d) of each sample was determined.

2.4.3. Chemical analyses

The effect of degradation experiments on polymers was evaluated by Fourier transformed infrared (FTIR) and ^1H Nuclear Magnetic Resonance (NMR) spectroscopy. FTIR spectra of the samples were recorded at room temperature by means of a Perkin Elmer Spectrum 100 FTIR spectrometer, equipped with an attenuated total reflectance accessory (ATR), in the range 4000–650 cm^{-1}. All spectra were recorded at a resolution of 4 cm^{-1}, 16 scans were averaged for each sample. ^1H NMR spectra were recorded on a Bruker Avance 400 spectrometer on samples dissolved in $CDCl_3$ (approximate concentration: 5mg/mL; internal standard: $CDCl_3$ signal at 7.26 ppm).

2.4.4. Surface morphology

Morphological analysis was performed using a FEI Quanta 200 FEG scanning electron microscope, SEM, (Eindhoven, The Netherlands) in high vacuum mode, equipped with a secondary electron detector. SEM analysis was carried out on film surfaces to evaluate the degradation phenomena occurring during the test. Before the analysis, samples were mounted on aluminum stubs and coated with an Au/Pd alloy using a sputtering device, Emitech K575X (Laughton, UK).

2.4.5. Release in sediments

In order to detect the presence of released fragments in the sand 600 g of sand in which the films were buried were collected and treated with 600 ml of chloroform, stirred for 24 h at room temperature. The solvent was recovered and concentrated to 2 ml using a rotary evaporator. The remaining solution was casted on KBr disks and analyzed by using a Nicolet iN10 MX Infrared Microscope (Thermo-Fisher Scientific, Madison, WI) equipped with a liquid nitrogen cooled in order to individuate traces of the buried polymer. All spectra were recorded at a resolution of 4 cm^{-1} in transmission in the range 4000–650 cm^{-1}.

3. Results and discussion

In Fig. 1 the three different exposure conditions at which the biodegradable polymers were exposed are shown. During aging, a biofilm grown on polyester films surface in all the tested conditions. The polyester films were washed with distilled water and dried under vacuum at room temperature for 4 h before characterization. Isolation and identification of bacterial strains which colonized the tested materials was evaluated in a previous paper [41].

3.1. Gravimetric determination

The WL curves of the different films during degradation experiments as function of time are reported in Fig. 2. The investigated polymers

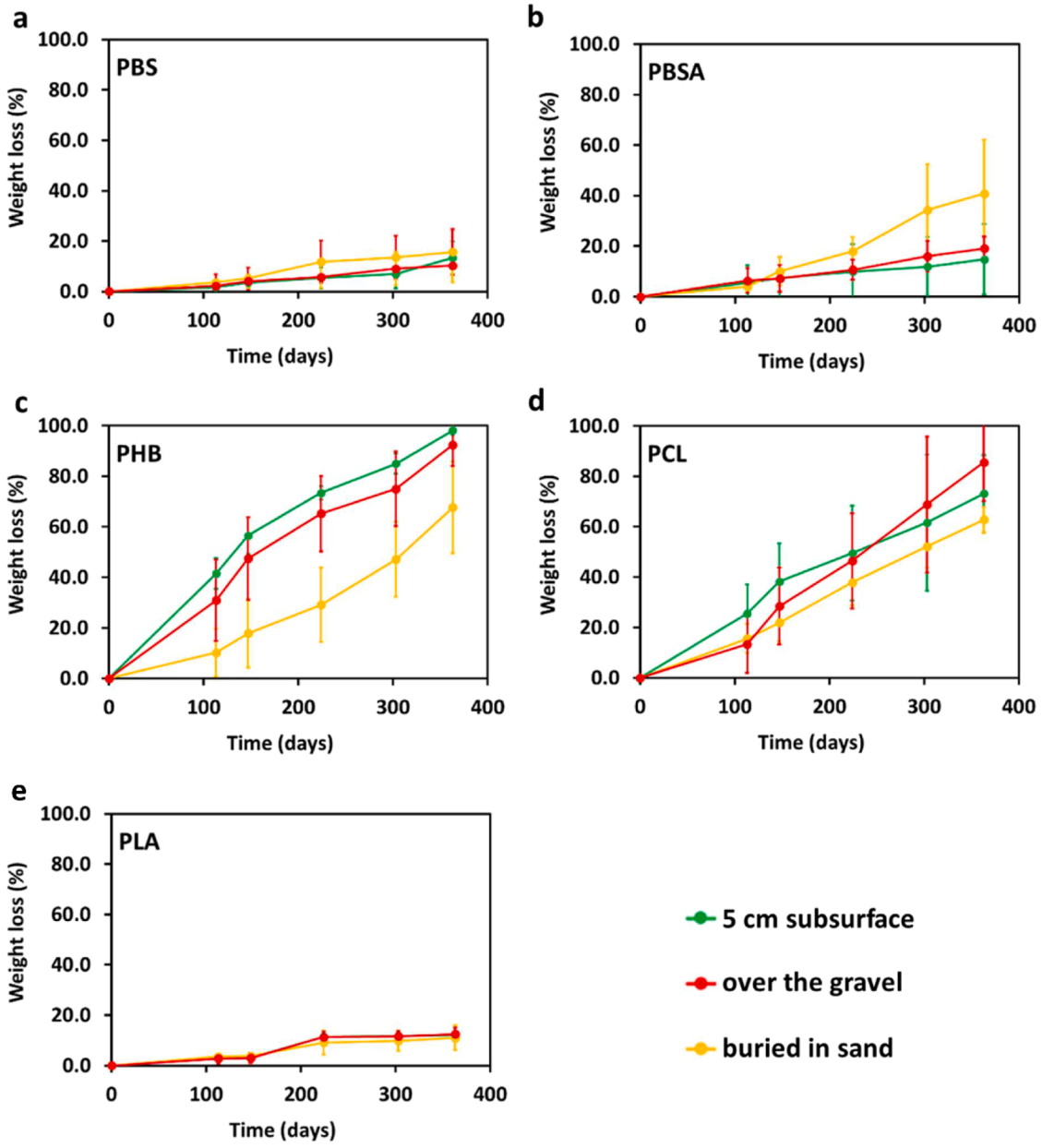

Fig. 2. Weight loss % (WL) versus time of the tested polymers in the three exposure conditions: i.e. 5 cm subsurface, over the gravel and buried in sand a) PBS; b) PBSA; c) PHB; d) PCL; e) PLA.

exhibited different WL and degradation behavior depending on their chemical composition and exposure in the mesocosm. PBS showed a very low WL in all the experimental conditions: after 363 days of permanence on 5 cm subsurface the materials lost about 13.4 % of the initial weight; a WL of 15.7 % was recorded in sample placed over the gravel and a WL of 10.3 % was obtained for samples buried in sand (Fig. 2a). PBSA presented a greater WL %, about 40.8 % of reduction of the initial weight, after 363 days of burial in sand, while PBSA films placed over the gravel and on 5 cm subsurface presented a WL of 19.1 % and 14.8 %, respectively (Fig. 2b). PBSA films presented a similar weight loss behavior across the three exposure conditions; there is a slow degradation during 224 days of exposition, then the weight loss decreased more rapidly for the buried samples. PHB exhibited a very high weight loss when aged over the gravel and 5 cm subsurface with value after 363 days of exposure equal to 92.5 % and 98.2 %, respectively. Lowest WL %, 67.7 %, was obtained after 363 days of burial PHB films in sand (Fig. 2c). Also PCL samples presented high weight loss during aging, WL 85.6 % was obtained for the samples placed over the gravel, WL 73.1 % was measured after 363 days of film exposure to 5 cm subsurface and WL 62.8 % was obtained after 363 days of burial in sand (Fig. 2d). Finally, PLA showed a very low weight loss in all conditions (Fig. 2e). In the first 147 days the weight remains almost unchanged with a weight loss below 4 %. After 363 days the loss was 12.5 % for the samples placed over the gravel, 12.1 % for the sample placed at 5 cm subsurface and 11.0 % for sample buried in sand.

The mean degradation rates, R, were determined experimentally in the three exposure conditions (Table 1). The values obtained, expressed in mg per day per unit area (mg day^{-1} cm^{-2}), show a clear variability between the different materials and the experimental conditions. The polymer that showed the highest degradation rate was PHB, with valuesranging from 0.0539 to 0.0806 mg $day^{-1}cm^{-2}$ .PCL (0.0277–0.0307) and PBSA (0.0104–0.0233) followed, while PBS and PLA were positioned significantly lower, with values lower than 0.0103 mg $day^{-1}cm^{-2}$. These experimental results are comparable with those reported in the

Table 1
Average degradation rates, R, (mg day^{-1} cm^{-2}) of the 5 polymers under the 3 exposure conditions.

Sample	R (mg day^{-1} cm^{-2})		
	Buried in sand	Over the gravel	5 cm subsurface
PBS	0.00587	0.01024	0.00775
PBSA	0.02327	0.01192	0.01048
PHB	0.05393	0.06942	0.08062
PCL	0.02788	0.03075	0.02766
PLA	0.00868	0.00902	0.00899

meta-analysis conducted by Dilkes-Hoffman et al. (2019), who collected quantitative data on the biodegradation of polyhydroxyalkanoates (PHAs) in the marine environment [47]. According to the authors, the average degradation rates of PHAs, with particular attention to PHB, are between 0.04 and 0.09 mg day^{-1}cm^{-2}, depending on the experimental conditions and sample morphology. The data obtained for PHB in the present study fall within this range, confirming its strong biodegradability in the marine environment. In contrast, the other polymers analyzed, in particular PLA and PBS, show degradation rates much lower than those of PHB and do not fall into the domain of materials commonly considered PHAs. It is important to note that a limitation of this calculation is that the degradation rate is calculated assuming that degradation occurs in a constant (linear) manner over time. This does not necessarily reflect the real behavior: in many cases, polymer degradation follows a non-linear pattern, for example with an initial lag phase or an acceleration in the final phase (e.g. due to fragmentation or biofilm). The use of a linear average may underestimate or overestimate the actual time required for complete degradation.

It is to be highlighted that the degradation of these materials was assessed through the weight loss of the samples, used as an indirect indicator of the material degradation. This methodological choice allows to estimate the material degradation and the potential release of microplastics into the environment, but does not allow to draw conclusions on biodegradation extent, i.e. on the mineralization of organic carbon into CO_2 by the microbial community.

Several works in the literature have addressed this distinction. The study by Nakayama et al. (2019) demonstrated that some polyesters, in particular PCL, can indeed biodegrade in the marine environment, but only under well-defined and monitored conditions, through BOD (biochemical oxygen demand) tests with natural inoculum [48]. However, many other materials show extremely slow or negligible degradation rates in similar conditions. In a complementary manner, López-Ibáñez and Beiras (2022) developed a rapid protocol to assess mineralization in realistic marine sediments, highlighting that many materials certified as "biodegradable" in compost do not degrade at all in the marine environment, although they may undergo fragmentation phenomena [49]. This discrepancy is fundamental for the interpretation of data based on mass loss alone. As also highlighted by Chinaglia et al. (2018), fragmentation and surface erosion of materials do not necessarily coincide with microbiologically active biodegradation [50]. In fact, polymers can undergo physical disintegration processes, often accelerated by environmental conditions such as solar radiation, mechanical action of waves or biofouling, which reduce the mass of the sample without effective carbon assimilation by microorganisms. In the specific case of biodegradable polyesters, this fragmentation can lead to the release of microplastics that, can persist in the environment for a long time and contribute to marine or terrestrial contamination. The study by Dilkes-Hoffman et al. (2019) estimated, through a meta-analysis, that the complete degradation of PHA objects in the marine environment can take years, suggesting that even biodegradable materials can constitute a source of microplastics if managed inadequately [47]. Weight loss can therefore be considered a useful indicator to describe degradation phenomena and potential release of microplastics.

3.2. Thermal analyses

The influence of degradation on thermal transitions, as well as on the thermal stability of the samples, was analyzed by using DSC and TGA.

As reported in Fig. 3, the melting temperatures (T_m) remain unchanged during the exposure period for all the samples analyzed and in all conditions. All polymers, except PHB and PBS, present a similar thermal behavior with an increase of the crystallinity index (X_c) of about 6–10 %. PLA samples, in all the tested conditions, present an increase of X_c during the first 100 days of aging, along with an increase in the glass transition temperature, Tg, as reported in Fig. 4. Such an increase could be associated to the degradation of the amorphous regions and microstructural rearrangements in the films that induce a rise in crystallinity. In the subsequent days, no significant differences in X_c were observed for PLA samples aged at 5 cm subsurface. A further increase of X_c was observed after 1 year of exposure in PLA sample aged over the gravel while a slight decrease was detected in samples buried in sediments, at the same time of testing. This reduction in the degree of crystallinity was already reported in literature [51,52], and ascribed to water diffusion within the polymer chains. An increase of X_c was noted in PCL and PBSA samples in all the exposure conditions, while no significant differences in X_c were measured in PBS samples. X_c value of PHB samples, independently from the aging conditions reach a minimum after 147 days of testing this could be attributed to an extended degradation involving amorphous and crystalline regions [29].

DSC curves of PLA during the exposition period in water surface, reported in Fig. 4, showed that after the first 100 days of exposure an increase of glass transition temperature (T_g) and a progressive broadening of the cold crystallization peak as a function of exposure time occur. It is interesting to note the development of a double melting peak during the exposition time. The double melting can be explained with the lamellar thickness model, which theorizes the existence of two kinds of crystal lamellae with different thicknesses [53,54]. Melting of thinner lamellae will be associated with lower temperature endotherms, while melting of thicker lamellae will be associated with higher temperature endotherms. In absence of changes in the chemical structure, as it was seen by FTIR analysis which will be discussed in Section 3.3, this thermal behavior can be explained by a physical aging process [29,55].

The thermal degradation temperature (T_d) of the samples analyzed by TGA was little affected by the different exposure conditions. TGA curves reported in Fig. 5, showed that the thermal degradation of all analysed materials occurred in a single-step process. After 1 year of aging, all the samples, except PBS, show a slight shift to lower temperatures of the weight loss, suggesting a worsening of thermal stability of the samples after aging with an anticipation of degradation compared to the unaged samples. This behavior is more evident for PHB, PCL and PLA (Fig. 5c-e), while PBS and PBSA the typical thermal degradation after aging (Fig. 5a-b). The lower thermal stability of aged PHB, PCL and PLA could be explained considering that the degradation (hydrolysis and/or microbial attack) results in the formation of polymer chains with lower molecular weight affecting their thermal behavior [28]. Moreover, in the case of PHB, a hydrolytic scission mechanism caused by water adsorption is reported in the literature, which accelerates the hydrolysis leading to a faster degradation of the polymer, reducing its thermal stability [56,57]. The same behavior was observed for the samples in all the exposure conditions (Figure S2).

3.3. Chemical analyses

The chemical modifications of the polymeric samples during exposure to the three different conditions, simulating their presence across the water column in marine environment, were monitored by FTIR-ATR and NMR spectroscopies.

Polyesters are sensitive to hydrolysis reactions of ester bonds in the polymer backbone which lead to the formation of alcohol and carboxylic acid groups [58].

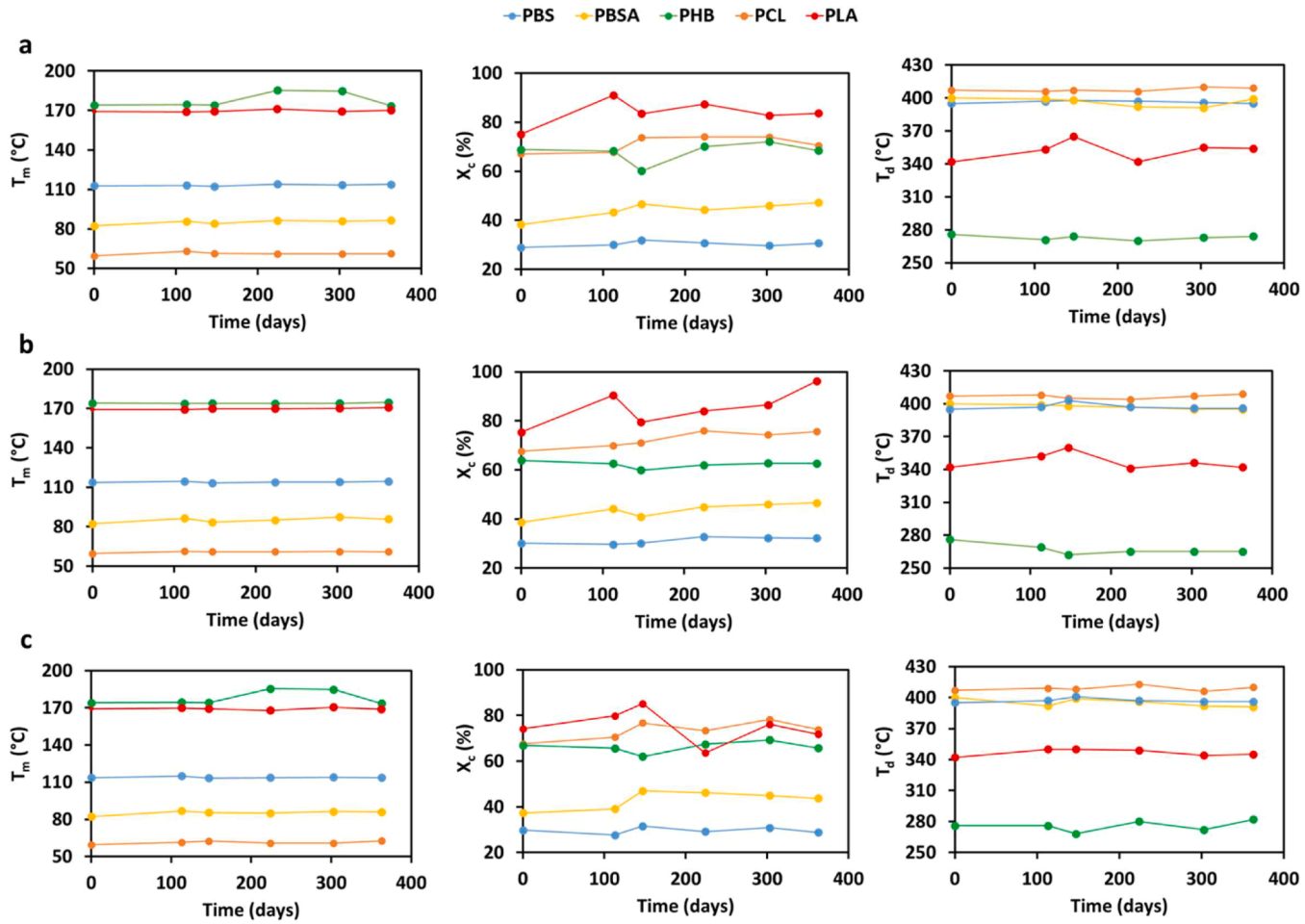

Fig. 3. Thermal parameters of polyesters as a function of exposure time: a) 5 cm subsurface; b) over the gravel; c) buried in sediments.

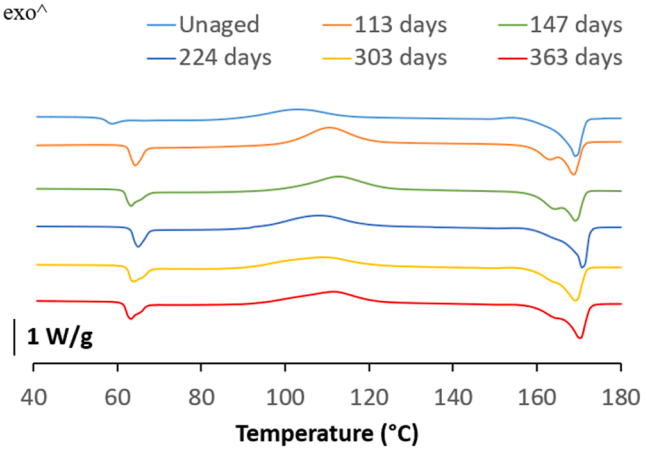

Fig. 4. DSC thermograms of PLA during exposition time at 5 cm subsurface; DSC of all the films exposed to the other three conditions are available in Figure S1 of the supporting material.

FTIR spectra of PBS and PBSA films showed three absorption bands of C=O stretching modes centered at 1736 cm^{-1}, associated with free amorphous region, 1720 cm^{-1} and 1713 cm^{-1} due to the formation of crystalline structure [59].

During exposure to 5 cm subsurface (Figs. 6a, b) is evident a progressive decrease of the C=O and -C-O—C- bands (at 1713 cm^{-1} and 1164 cm^{-1} respectively) and an increase in the OH group stretching vibration, as a result of a progressive hydrolysis of the ester bonds during aging [29]. This behavior suggests that the effect of remaining to 5 cm subsurface resulted in structural changes in PBS and PBSA [60]. Different mechanisms of scission of the PBS and PBSA chain have been proposed in the literature: among these, the extraction of α-hydrogen which leads to the formation of carboxyl and aldehyde groups via hydroperoxides, the Norrish I of chain scission which leads to carboxyl, aldehyde and ethereal, the oxidation of the terminal hydroxyl groups leading to carboxyl groups and the extraction of β-hydrogen resulting in the formation of unsaturated compounds [61–63]. The aging of PBS and PBSA in all exposure conditions results in the hydrolysis of the ester bonds in the main chains. PHB spectra (Fig. 6c) presented an increase in the absorption band in the range 3000–3500 cm^{-1}, related to the O—H stretching. The band at 3437 cm^{-1} increased with exposure time in all conditions due to an increase in the OH groups as consequence of the formation of carboxylic acid and unsaturated groups, representing an indication of PHB degradation [64]. In the C—H stretching region (2800–3200 cm^{-1}), six bands of semicrystalline PHB were identified: 3007 cm^{-1}, 2997 cm^{-1}, 2976 cm^{-1}, 2935 cm^{-1}, 2873 cm^{-1} and 2850 cm^{-1} [65]. A gradual increase in the intensity of these bands was observed with increasing exposure time suggesting the development of PHB crystalline structure and the reorganization of crystal phase due to the degradation of the material. The appearance of a band at 2920 cm^{-1} was highlighted after exposure period, more intense in the films over the gravel and buried in the sediment. This band is associated with the aliphatic stretching of C—H and may be due to a scission of the chain in the crystalline and amorphous regions [66]. Weak intramolecular interactions such as hydrogen bonding C–H···O=C between two helical

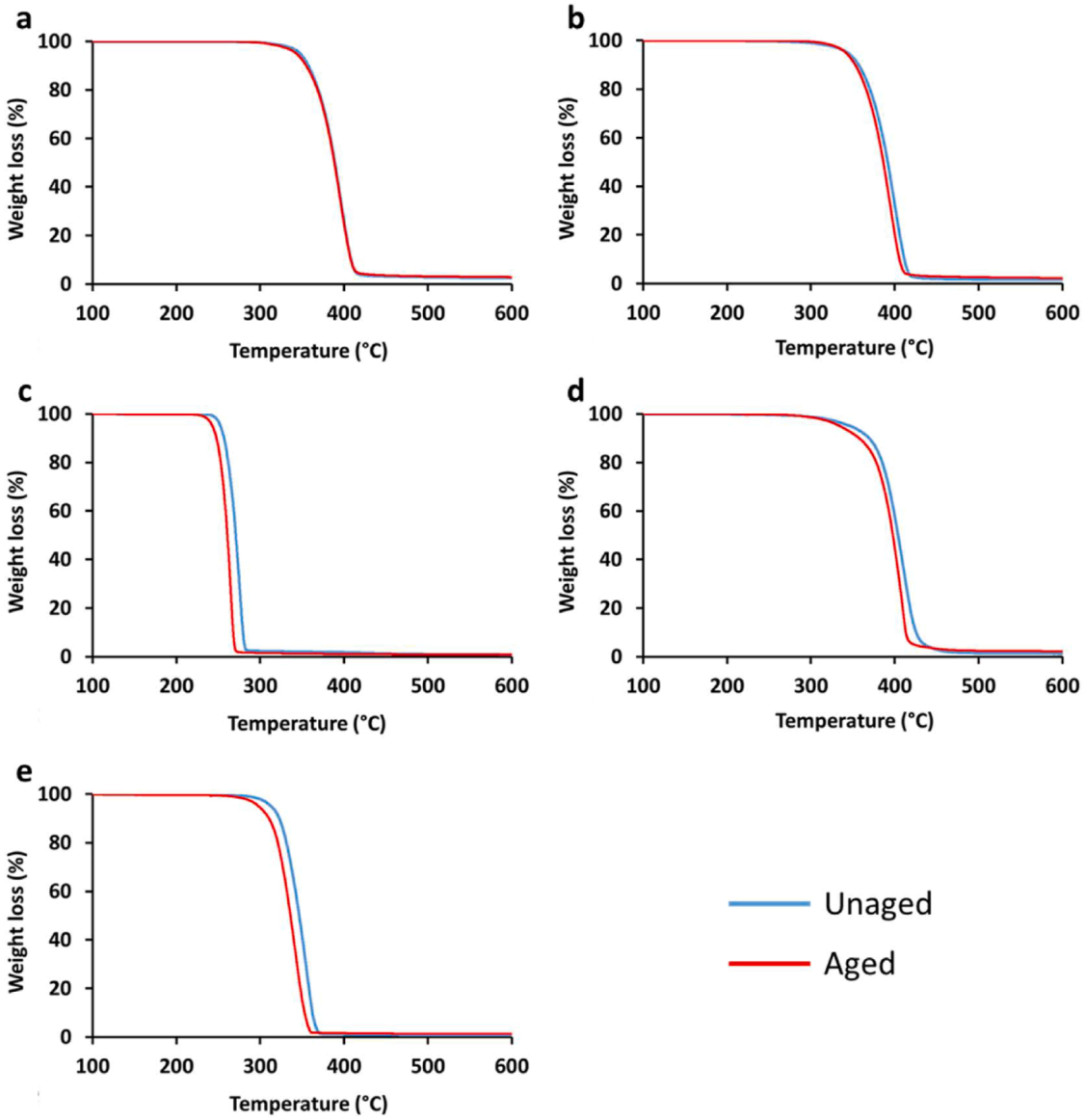

Fig. 5. TGA thermograms of the films before and after 1 year of exposition at 5 cm subsurface; a) PBS, B) PBSA, C) PHB, D) PCL, E) PLA.

structures in PHB were also reported [67]. At 1720 cm^{-1} is visible the absorption band due to C=O stretching vibration of PHB in the crystalline phase together with a broad band at 1740 cm^{-1} arising from the C=O stretching of amorphous PHB. The increase in the band at 1740 cm^{-1}, during exposure, could suggest the formation of intermolecular hydrogen bonding between PHB chains in the amorphous phase [67]. Moreover, the presence of OH and amide I (1650 cm^{-1}) and II (1520 cm^{-1}) groups further suggest the occurrence of biodegradation process on plastic surfaces with accumulation of nitrogen groups [68].

As shown in Fig. 6d the PCL characteristic bands are recorded at 2943 cm^{-1} and 2865 cm^{-1} related to the asymmetric and symmetric stretching of CH_2 respectively, 1720 cm^{-1} associated with the stretching of carbonyl groups, 1294 cm^{-1} ascribed to C—O and C—C stretching, 1239 cm^{-1} and 1169 cm^{-1} related to the asymmetric and symmetric stretching of C—O-C. After exposure period, the peak intensity decreases, thus showing degradation up to the molecular level [69]. The increase in the intensity of the bands associated with the absorption of hydroxyl (between 3600 and 3300 cm^{-1} and between 710 and 600 cm^{-1}), combined with the reduction in the intensity of the band at 1720 cm^{-1} associated with the ester groups, visible in the PCL spectra during the exposure period (Fig. 6d), suggests the formation of hydroxyl terminal groups following the scission of macromolecular chains typical of hydrolytic degradation [70], confirming the effective process of degradation of PCL.

The PLA spectra (Fig. 6e) during degradation in all conditions do not show any significant changes in the C=O and OH absorption bands, that indicates the no significant change in the chemical structure. This result is in line with the absence of degradation observed during all the experimental periods.

The results are the same in all conditions. FTIR spectra of the films exposed to water bottom and buried in sediment are available in Figure S3 of the supporting material.

^1H NMR analysis was carried out on the materials showing the highest weight loss: PHB, PCL and PBSA. In the ^1H spectrum of PHB before and after exposure to water surface, see Fig. 7, it was possible to identify, besides the main PHB signals [71] at 1.28 ppm ($–CH_3$), 2.48–2.62 ($–CH_2–$) and 5.26 ppm ($–\underline{CH}(CH_3)–$), also the signals attributed to chain end groups. In particular, the signal of $–\underline{CH}(CH_3)–OH$ of hydroxyl end groups is identified at 4.17 – 4.21 ppm, while the signals of unsaturated (propenyl) end groups, generated by chain scissions, are observed at 5.80 and 6.95 ppm [72].

Although the presence of overlapping signals, due to trace

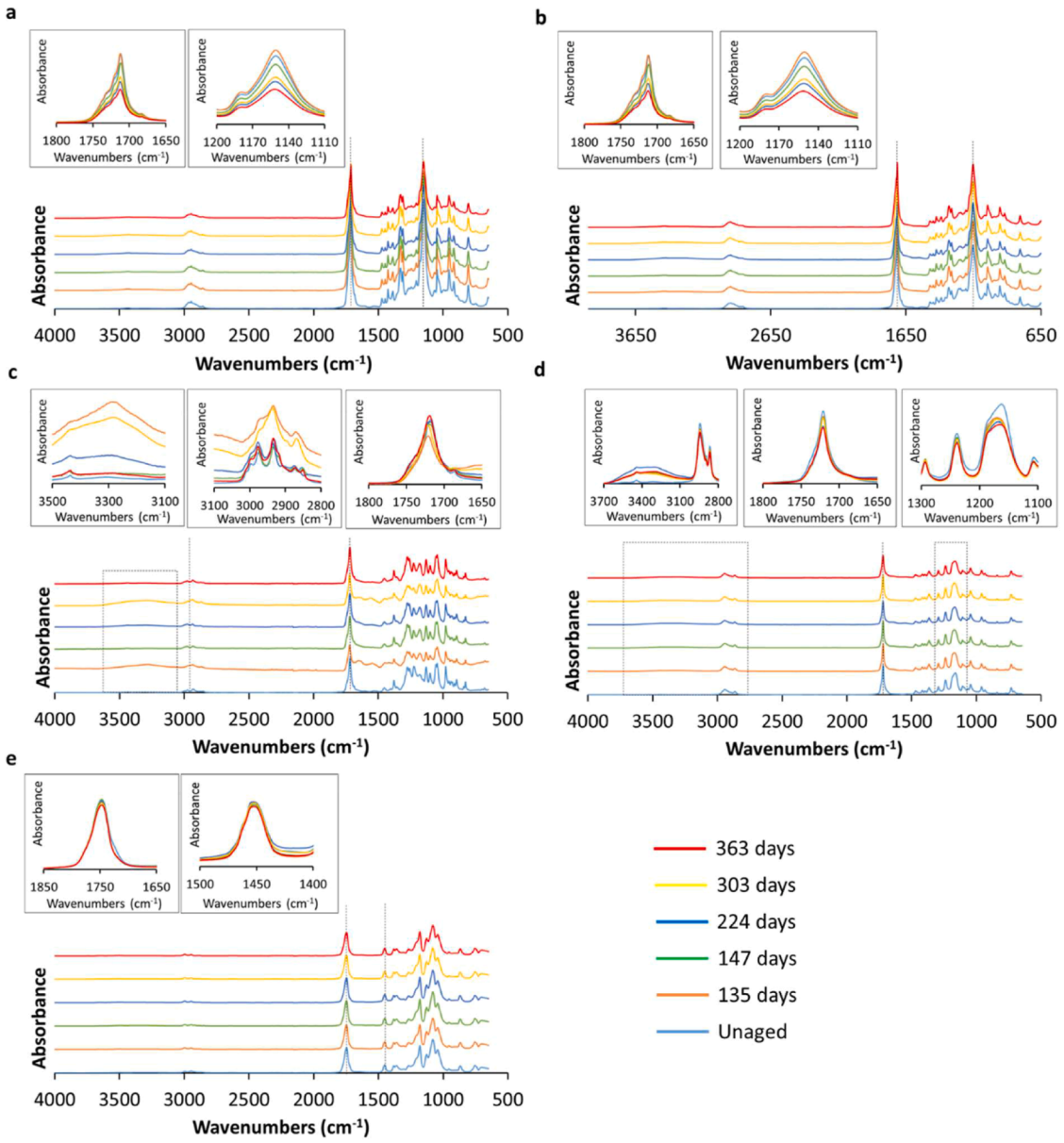

Fig. 6. FTIR spectra of analysed films during exposure to 5 cm subsurface at different degradation time: a) PBS; b) PBSA; c) PHB; d) PCL; e) PLA.

impurities, hinders a reliable determination of molecular weight by peak integration, the relative intensity of terminal groups increases by about 75 % in the degraded PHB sample, indicating a substantial decrease in molecular weight.

On the contrary, for PCL and PBSA, the spectra of samples before and after exposure to the marine environment do not show significant differences (Figure S4). For PCL, the main signals are identified at 1.38 ppm (–C(O)OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$–), 1.64 ppm (–C(O)OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$–), 2.30 ppm (–C(O)OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$–) and 4.05 ppm ((–C(O)OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$–) [73]. The signal attributed to the -CH$_2$OH of hydroxyl chain ends is observed at 3.64 ppm [74]and its relative intensity is almost unchanged after exposure. Likewise, for PBSA, the main signals attributed to the –CH$_2$CH$_2$O– (1.72 ppm) and –CH$_2$CH$_2$O– (4.13 ppm) of butylene units, along with the CH$_2$ of succinic units (2.64 ppm) and adipic units (1.67, 2.34 ppm) are readily identified [75]. Methylenes of hydroxyl chain ends are observed at 3.68 ppm and also in this case their relative intensity is unchanged. Moreover, there is no evidence of a preferential degradation of adipate segments, as sometimes observed [76] as the succinate/adipate ratio was mot modified after marine exposure.

In the case of PCL and PBSA, then, NMR data did not show a strong evidence of molecular weight degradation, in apparent contrast with FTIR data discussed above. However, it must be considered that ATR-FTIR analyses are focused on the surface of samples, while for NMR analyses whole films were sampled and dissolved. This difference can explain the fact that FTIR did show some sign of hydrolysis: these effects can be essentially concentrated at the surface, while are not so strong if mediated over the entire thickness of the sample.

3.3.1. *Surface morphology*

SEM micrographs of the samples after 363 days of degradation in the different exposure conditions, reported in Fig. 8, allowed the detection of the degradation phenomena occurring on film surfaces. The formation of numerous heterogeneous pinholes, cracks and grooves were observed on the PBS, PBSA and PCL surface suggesting the occurrence of degradation (Figs. 8a, b, d). Degradation phenomena were clearly observable on PHB film surface after 363 days of burial in sand (Fig. 8c) where holes with a diameter of about 100 μm and grooves are visible.

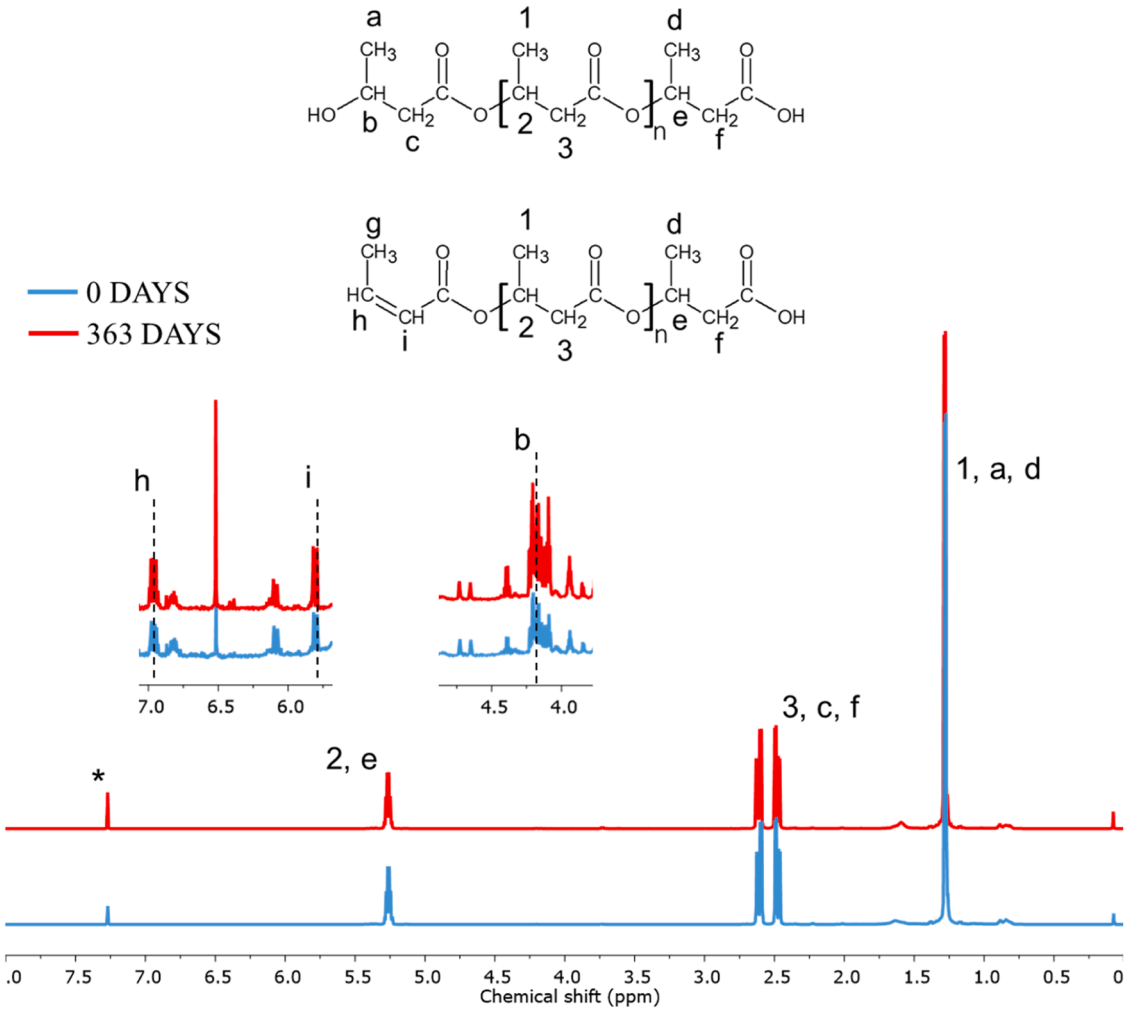

Fig. 7. ^{1}H spectrum of PHB before and after exposure to 5 cm subsurface, with assignment of mainchain peaks and of the peaks attributed to two possible chain terminal groups, hydroxyl and propenyl (reported at high magnification in the inserts). The residual signal of chloroform is marked by a star.

PCL film surface, after 363 days of exposure to surface water, bottom surface and burial in sand (Figs. 8d) presented several spherulites with an average diameter of about 10 μm and 20 μm this last in the case of the sample exposed to water bottom. PLA film surfaces were slightly affected by exposure to the three conditions, especially films exposed to 5 cm subsurface and over the gravel (Fig. 8e), thus confirming that limited degradation phenomena occur and affect surface morphology and integrity.

3.3.2. *Release in sediments*

In order to verify the presence of degradation products of tested polymers in the sediment present in the mesocosms, knowing the solubility od these polymers in chloroform, extractions of sediment with chloroform were performed and the recovered solutions were analysed with FTIR spectroscopy. For each sample three replicates were extracted and analysed. FTIR spectroscopy allows to identify the presence of traces of PBS and PBSA (1 positive over three replicates) and PCL (3 positives over three replicates). PLA and PHB were not found in sediments. FTIR spectra of PBS and PBSA extracted from sediment are reported in Fig. 9a, b. Spectra presented the typical absorption bands of PBS and PBSA: 1719 cm^{-1}, C=O stretching vibrations; 1151 cm^{-1}, C—O stretching mode; 1046 cm^{-1}, $O(CH_2)_4O$ vibration; 955 cm^{-1}, C–O symmetric stretching mode [77]. PCL was extracted form the sediments in all replicates as highlighted by FTIR spectrum reported in Fig. 9c, where the characteristic absorption bands of PCL were detectable: 1726 cm^{-1} (C=O stretching), 1190 cm^{-1} (OC—O stretching) and 1294 cm^{-1} (C—O and C—C stretching in crystalline phase) [78].

These results allowed to conclude that during aging small fragments of PBS, PBSA and PCL are released in sediment confirming the hypothesis of breakup caused by environmental factors induced by the exposure conditions.

4. Conclusions

The degradation of biodegradable polyesters such as PBS, PBSA, PHB, PCL and PLA was studied for 363 days in simulated marine environment under three different conditions (in the water surface, over the gravel and buried in the sand). After 363 days of exposure in the marine environment, the polymers show variable weight losses, depending on polymer nature and the exposure conditions. Indeed, the mass loss rate is significantly stronger and faster for PCL and PHB while the mass loss rate for PBA, PBSA and PLA is very slow during time. The degradation appears almost complete for PCL and PHB but for the PBS, PBSA and PLA the weight loss does not exceed 20 % after one year of exposure in all the tested conditions, except for PBSA buried in the sand which lose 40 % of its initial weight at the end of the test.

The surface morphologies of the films during aging confirm the occurring of the degradation in all the tested conditions. Numerous cracks, grooves and holes were observed on the PBS, PBSA, PCL and PHB films after one year of exposure while at the initial stage, the film was smooth and did not show any specific observation. On the contrary, PLA films show very little change on its surface after the same exposure time.

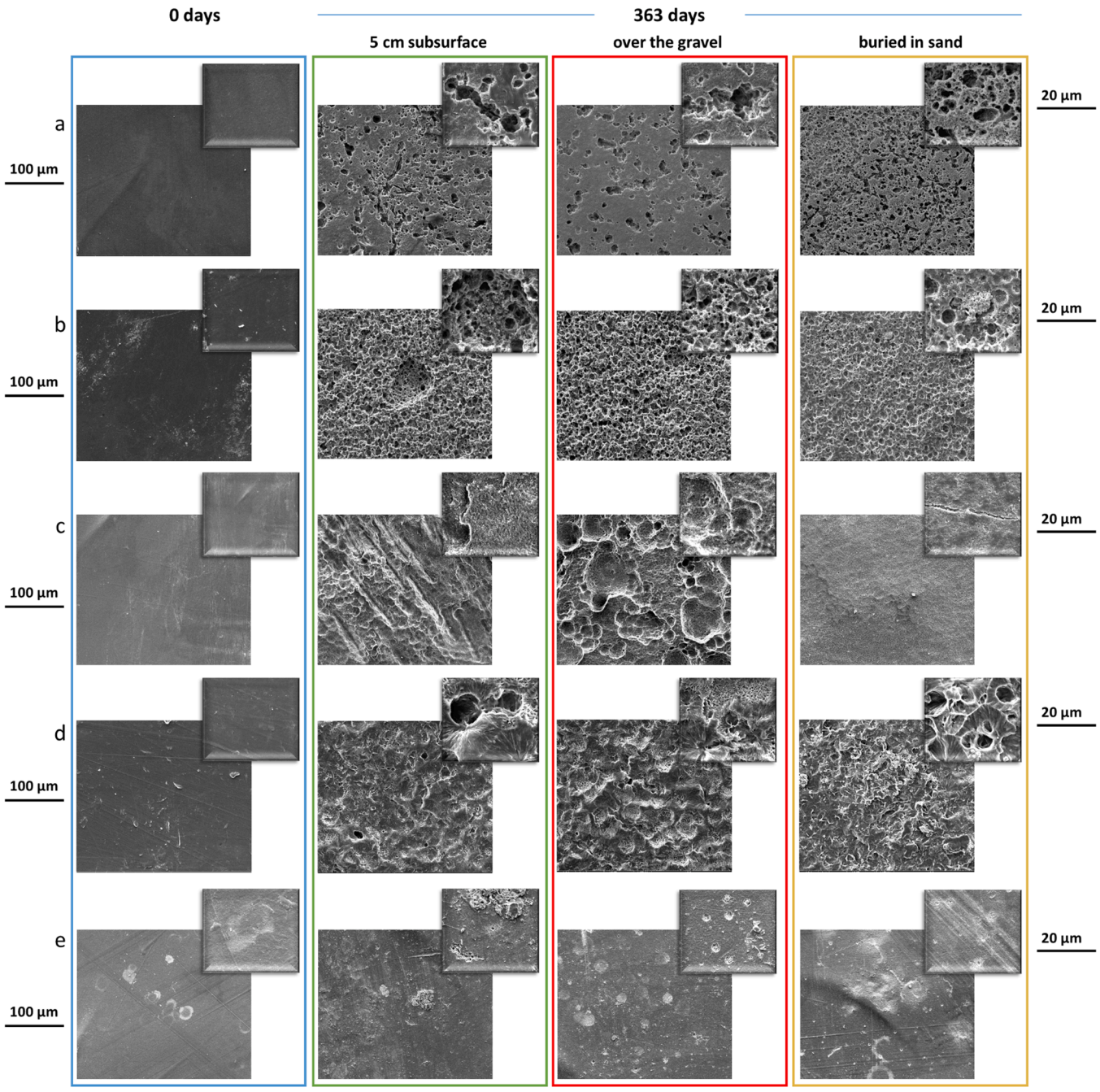

Fig. 8. SEM micrographs of the films exposed at 5 cm subsurface, over the gravel and buried in sand at t0 and after 363 days for: a) PBS; b) PBSA; c) PHB; d) PCL; e) PLA. 100 µm scale bare indicates the dimension of larger SEM micrographs while scale bar of 20 µm is for smaller SEM micrographs in the upper right.

During the exposure period, PLA was mainly subjected to physical aging, as confirmed by DSC and FTIR analyses. FTIR, highlighted chemical changes in all the samples, except in PLA. Exposure to the marine environment induces hydrolytic degradation confirmed by a progressive decrease, during the year of the experiment, of the absorption bands ascribed to the stretching vibration of the C=O and an increase of the absorption bands ascribed to OH vibration. NMR spectra further confirmed a change in signals attributable to terminal groups, probably produced by chain scission reactions through hydrolysis of ester groups.

The FTIR analysis of materials extracted from sediment confirmed the hypothesis of fragmentation phenomena of the films samples during ageing. In fact, traces of some polymers, in particular of PCL, into the sediment were found, a sign of the fragmentation and migration of small pieces of the samples in the sediment.

In conclusion, the tested polyesters showed different degradation kinetics and mechanisms during aging. In any case, the comparison of the degradation behavior among the biodegradable polyesters allowed to conclude that not all the biodegradable polyesters biodegrade in marine environment thus their mismanagement at the end of life could induce accumulation of plastic in the environment.

CRediT authorship contribution statement

Thomas Viel: Investigation, Formal analysis, Data curation. **Immacolata Liotta:** Writing – original draft, Investigation, Data curation. **Roberto Avolio:** Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Maria Emanuela Errico:** Writing – original draft, Methodology, Formal analysis, Data curation,

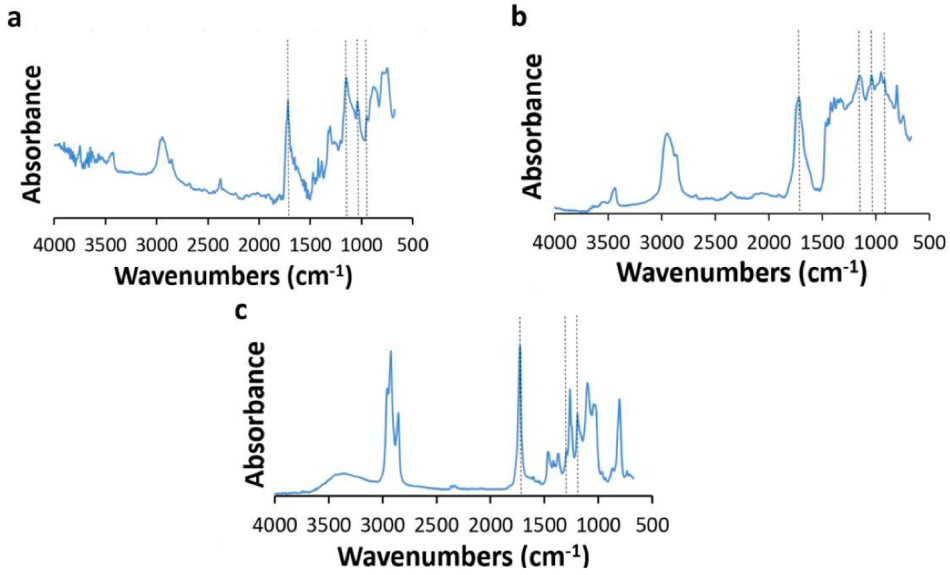

Fig. 9. FTIR spectra of chloroform used to extract from sand a) PBS; b) PBSA and c) PCL.

Conceptualization. **Loredana Manfra:** Writing – original draft, Funding acquisition, Formal analysis, Data curation. **Giovanni Libralato:** Writing – original draft, Funding acquisition, Conceptualization. **Valerio Zupo:** Writing – original draft, Formal analysis, Data curation. **Maria Costantini:** Writing – original draft, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Mariacristina Cocca:** Writing – original draft, Supervision, Funding acquisition, Formal analysis, Data curation, 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.

Acknowledgements

The authors kindly thank Dr. Cristina Del Barone of IPCB-CNR for the support in the acquisition of SEM images. Thomas Viel was supported by a PhD fellowship (PhD in Biology, University of Naples Federico II) co-funded by the Stazione Zoologica Anton Dohrn (Naples, Italy) and the Institute of Polymers, Composites and Biomaterials - National Research Council of Italy (Pozzuoli, NA, Italy).

This research was conducted in the framework of the Project – Bio-monitoraggio di micro e nanoplastiche biodegradabili: dall'ambiente all'uomo in una prospettiva one health (BioPlast4Safe) – with the technical and economic support of the Italian Ministry of Health- PNC.

R. Avolio, M.E. Errico and M. Cocca thank the project "Co-creating strong uptake of REMEDIES for the future of our oceans through deploying plastic litter valorisation and prevention pathways" funded by the European Union's HORIZON EUROPE Innovation program under grant agreement No 101093964.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2025.111539.

Data availability

Data will be made available on request.

References

[1] A.L. Andrady, M.A. Neal, Applications and societal benefits of plastics, Phil. Trans. R. Soc. B 364 (2009) 1977–1984, https://doi.org/10.1098/rstb.2008.0304.
[2] Plastics – the fast facts 2024 • Plastics Europe, Plastics Europe (n.d.). https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2024/(accessed June 19, 2025).
[3] A. Barron, T.D. Sparks, Commercial marine-degradable polymers for flexible packaging, iScience 23 (2020) 101353, https://doi.org/10.1016/j.isci.2020.101353.
[4] M.B. Paul, V. Stock, J. Cara-Carmona, E. Lisicki, S. Shopova, V. Fessard, A. Braeuning, H. Sieg, L. Böhmert, Micro- and nanoplastics – current state of knowledge with the focus on oral uptake and toxicity, Nanoscale Adv. 2 (2020) 4350–4367, https://doi.org/10.1039/D0NA00539H.
[5] A.J. Jamieson, L.S.R. Brooks, W.D.K. Reid, S.B. Piertney, B.E. Narayanaswamy, T. D. Linley, Microplastics and synthetic particles ingested by deep-sea amphipods in six of the deepest marine ecosystems on Earth, R. Soc. Open Sci. 6 (2019) 180667, https://doi.org/10.1098/rsos.180667.
[6] R.C. Thompson, Y. Olsen, R.P. Mitchell, A. Davis, S.J. Rowland, A.W.G. John, D. McGonigle, A.E. Russell, Lost at sea: where is all the plastic? Science 304 (2004) https://doi.org/10.1126/science.1094559, 838–838.
[7] GESAMP, Sources, fate and effects of microplastics in the marine environment: part 2 of a Global assessment, Joint Group of Experts on the scientific aspects of marine environmental protection (GESAMP), London, UK, 2016. http://www.gesamp.org/site/assets/files/1275/sources-fate-and-effects-of-microplastics-in-the-marine-environment-part-2-of-a-global-assessment-en.pdf.
[8] C. Arthur, H. Bamford, J. Baker, The occurrence, effects and fate of small plastic debris in the oceans, (2008).
[9] M. Poulain, M.J. Mercier, L. Brach, M. Martignac, C. Routaboul, E. Perez, M. C. Desjean, A. Ter Halle, Small microplastics As a main contributor to plastic mass balance in the North Atlantic subtropical gyre, Environ. Sci. Technol. 53 (2019) 1157–1164, https://doi.org/10.1021/acs.est.8b05458.
[10] A. Ter Halle, L. Ladirat, X. Gendre, D. Goudouneche, C. Pusineri, C. Routaboul, C. Tenailleau, B. Duployer, E. Perez, Understanding the fragmentation pattern of marine plastic debris, Environ. Sci. Technol. 50 (2016) 5668–5675, https://doi.org/10.1021/acs.est.6b00594.
[11] M.L. Taylor, C. Gwinnett, L.F. Robinson, L.C. Woodall, Plastic microfibre ingestion by deep-sea organisms, Sci. Rep. 6 (2016) 33997, https://doi.org/10.1038/srep33997.
[12] R. Mercogliano, C.G. Avio, F. Regoli, A. Anastasio, G. Colavita, S. Santonicola, Occurrence of microplastics in commercial seafood under the perspective of the Human food chain. A review, J. Agric. Food Chem. 68 (2020) 5296–5301, https://doi.org/10.1021/acs.jafc.0c01209.
[13] S. Santonicola, M. Volgare, E. Di Pace, M. Cocca, R. Mercogliano, G. Colavita, Occurrence of potential plastic microfibers in mussels and anchovies sold for human consumption: preliminary results, Ital J. Food Saf. 10 (2021), https://doi.org/10.4081/ijfs.2021.9962.
[14] S.L. Wright, R.C. Thompson, T.S. Galloway, The physical impacts of microplastics on marine organisms: a review, Environ. Pollut. 178 (2013) 483–492, https://doi.org/10.1016/j.envpol.2013.02.031.
[15] M. Vighi, J. Bayo, F. Fernández-Piñas, J. Gago, M. Gómez, J. Hernández-Borges, A. Herrera, J. Landaburu, S. Muniategui-Lorenzo, A.-R. Muñoz, A. Rico, C. Romera-Castillo, L. Viñas, R. Rosal, Micro and nano-plastics in the environment: research priorities for the near future, in: P. De Voogt (Ed.), Reviews of Environmental

Contamination and Toxicology Volume 257 (2021), Springer International Publishing, Cham, 2021: pp. 163–218. https://doi.org/10.1007/398_2021_69.
[16] L. Manfra, V. Marengo, G. Libralato, M. Costantini, F. De Falco, M. Cocca, Biodegradable polymers: a real opportunity to solve marine plastic pollution? J. Hazard. Mater. 416 (2021) 125763 https://doi.org/10.1016/j.jhazmat.2021.125763.
[17] N. Lucas, C. Bienaime, C. Belloy, M. Queneudec, F. Silvestre, J.-E. Nava-Saucedo, Polymer biodegradation: mechanisms and estimation techniques – A review, Chemosphere 73 (2008) 429–442, https://doi.org/10.1016/j.chemosphere.2008.06.064.
[18] R. Chandra, Biodegradable polymers, Prog. Polym. Sci. 23 (1998) 1273–1335, https://doi.org/10.1016/S0079-6700(97)00039-7.
[19] F. Degli Innocenti, T. Breton, Intrinsic biodegradability of plastics and ecological risk in the case of leakage, ACS Sustain. Chem. Eng. 8 (2020) 9239–9249, https://doi.org/10.1021/acssuschemeng.0c01230.
[20] F. Convertino, S.C. Carroccio, M.C. Cocca, S. Dattilo, A.C. Dell'Acqua, L. Gargiulo, L. Nizzetto, P.M. Riccobene, E. Schettini, G. Vox, D. Zannini, P. Cerruti, The fate of post-use biodegradable PBAT-based mulch films buried in agricultural soil, Sci. Total Environ. 948 (2024) 174697, https://doi.org/10.1016/j.scitotenv.2024.174697.
[21] M. Tosin, A. Pischedda, F. Degli-Innocenti, Biodegradation kinetics in soil of a multi-constituent biodegradable plastic, Polym. Degrad. Stab 166 (2019) 213–218, https://doi.org/10.1016/j.polymdegradstab.2019.05.034.
[22] G. Suaria, C.G. Avio, A. Mineo, G.L. Lattin, M.G. Magaldi, G. Belmonte, C.J. Moore, F. Regoli, S. Aliani, The Mediterranean Plastic Soup: synthetic polymers in Mediterranean surface waters, Sci. Rep. 6 (2016) 37551, https://doi.org/10.1038/srep37551.
[23] T. Morohoshi, K. Ogata, T. Okura, S. Sato, Molecular characterization of the bacterial community in biofilms for degradation of poly(3-Hydroxybutyrate-*co*-3-Hydroxyhexanoate) films in seawater, Microbes Environ. 33 (2018) 19–25, https://doi.org/10.1264/jsme2.ME17052.
[24] T. Sekiguchi, A. Saika, K. Nomura, T. Watanabe, T. Watanabe, Y. Fujimoto, M. Enoki, T. Sato, C. Kato, H. Kanehiro, Biodegradation of aliphatic polyesters soaked in deep seawaters and isolation of poly(ε-caprolactone)-degrading bacteria, Polym. Degrad. Stab. 96 (2011) 1397–1403, https://doi.org/10.1016/j.polymdegradstab.2011.03.004.
[25] T. Omura, N. Isobe, T. Miura, S. Ishii, M. Mori, Y. Ishitani, S. Kimura, K. Hidaka, K. Komiyama, M. Suzuki, K. Kasuya, H. Nomaki, R. Nakajima, M. Tsuchiya, S. Kawagucci, H. Mori, A. Nakayama, M. Kunioka, K. Kamino, T. Iwata, Microbial decomposition of biodegradable plastics on the deep-sea floor, Nat. Commun. 15 (2024) 568, https://doi.org/10.1038/s41467-023-44368-8.
[26] L. Manfra, L. Albarano, A. Rotini, F. Biandolino, E. Prato, F. Carraturo, G. Chiaretti, O. Faraponova, M. Salamone, C. Sebbio, A. Siciliano, A. Tornambè, G. Libralato, Can biodegradable plastics mitigate plastamination? Feedbacks from marine organisms, J. Hazard. Mater. 487 (2025) 137179, https://doi.org/10.1016/j.jhazmat.2025.137179.
[27] M. Tosin, M. Weber, M. Siotto, C. Lott, F.Degli Innocenti, Laboratory test methods to determine the degradation of plastics in marine environmental conditions, Front. Microbio. (2012) 3, https://doi.org/10.3389/fmicb.2012.00225.
[28] P. Feijoo, A. Marín, E. Sánchez-Safont, J. Tena-Medialdea, J.R. García-March, J. Gámez-Pérez, L. Cabedo, Marine degradation of plastics in Western Mediterranean Sea: comparison between biodegradable and conventional polymers, Polym. Degrad. Stab. 234 (2025) 111222, https://doi.org/10.1016/j.polymdegradstab.2025.111222.
[29] F. De Falco, R. Avolio, M.E. Errico, E. Di Pace, M. Avella, M. Cocca, G. Gentile, Comparison of biodegradable polyesters degradation behavior in sand, J. Hazard. Mater. 416 (2021) 126231, https://doi.org/10.1016/j.jhazmat.2021.126231.
[30] M. Shin, H. Kim, S. Kim, H.J. Kim, D.X. Oh, J. Park, Biodegradation behavior of polyesters with various internal chemical structures and external environmental factors in real seawater, Polym. Test. 132 (2024) 108357, https://doi.org/10.1016/j.polymertesting.2024.108357.
[31] International Organization for Standardization, Plastics - Determination of Aerobic Biodegradation of Non-Floating Plastic Materials in a Seawater/Sandy Sediment Interface - Method by Measuring the Oxygen Demand in Closed Respirometer, International Organization for Standardization, Geneva, Switzerland, 2016.
[32] International Organization for Standardization, Plastics - Determination of Aerobic Biodegradation of Non-Floating Plastic Materials in a Seawater/Sediment Interface - Method by Analysis of Evolved Carbon Dioxide, International Organization for Standardization, Geneva, Switzerland, 2020.
[33] International Organization for Standardization, Plastics - Determination of the Aerobic Biodegradation of Non-floating Materials Exposed to Marine Sediment - Method by Analysis of Evolved Carbon Dioxide, International Organization for Standardization, Geneva, Switzerland, 2019.
[34] ASTM International, Standard Test Method For Determining Aerobic Biodegradation of Plastic Materials in Soil, ASTM International, West Conshohocken, PA, 2018.
[35] International Organization for Standardization, Plastics - Determination of the aerobic biodegradation of plastic materials exposed to seawater, International Organization for Standardization, Geneva, Switzerland, 2020.
[36] D. Briassoulis, A. Pikasi, N.G. Papardaki, A. Mistriotis, Biodegradation of plastics in the pelagic environment of the coastal zone – Proposed test method under controlled laboratory conditions, Sci. Total Environ. 912 (2024) 168889, https://doi.org/10.1016/j.scitotenv.2023.168889.
[37] P. Jariyasakoolroj, P. Kumsang, S. Phattarateera, N. Kerddonfag, Enhanced impact resistance, oxygen barrier, and thermal dimensional stability of biaxially processed miscible poly(Lactic Acid)/poly(Butylene Succinate) thin films, Polym. (Basel) 16 (2024) 3033, https://doi.org/10.3390/polym16213033.
[38] M. Gammino, C. Gioia, A. Maio, R. Scaffaro, G. Lo Re, Chemical-free reactive melt processing of biosourced poly(butylene-succinate-adipate) for improved mechanical properties and recyclability, ACS Appl. Polym. Mater. 6 (2024) 5866–5877, https://doi.org/10.1021/acsapm.4c00514.
[39] N. Ruocco, I. Bertocci, M. Munari, L. Musco, D. Caramiello, R. Danovaro, V. Zupo, M. Costantini, Morphological and molecular responses of the sea urchin paracentrotus lividus to highly contaminated marine sediments: the case study of Bagnoli-Coroglio brownfield (Mediterranean Sea), Mar. Environ. Res. 154 (2020) 104865, https://doi.org/10.1016/j.marenvres.2019.104865.
[40] L. Albarano, V. Zupo, D. Caramiello, M. Toscanesi, M. Trifuoggi, M. Guida, G. Libralato, M. Costantini, Sub-chronic effects of slight PAH- and PCB-contaminated mesocosms in Paracentrotus lividus Lmk: a multi-endpoint approach and De novo transcriptomic, IJMS 22 (2021) 6674, https://doi.org/10.3390/ijms22136674.
[41] R. Esposito, S. Federico, A. Amato, T. Viel, D. Caramiello, A. Macina, M. Miralto, L. Ambrosino, M.L. Chiusano, M. Cocca, L. Manfra, G. Libralato, V. Zupo, M. Costantini, Isolation and identification of bacterial strains colonizing the surface of biodegradable polymers, Microorganisms 13 (2025) 609, https://doi.org/10.3390/microorganisms13030609.
[42] E.W. Fischer, H.J. Sterzel, G. Wegner, Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions, Kolloid-Z.u.Z. Polym. 251 (1973) 980–990, https://doi.org/10.1007/BF01498927.
[43] V. Crescenzi, G. Manzini, G. Calzolari, C. Borri, Thermodynamics of fusion of poly-β-propiolactone and poly-ϵ-caprolactone. Comparative analysis of the melting of aliphatic polylactone and polyester chains, Eur. Polym. J. 8 (1972) 449–463, https://doi.org/10.1016/0014-3057(72)90109-7.
[44] S. Pradeep, H. Kharbas, L.-S. Turng, A. Avalos, J. Lawrence, S. Pilla, Investigation of thermal and thermomechanical properties of biodegradable PLA/PBSA composites processed via supercritical fluid-assisted foam injection molding, Polym. (Basel) 9 (2017) 22, https://doi.org/10.3390/polym9010022.
[45] C. Thellen, M. Coyne, D. Froio, M. Auerbach, C. Wirsen, J.A. Ratto, A. Processing, Characterization and marine biodegradation study of melt-extruded polyhydroxyalkanoate (PHA) films, J. Polym. Environ. 16 (2008) 1–11, https://doi.org/10.1007/s10924-008-0079-6.
[46] M.C. Righetti, M.L. Di Lorenzo, P. Cinelli, M. Gazzano, Temperature dependence of the rigid amorphous fraction of poly(butylene succinate), RSC Adv. 11 (2021) 25731–25737, https://doi.org/10.1039/D1RA03775G.
[47] L.S. Dilkes-Hoffman, P.A. Lant, B. Laycock, S. Pratt, The rate of biodegradation of PHA bioplastics in the marine environment: a meta-study, Mar. Pollut. Bull. 142 (2019) 15–24, https://doi.org/10.1016/j.marpolbul.2019.03.020.
[48] A. Nakayama, N. Yamano, N. Kawasaki, Biodegradation in seawater of aliphatic polyesters, Polym. Degrad. Stab. 166 (2019) 290–299, https://doi.org/10.1016/j.polymdegradstab.2019.06.006.
[49] S. López-Ibáñez, R. Beiras, Is a compostable plastic biodegradable in the sea? A rapid standard protocol to test mineralization in marine conditions, Sci. Total Environ. 831 (2022) 154860, https://doi.org/10.1016/j.scitotenv.2022.154860.
[50] S. Chinaglia, M. Tosin, F. Degli-Innocenti, Biodegradation rate of biodegradable plastics at molecular level, Polym. Degrad. Stab. 147 (2018) 237–244, https://doi.org/10.1016/j.polymdegradstab.2017.12.011.
[51] O. Gil-Castell, J.D. Badia, S. Ingles-Mascaros, R. Teruel-Juanes, A. Serra, A. Ribes-Greus, Polylactide-based self-reinforced composites biodegradation: individual and combined influence of temperature, water and compost, Polym. Degrad. Stab. 158 (2018) 40–51, https://doi.org/10.1016/j.polymdegradstab.2018.10.017.
[52] P. Cabrera-García, M.D. Marrero, A.N. Benítez, Disintegration and marine biodegradability of biocomposite using Pennisetum setaceum fiber and PLA as matrix, Polym. Degrad. Stab. 230 (2024) 111026, https://doi.org/10.1016/j.polymdegradstab.2024.111026.
[53] C.A. Gracia-Fernández, S. Gómez-Barreiro, J. López-Beceiro, S. Naya, R. Artiaga, New approach to the double melting peak of poly(L -lactic acid) observed by DSC, J. Mater. Res. 27 (2012) 1379–1382, https://doi.org/10.1557/jmr.2012.57.
[54] Z. Su, Q. Li, Y. Liu, G. Hu, C. Wu, Multiple melting behavior of poly(lactic acid) filled with modified carbon black, J. Polym. Sci. B Polym. Phys. 47 (2009) 1971–1980, https://doi.org/10.1002/polb.21790.
[55] R. Avolio, R. Castaldo, G. Gentile, V. Ambrogi, S. Fiori, M. Avella, M. Cocca, M. E. Errico, Plasticization of poly(lactic acid) through blending with oligomers of lactic acid: effect of the physical aging on properties, Eur. Polym. J. 66 (2015) 533–542, https://doi.org/10.1016/j.eurpolymj.2015.02.040.
[56] N. Altaee, G.A. El-Hiti, A. Fahdil, K. Sudesh, E. Yousif, Biodegradation of different formulations of polyhydroxybutyrate films in soil, SpringerPlus 5 (2016) 762, https://doi.org/10.1186/s40064-016-2480-2.
[57] E.-R. Radu, D.M. Panaitescu, C.-A. Nicolae, R.A. Gabor, V. Rădiţoiu, S. Stoian, E. Alexandrescu, R. Fierăscu, I. Chiulan, The soil biodegradability of structured composites based on cellulose cardboard and blends of polylactic acid and polyhydroxybutyrate, J. Polym. Environ. 29 (2021) 2310–2320, https://doi.org/10.1007/s10924-020-02017-x.
[58] Naznin Sultana, Study of in vitro degradation of biodegradable polymer based thin films and tissue engineering scaffolds, Afr. J. Biotechnol. 10 (2011), https://doi.org/10.5897/AJB11.2742.
[59] S.-F. Yao, X.-T. Chen, H.-M. Ye, Investigation of structure and crystallization behavior of poly(butylene succinate) by fourier transform infrared spectroscopy, J. Phys. Chem. B 121 (2017) 9476–9485, https://doi.org/10.1021/acs.jpcb.7b07954.

[60] E. Sasimowski, Ł. Majewski, M. Grochowicz, Artificial ageing, chemical resistance, and biodegradation of biocomposites from poly(Butylene Succinate) and wheat bran, Mater. (Basel) 14 (2021) 7580, https://doi.org/10.3390/ma14247580.
[61] L. Cai, Z. Qi, J. Xu, B. Guo, Z. Huang, Study on the photodegradation stability of poly(butylene Succinate- *co* -butylene Adipate)/TiO_2 nanocomposites, J. Chem. 2019 (2019) 1–9, https://doi.org/10.1155/2019/5036019.
[62] S. Carroccio, P. Rizzarelli, C. Puglisi, G. Montaudo, MALDI investigation of photooxidation in aliphatic polyesters: poly(butylene succinate), Macromolecules 37 (2004) 6576–6586, https://doi.org/10.1021/ma049633e.
[63] Y. Zhang, J. Xu, B. Guo, Photodegradation behavior of poly(butylene succinate-co-butylene adipate)/ZnO nanocomposites, Colloids Surf. A: Physicochem. Eng. Asp. 489 (2016) 173–181, https://doi.org/10.1016/j.colsurfa.2015.10.038.
[64] M. Julinová, D. Šašinková, A. Minařík, M. Kaszonyiová, A. Kalendová, M. Kadlečková, A. Fayyazbakhsh, M. Koutný, Comprehensive biodegradation analysis of chemically modified poly(3-hydroxybutyrate) materials with different crystal structures, Biomacromolecules 24 (2023) 4939–4957, https://doi.org/10.1021/acs.biomac.3c00623.
[65] J. Zhang, H. Sato, I. Noda, Y. Ozaki, Conformation rearrangement and molecular dynamics of poly(3-hydroxybutyrate) during the melt-crystallization process investigated by infrared and two-dimensional infrared correlation spectroscopy, Macromolecules 38 (2005) 4274–4281, https://doi.org/10.1021/ma0501343.
[66] R.V. Chernozem, I.O. Pariy, A. Pryadko, A.P. Bonartsev, V.V. Voinova, V. A. Zhuikov, T.K. Makhina, G.A. Bonartseva, K.V. Shaitan, V.V. Shvartsman, D. C. Lupascu, K.N. Romanyuk, A.L. Kholkin, R.A. Surmenev, M.A. Surmeneva, A comprehensive study of the structure and piezoelectric response of biodegradable polyhydroxybutyrate-based films for tissue engineering applications, Polym. J. 54 (2022) 1225–1236, https://doi.org/10.1038/s41428-022-00662-8.
[67] K.R.Reddy Khasanah, H. Sato, I. Takahashi, Y. Ozaki, Intermolecular hydrogen bondings in the poly(3-hydroxybutyrate) and chitin blends: their effects on the crystallization behavior and crystal structure of poly(3-hydroxybutyrate), Polym. (Guildf) 75 (2015) 141–150, https://doi.org/10.1016/j.polymer.2015.08.011.
[68] Y. Cao, B. Zhang, X. Song, G. Dong, Y. Zhang, B. Chen, Polyhydroxybutyrate plastics show rapid disintegration and more straightforward biogeochemical impacts than polyethylene under marine biofragmentation, Environ. Sci. Technol. 58 (2024) 14496–14505, https://doi.org/10.1021/acs.est.4c04639.
[69] R. Sachan, R. Purwar, Soil burial degradation studies of photo-crosslinked PCL-PDMS-PCL triblock copolymer films, Polym. Eng. Sci. 63 (2023) 4107–4117, https://doi.org/10.1002/pen.26511.
[70] N.B. Erdal, G.A. Lando, A. Yadav, R.K. Srivastava, M. Hakkarainen, Hydrolytic degradation of porous crosslinked poly(ε-Caprolactone) synthesized by high internal phase emulsion templating, Polym. (Basel) 12 (2020) 1849, https://doi.org/10.3390/polym12081849.
[71] P. Chaber, M. Kwiecień, M. Zięba, M. Sobota, G. Adamus, The heterogeneous selective reduction of PHB as a useful method for preparation of oligodiols and surface modification, RSC Adv. 7 (2017) 35096–35104, https://doi.org/10.1039/C7RA06111K.
[72] G. Yu, R.H. Marchessault, Characterization of low molecular weight poly (β-hydroxybutyrate)s from alkaline and acid hydrolysis, Polym. (Guildf) 41 (2000) 1087–1098, https://doi.org/10.1016/S0032-3861(99)00230-X.
[73] J. Pal, S. Sanwaria, A. Choudhary, K. Thakur, B. Nandan, R.K. Srivastava, Thermally initiated trans-esterification in poly(ε-caprolactone) and its dependence on molecular weight, J. Polym. Environ. 22 (2014) 479–487, https://doi.org/10.1007/s10924-014-0669-4.
[74] K. Żółtowska, M. Sobczak, E. Olędzka, Novel zinc-catalytic systems for ring-opening polymerization of ε-caprolactone, Molecules 20 (2015) 2816–2827, https://doi.org/10.3390/molecules20022816.
[75] T. Debuissy, E. Pollet, L. Avérous, Synthesis and characterization of biobased poly (butylene succinate- ran -butylene adipate), Anal. Compos.-Depend. Physicochem. Prop. Eur. Polym. J. 87 (2017) 84–98, https://doi.org/10.1016/j.eurpolymj.2016.12.012.
[76] J.-H. Zhao, X.-Q. Wang, J. Zeng, G. Yang, F.-H. Shi, Q. Yan, Biodegradation of poly (butylene succinate-co-butylene adipate) by Aspergillus versicolor, Polym. Degrad. Stab. 90 (2005) 173–179, https://doi.org/10.1016/j.polymdegradstab.2005.03.006.
[77] I.-N. Georgousopoulou, S. Vouyiouka, P. Dole, C.D. Papaspyrides, Thermo-mechanical degradation and stabilization of poly(butylene succinate), Polym. Degrad. Stab. 128 (2016) 182–192, https://doi.org/10.1016/j.polymdegradstab.2016.03.012.
[78] S. Ali, Z. Khatri, K.W. Oh, I.-S. Kim, S.H. Kim, Preparation and characterization of hybrid polycaprolactone/cellulose ultrafine fibers via electrospinning, Macromol. Res. 22 (2014) 562–568, https://doi.org/10.1007/s13233-014-2078-x.