



(Bio)degradation of biopolymer and biocomposite in deep-sea environments

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ARTICLE INFO

Keywords:

Marine pollution
Deep sea
Biopolymer
Biodegradation
Biocomposite
PHBV
Natural fibres

ABSTRACT

In order to reduce the contamination of marine ecosystems by plastic materials, the scientific community is engaged in the development of biodegradable substitutes for conventional plastics. While certain candidates have been successfully tested in coastal marine environments, the degradation process in deep-sea environments remains poorly understood. This study examined the degradation of two industrial biopolyesters, a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and a polybutylene-succinate (PBS), in two deep marine environments of the Middle and Eastern Atlantic, at depths of 780 and 1740 m, as well as under laboratory conditions under hydrostatic pressure and without micro-organisms. The findings reveal a considerable biodeterioration of PHBV and a pronounced influence of flax fibre reinforcement on the degradation mechanisms. Conversely, PBS exhibits minimal to no indications of degradation. Additionally, the results confirm that biotic factors are the primary determinants of the degradation processes, with no degradation observed under abiotic conditions.

1. Introduction

The consumption of plastic materials in modern societies is extremely high, encompassing the vast majority of consumer goods (Abrahms-Kavunenko, 2023; Rothman and Ryan, 2023). Since the advent of these inexpensive and easily processable materials in the 1960s, production has continuously increased (Plastics Europe, 2022). This increase in consumption is accompanied by widespread pollution of the planet's environments. The pervasive nature of plastic pollution has led to its designation as an indicator of a new geological era, the Anthropocene (Rangel-Buitrago and Neal, 2023) and the United Nations has declared it one of the most significant challenges of the 21st century (United Nations Environment Assembly, 2022). One particularly vulnerable ecosystem is the marine environment. A substantial body of evidence now exists which demonstrates the extent of plastic pollution in this environment. All the environments of the five oceans are affected, including coastal regions (Lebreton et al., 2019), surface waters (Eriksen et al., 2014), water columns (Pabortsava and Lampitt, 2020), and the deep sea (Harris et al., 2023). This pollution has been demonstrated to

have severe impacts on marine ecosystems, with macroplastics (e.g., plastic debris) causing suffocation and depletion of marine macrofauna (e.g., large marine organisms such as fish, crabs, and sea turtles) (Kühn et al., 2015), and microplastics (e.g., plastic particles less than 5 mm in size) being found in all marine species (Worm et al., 2017). The consequences of this contamination remain poorly understood, although negative impacts have been identified (Hermabessiere et al., 2017; Worm et al., 2017).

When loss at sea is unavoidable, one potential solution to reduce the impact of plastic pollution on the environment while maintaining a certain level of plastic consumption is to substitute conventional plastic materials with biodegradable polymers that present similar mechanical properties and processing methods (Shen et al., 2020). In coastal marine environments, the most promising candidates are biopolyesters, cellulose and starch derivatives (Haider et al., 2019; Wang et al., 2021). The biodegradation process of these materials is relatively well understood, comprising three interdependent and simultaneous stages: deterioration, fragmentation, and assimilation. These stages are detailed in the following reviews (Laycock et al., 2017; Lucas et al., 2008; Wang et al.,

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<https://doi.org/10.1016/j.marpolbul.2024.117230>

Received 20 September 2024; Received in revised form 28 October 2024; Accepted 28 October 2024

Available online 12 November 2024

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2021). The deterioration and fragmentation of these materials can result from abiotic processes, such as mechanical stresses or hydrolytic ageing. However, the rates of these processes are significantly accelerated when they are catalysed by biotic factors, the most common of which is enzymatic hydrolysis. Conversely, the final stage of biodegradation, namely assimilation, which enables the reintroduction of the material's constitutive elements into the natural biogeochemical cycles, is only possible with the requisite microorganisms. Therefore, living microbial communities in the degradation environment represent the predominant factor. The methods developed by standardising bodies to evaluate biodegradation rates (e. g., (ASTM, 2017; ISO, 2017, 2020)) have been the subject of criticism by the scientific community, which has not yet developed a consensus methodology (Harrison et al., 2018; Wang et al., 2021). The latest studies and reviews on the subject recommend conducting multidisciplinary studies linking biology and polymer science (Briassoulis et al., 2024; Hyodo et al., 2024; Omura et al., 2024; Shah et al., 2008) and to maintain a strong connection with real environmental conditions (Cheng et al., 2022; Harrison et al., 2018; Lott et al., 2020; Royer et al., 2023).

Biodegradable polymers can be reinforced with plant fibres to create materials that are more rigid and stronger, thereby enabling their use in structural applications (Bodros et al., 2007). The reinforcement with natural fibres has also a positive impact on the life cycle analyses of the final material (Ahmad et al., 2022; Gomez-Campos et al., 2021; Le Duigou et al., 2011). Concerning their biodegradation, the reinforcement has been demonstrated to enhance the biodegradation kinetics in compost or terrestrial conditions but its impact on marine biodegradation has been barely studied; the few studies conducted on miscanthus or algae showed similar results in coastal marine environments (Meereboer et al., 2021; Rajeshkumar et al., 2023). Plant fibres are naturally biodegradable in a wide range of environments (Erdal and Hakkarainen, 2022). Therefore the biodegradation of a biocomposite in a given environment is assumed to be contingent upon the matrix's ability to biodegrade in that environment. A multitude of fibre-producing plants have been employed by humans for an extended period of time, with some yielding cells that possess exceptional characteristics (Bourmaud et al., 2018). Notably, the supporting tissues of flax stems, which are available in Europe, exhibit excellent mechanical properties, a high aspect ratio, and the potential to create high-performance composites (Baley et al., 2019) without significant adhesion issues with biopolymers (Pantaloni et al., 2021). Additionally, they possess a biochemical composition conducive to biodegradation, exhibiting a low lignin content of approximately 2 % (Day et al., 2005; Love et al., 1994; Zambrano et al., 2020), content that has been demonstrated to influence the degradation rate negatively in aquatic environments (Kwon et al., 2021).

Recent studies and models of marine pollution indicate that deep-sea environments may act as a final sink for the majority of marine debris entering the world's oceans (Harris et al., 2023; Woodall et al., 2014) either transported by currents, or through processes of fragmentation and aggregation (Kane and Clare, 2019). However, a large majority of biodegradation studies are still conducted in coastal environments or using coastal environment microorganisms and environmental parameters. Consequently, the state of knowledge regarding biodegradation mechanisms in deep-sea environments is extremely limited (Chamley et al., 2024). Only two studies on biodegradation have been conducted in situ, in the Pacific Ocean, in five different deep-sea environments (Hyodo et al., 2024; Omura et al., 2024). These environments are characterised by a high degree of diversity, encompassing a wide range of environmental conditions and their ecosystems remain largely unknown (Harris et al., 2014; Ramirez-Llodra, 2020). The diversity and quantity of the organisms that inhabit these environments are influenced by a number of factors, including the location within an ocean basin and the geological features of the surrounding area, the input of nutrients, pressure, and temperature (Harris, 2020; Ramirez-Llodra et al., 2010; Wang et al., 2013). Given the absence of UV and the low

temperatures, abiotic degradation pathways are negligible, and degradation mechanisms are contingent upon the presence of living degraders (Laycock et al., 2017). To confirm the presence of these organisms across all ocean basins, further studies are therefore required, with a particular focus on other deep ocean locations.

The present study aims to characterize the biodegradation in deep ocean environments of two industrial biopolymers for which biodegradation has been observed in terrestrial and coastal marine environments: a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and a polybutylene succinate (PBS) (Table 1). In order to cover a wider range of mechanical properties and to potentially increase the biodegradation kinetics, the impact of a reinforcement with natural fibres is also studied. Specimens were immersed at two deep-sea locations of the Middle and Eastern Atlantic, at depths of 780 and 1740 m. In situ ageing is compared to abiotic ageing in the laboratory under similar hydrostatic pressures, in order to better understand degradation mechanisms. Various material properties including weight, surface aspect, porosity, tensile properties, thermal properties and molecular chain length, are investigated throughout the different ageing periods to characterize the degradation.

2. Materials and methods

2.1. Materials

The materials studied are described in Table 1. Two polyesters, which are candidates for biodegradation in deep-sea environments, and a conventional polycarbonate plastic are investigated. Composite specimens with flax fibre reinforcement were also produced for the two polyester materials. The latter are referenced as PHBV-Flax and PBS-Flax in this document.

The injection moulding process was performed using an 80-tonne Battenfeld injection moulding machine (Wittman Battenfeld, Kottlingbrunn, Austria). The samples were injected in accordance with the standard ISO 527 procedure (ISO, 2012), with an initial step of drying of the pellets, to produce specimens of the H3 shape (see Table S1 for more processing information). To reinforce the material with flax fibres, granulates were produced by compounding with 30 % by weight of flax fibres using a Fairex single-screw extruder machine (Fairex, England). The length and diameter of the screw were 600 mm and 20 mm, respectively, resulting in an L/D ratio of approximately 30. The same parameters used for the pure material were then employed for the injection moulding process.

2.2. In situ ageing

This study investigated natural environmental degradation at two distinct deep-sea locations: CHEREEF-OBS, which is located within Lampaul Canyon at an approximate depth of 780 m, and the EMSO Azores site, which is positioned along the mid-Atlantic ridge at a depth of 1742 m. More details and environmental parameters are given in Table 2.

The samples were immersed during the 2022 campaign (Menot and Tourolle, 2022; Sarradin and Matabos, 2022) and subsequently

Table 1
Materials studied.

	Formal name	Abbr.	Supplier
Injected material	Poly[(R)-3-hydroxybutyrate-co-3-mol%-(R)-3-hydroxyvalerate]	PHBV	NaturePlast PHI002
	Poly(butylene succinate)	PBS	NaturePlast PBI002
	Polycarbonate – Polybutylene terephthalate (Makroblend)	MkB	Covestro UT6005
Reinforcement fibres	Flax fibres	FF	Van Robaey 2 mm

Table 2
Ageing conditions.

Site name	Localisation	Abbr.	Environment	Depth (m)	P (bar)	T (°C)	Longitude	Latitude
CHEREEF-OBS	Lampaul canyon, bay of Biscay	S1-780	Submarine canyon	778	79	[9.9–10.3]	−7.5363	47.6116
EMSO Azores	SEAMON WEST station, Mid Atlantic ridge	S2-1740	Lava lake	1742	177	[4.4–4.6]	−32.2798	37.2912
IFREMER	Brest, France	L1-Abio	Laboratory, Pressure chamber	0	177	15		

recovered during the 2023 campaign (Matabos, 2023; Menot and Tourolle, 2023), for a total period of 377 days for S1-780 and 401 days for S2-1740. They were immersed in oyster bags secured with nylon rope. Each bag contained between seven and ten samples of each material. At S1-780, the bags were fixed to a deep-sea observation platform, which is brought to the surface for annual maintenance. At S2-1740, the samples were deployed on the seabed and subsequently retrieved using a remotely operated underwater vehicle (ROV). Upon retrieval, three distinct sampling procedures were applied. First, four or five samples were rinsed with distilled water, dried, and stored at 4 °C in zip lock bags. These samples were designated for mechanical and physico-chemical investigation. Second, a sample was taken from the remaining samples and stored in a flask containing sterile seawater and glutaraldehyde (concentration 2.5 %) for biofilm fixing. After 15 h these samples were transferred to a storage solution (sterile seawater and sodium azide at a concentration of 0.5 g.L^{−1}). The remaining samples were flash-frozen and stored at −80 °C in sterile zip lock bags for microbiological investigations that are not presented in this paper.

2.3. Laboratory ageing

In order to enhance the comprehension of the degradation observed in situ, abiotic degradation was investigated in the laboratory. This ageing campaign was performed exclusively on the samples PHBV and PHBV-Flax (which demonstrate significant degradation signs after in situ ageing) and the material of reference (MkB). The samples were immersed in sterilised seawater at the hydrostatic pressure of S2-1740 (177 bar) using a hyperbaric pressure chamber designed for seawater pressure ageing. The ageing process was conducted over a period of one year, with samples removed for testing at M1, M3, M6 and M12. Depressurisation and repressurisation were required for each sampling operation. For sterilisation, seawater was autoclaved and antibiotics, chloramphenicol and penicillin G, were added to the seawater at concentrations of 50 mg.L^{−1} and 10 mg.L^{−1}, respectively. This ageing condition is referred to as L1-Abio later in this document.

2.4. Weight-loss

The weights of each sample were measured before and after the ageing processes, using an electronic balance with a precision of 10^{−3} g. Three to five samples were studied for each sampling. The percentage of weight loss and the degradation rate are calculated using Eqs. (1) and (2). The degradation rate is defined as the mass loss ($\Delta W_{(g)}$) per day normalised by the initial area ($S_{initial (cm^2)}$), as previously defined in other degradation studies (Dilkes-Hoffman et al., 2019; Omura et al., 2024).

$$\text{Weight loss}_{(\%)} = \frac{W_{\text{initial}} - W_{\text{aged}}}{W_{\text{initial}}} \times 100 \quad (1)$$

$$D_{(\mu\text{g.cm}^{-2}.\text{day}^{-1})} = \frac{\Delta W_{(g)}}{S_{\text{initial (cm}^2)} \times t_{\text{ageing (day)}}} \times 10^{-6} \quad (2)$$

2.5. Mechanical properties

Tensile tests were conducted on an Instron™ test machine (10kN) equipped with a 10kN load cell and a laser extensometer. At least three tests were performed for each sampling point. For the injected moulded samples, the tensile test loading rates were at 1 mm.min^{−1} from 0 to 0.5 % strain, and then at 10 mm.min^{−1} until failure. The Young's modulus was calculated by linear regression of the stress-strain curve at low strain (0.1–0.4 %) [26].

2.6. X-ray tomography

Tomography is a technology based on the assembly of X-ray radiographs, which enables the digital reconstruction of the volume of the specimen under analysis. A Tomoscope XS Plus™ 200 kV tomograph from WERTH, equipped with a transmission microfocus tube, was employed. Given the dimensions of the specimens (18cm x 2cm x 4mm) and the resolution of 36 μm, eight acquisitions were necessary, with a power of 80 W, a voltage of 160 kV, and a current of 500 μA. Subsequently, porosity analyses were performed using VG Studio Max.

2.7. SEM observations

An FEI Quanta 200 scanning electron microscope (SEM) was used for surface observations. Prior to observation, each sample was coated with a thin coating (60:40 ratio of gold and palladium) to avoid surface charging.

Biofilm observations were conducted using the same scanning electron microscope. Samples from in situ ageing were dehydrated in seven successive baths of distilled water and ethanol, with an increasing proportion of ethanol (20-50-70-80-90-100-100 %) for 30 min in each bath. Subsequently, the ethanol was expelled from the sample using the critical point method, performed with a LEICA CPD 300. The samples were then observed in the SEM as described above.

2.8. Thermal properties

The thermal properties of the samples were analysed using differential scanning calorimetry (DSC) with a Discovery DSC 25, manufactured by TA Instruments. For each ageing condition, three samples of approximately 8 mg were subjected to analysis in a sealed aluminium pan. The test comprised two heating ramps at 10 °C per minute until the melting point, followed by a cooling ramp at 5 °C per minute, with a five-minute stabilisation period between the ramps. The temperature range for PHBV was set at [0; 200] °C, and at [−40; 130] °C for PBS. The degree of crystallinity (χ_c) was calculated using the Eq. (3) with the theoretical melting enthalpy values for 100 % crystallinity derived from the literature: 146 J.g^{−1} for PHBV (Deroiné et al., 2014a) and 200 J.g^{−1} for PBS (Papageorgiou and Bikiaris, 2005). For fibre-reinforced samples, crystallinity was normalised with respect to the proportion of fibres added (30 % by weight).

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (3)$$

2.9. Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) was conducted with GPC Agilent Technologies 1260 Infinity II High Temperature equipment at 40 °C, with an injection volume of 2 mL, a flow rate of 1 mL·min⁻¹, an Agilent-DRI refractive index detector, and two columns (two PL Gel Mixed B 10 µm). Calibration was conducted using chloroform and polystyrene standards. Prior to analysis, the samples were dissolved in a chloroform solution for a period of 10 h at 50 °C, after which they were filtered through a 1-micrometre filter. The weight-average molecular weight (Mw) and number-average molecular weight (Mn) were obtained from the GPC analysis. The polydispersity index (PI) was calculated as Mw/Mn.

3. Results

3.1. Biofilm observations

The SEM images of fixed biofilms on specimens aged under both in situ conditions revealed a considerable number of organisms on PHBV-Flax and PBS-Flax, and fewer on PHBV (Fig. 1, Fig. S1). The levels of colonisation were considerably lower for both PBS and MkB (Fig. S2). In the case of PBS, some bacterial aggregates are present in very localised regions (Fig. S4.A–B). Concerning the diversity of organisms identified, the majority were bacteria on the pure materials (PHBV, PBS, MkB). A greater diversity of organisms was observed in the flax fibre-reinforced specimens, including a wider variety of bacterial forms such as bacterial chains and filamentous bacteria, as well as potential fungi, archaea, and nematodes. The latter were observed exclusively at site S1-780. Another

notable difference between the two sites is the morphology of the bacteria, which were predominantly bacillus-shaped at S1-780 and cocci-shaped at S2-1740 (Fig. S4.C–D).

3.2. Surface degradation

The results of the scanning electron microscopy (SEM) observations indicate the presence of substantial surface degradation on the in situ samples of PHBV, PHBV-flax, and to a lesser extent, on PBS-flax (Fig. 2 and Fig. S5). The degradation observed on the PHBV and PHBV-flax samples is homogeneous across the surface, with some differences in morphology. In the case of the PHBV samples, the formation of circular holes is observed, with a notable difference of scale between the two in situ sites: holes observed in S1-780 samples are larger and deeper (Fig. 2). For PHBV-Flax samples, the surface degradation is characterised by crevices (Fig. 2). Notable differences are observed in the surface degradation of the PBS and the PBS-Flax samples between the two sites (Figs. S5–S6). For PBS-Flax samples, the S1-780 samples display homogeneous degradation, characterised by the formation of small cracks and a limited number of holes. Conversely, the surface degradation observed in the S2-1740 samples is significantly less pronounced, with only a few cracks present (Fig. S5). For the PBS samples, few signs of degradation were observed in the S1-780 samples, with the majority of the surface remaining intact and no degradation was observed for the S2-1740 samples (Fig. S6). No surface degradation was observed on any of the samples of MkB. The materials did not exhibit any indications of surface degradation following laboratory ageing under abiotic conditions (L1-Abio).

3.3. Weight loss

The gravimetric monitoring revealed a significant weight loss for PHBV-Flax, PHBV and PBS-Flax samples aged in S1-780 and S2-1740

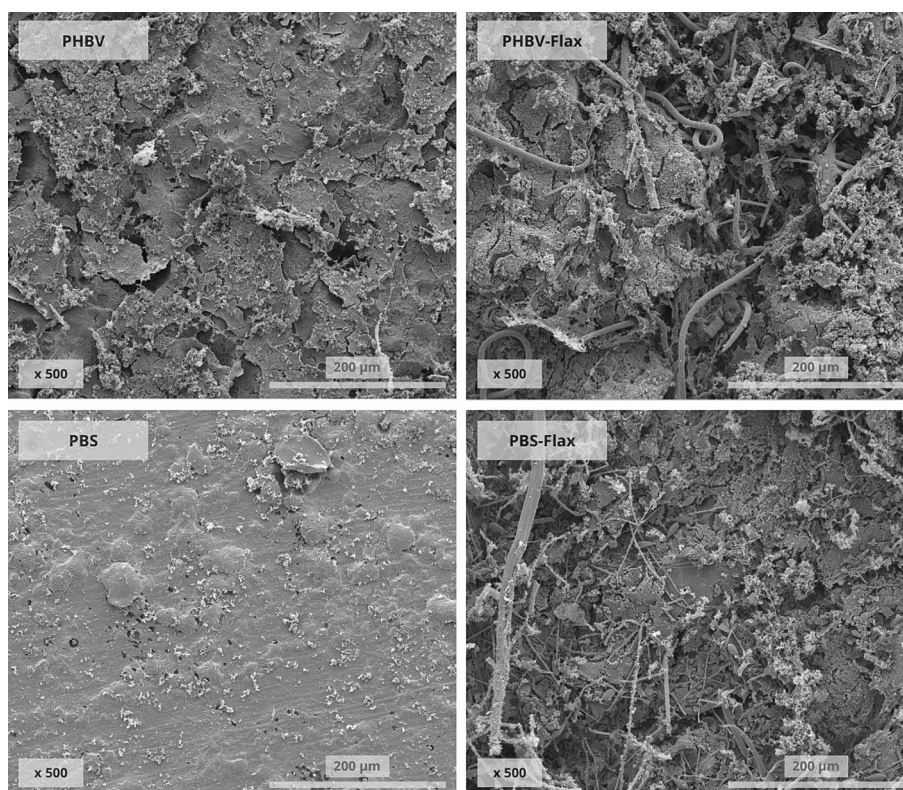


Fig. 1. SEM observations of S1-780 samples after fixing biofilm.

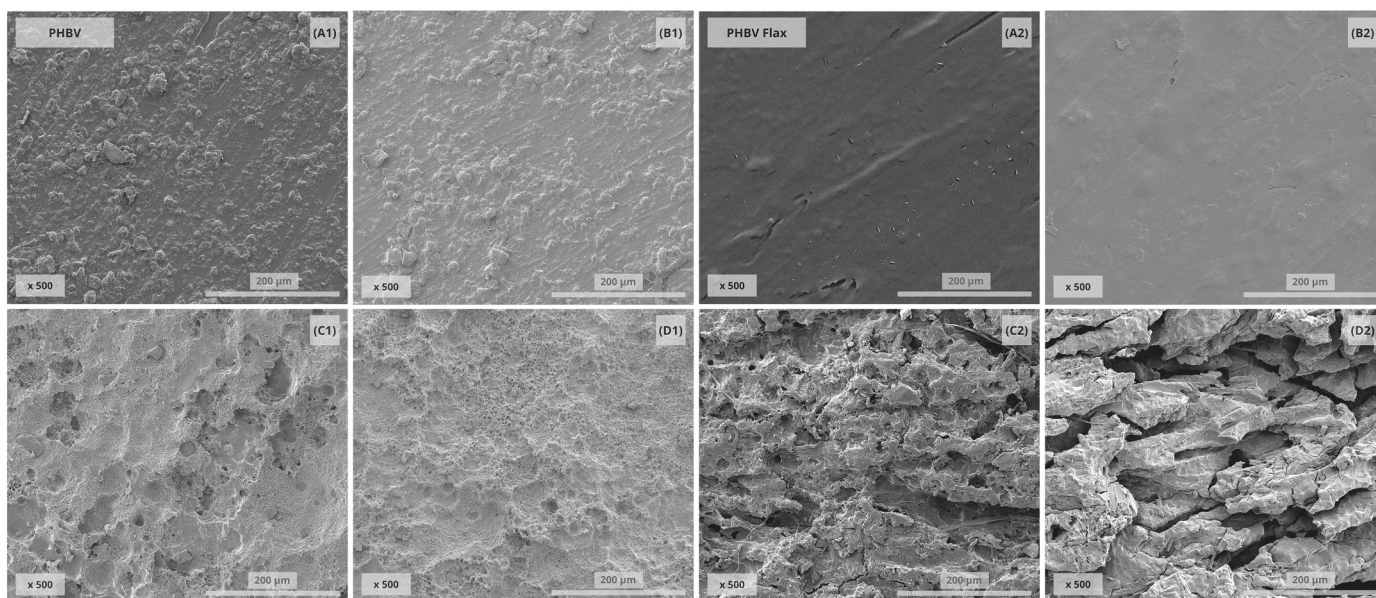


Fig. 2. SEM Pictures of PHBV (1) and PHBV-Flax (2) before and after ageing. A: Reference; B: L1-Abio; C: S1-780; D: S2-1740.

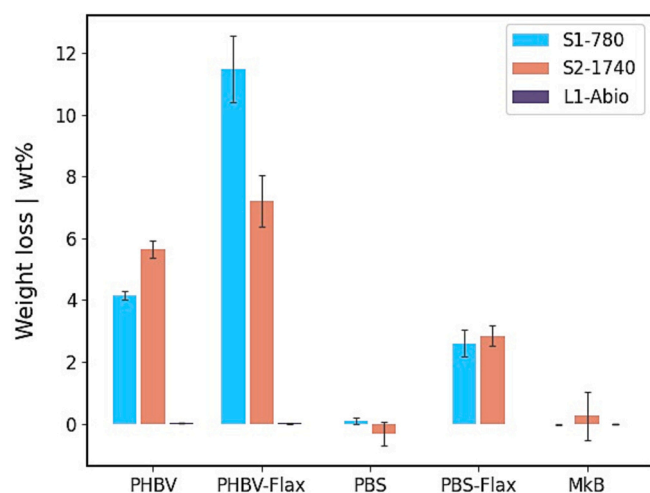


Fig. 3. Weight loss of the studied materials after ageing.

conditions (Fig. 3). Conversely, no weight variations have been measured for Makroblend and PBS samples under the same conditions. Under abiotic conditions (L1-Abio) no weight loss was observed (Fig. 3, third column, not calculated for PBS and PBS-Flax).

3.4. Tensile properties

The complete set of results from the tensile tests is presented in Table S2, and the corresponding curves are provided in the Fig. S8, both in the supplementary material section. The principal results are presented in this paragraph. The tensile tests conducted on PHBV specimens revealed no significant changes in mechanical behaviour after ageing for each condition (Fig. 4.A). Similar observations are made for the reference material (MkB, Fig. S8). The plasticity of PBS specimens is lost after ageing, as evidenced by the significant decrease in elongation at break resulting from the absence of necking; no major changes in behaviour are observed prior to failure (Young's modulus, yield strength and yield elongation) (Fig. S8). The mechanical properties of flax-reinforced specimens exhibit considerable variability: after in situ ageing, the

values of strain at break and Young's modulus decrease significantly for both PHBV-Flax and PBS-Flax (Fig. 4.C–D) and several premature failures were observed. A slight plasticization is observed for the PHBV-Flax specimens during the L1-Abiotic ageing, with an increase in elongation at break and a significant decrease in Young's modulus (Fig. 4.A–B).

3.5. Tomography

In order to enhance the comprehension of the degradation observed via gravimetry, surface observation, and tensile properties characterisation, tomographic observations were conducted on PHBV and PHBV-Flax samples. These revealed the presence of significant internal defects in the PHBV-Flax specimens aged under both conditions S1-780 and S2-1740 (Fig. 5). These defects are not observed in specimens aged under abiotic conditions (L1-Abio) nor in the initial state (Fig. 5). PHBV samples demonstrate no internal defects (Fig. S9). The appearance of these defects is characterised by a substantial increase in measured porosity (Table 3).

3.6. Thermal properties

The thermal properties of the specimens measured before and after ageing are available in the supplementary material section (Table S3). This paragraph focuses solely on the characteristics obtained during the first heating, which reflects the impact of ageing (Lucas et al., 2008). The tested materials do not exhibit significant changes in their melting temperatures, except for PHBV, which shows a slight decrease only in the case of in situ ageing (S1-780 and S2-1740). This change is also observed for PHBV-Flax and PBS-Flax but only for the S2-1740 ageing condition (Fig. 6a, Table S3). The enthalpy of fusion, and therefore the degree of crystallinity of all materials, increases slightly after ageing in most cases. Only PHBV aged under S2-1740 and L1-Abio conditions shows stable crystallinity values (Fig. 6b, Table S3).

3.7. GPC

GPC tests were performed exclusively on PHBV and PHBV-flax specimens before and after ageing under S1-780 and S2-1740 conditions. The results from the initial specimens demonstrate considerable variability despite the large number of tests conducted, particularly with

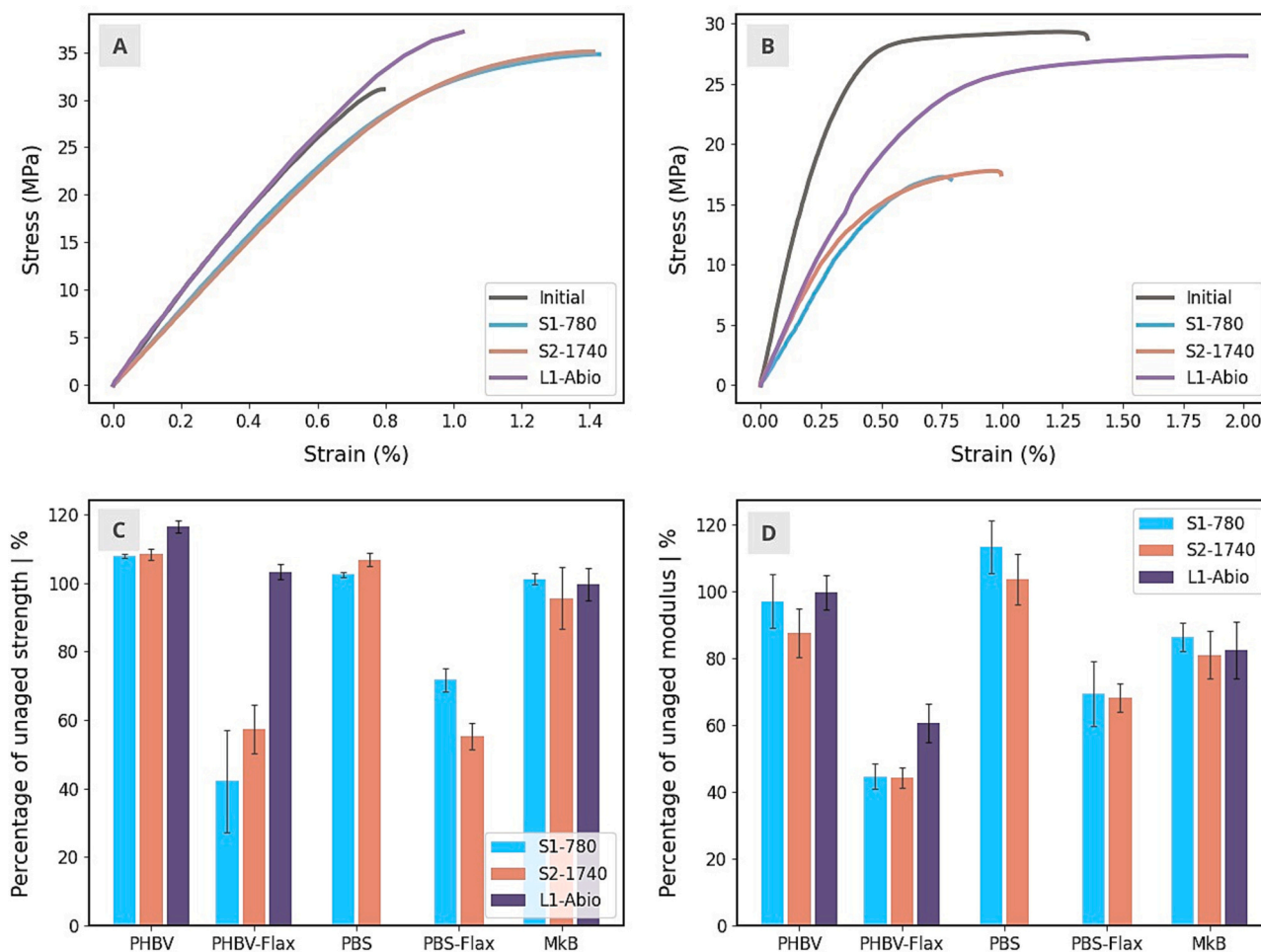


Fig. 4. Modification of mechanical properties after ageing.

(A) Tensile graph of PHBV; (B) Tensile graph of PHBV-Flax; (C) Percentage of unaged maximum strength for each material after ageing; (D) Percentage of unaged Young's modulus for each material after ageing.

regard to the number-average molecular weight (M_w) (Table 4, Table S4). Given this variability, no definitive conclusions can be drawn regarding the PHBV-Flax specimens. In contrast, the molecular weights measured on PHBV after ageing remain consistent; no reduction in chain length was observed in our specimens.

4. Discussion

4.1. Evidence of bio-deterioration

The results of the mass loss test are consistent with the SEM observations: the materials that exhibited the most significant surface degradation were also those that demonstrated the greatest mass loss (in order: PHBV-Flax, PHBV, PBS-Flax). The absence of any indications of degradation under L1-Abio conditions indicates that the mass loss and surface degradation observed in situ are not attributable to the abiotic effects of pressure or water ageing of the materials under investigation. Consequently, biological factors appear to be the dominant cause of degradation. This finding corroborates previous observations regarding the stability of PHBV in water at temperatures representative of natural environments, in the absence of microorganisms (Deroiné et al., 2014b).

4.1.1. PBS

PBS specimens displayed no significant indications of biodegradation. Following ageing under S1-780 and S2-1740 conditions, no mass loss was observed, and the surface aspect remained unaltered, with the

exception of very localised areas at S1-780 (Figs. S1, S6). The observed changes in mechanical properties (loss of ductility with very small yield property changes) can be explained by a reduction in chain length, which is characteristic of typical hydrothermal ageing (Xu and Guo, 2010). This reduction in chain length without mass losses can induce a recrystallization that could explain the slight increase of crystallinity (Fig. 6b) and stiffness observed for this material (Fig. 4) (Foulc et al., 2005). The characterisation of ageing under abiotic conditions and the evolution of the chain lengths could have provided further insight to support these hypotheses; however, this was not possible within the scope of this study. Further research is therefore required to elucidate the mechanisms underlying the observed losses in the mechanical properties of PBS.

The absence of signs of biodeterioration (mass loss and surface degradation) is corroborated by a substantial body of research indicating minimal or no biodeterioration of PBS in marine environments (Kasuya et al., 1998; Nakayama et al., 2019; Omura et al., 2024; Sashiwa et al., 2018; Sekiguchi et al., 2011). The aforementioned studies, conducted under different conditions, indicate that the conditions required for the biodegradation of PBS grades are not met in many marine environments. Consequently, it may be concluded that most currently commercialised PBS are not viable substitutes for conventional plastics in biodegradable marine applications. Nevertheless, further studies are needed to ascertain if modifications to the structural properties of PBS, for example in terms of chain length or crystallinity, could facilitate the biodegradation of the polymer across these environmental conditions.

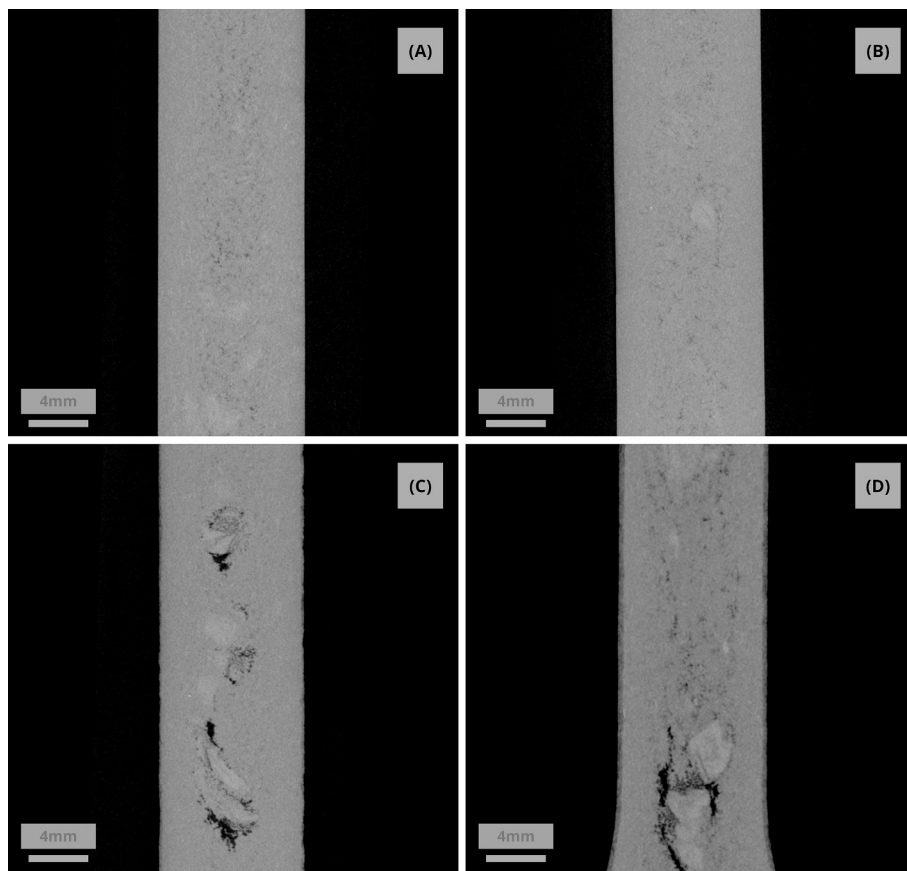


Fig. 5. Tomography images of PHBV-Flax samples before and after ageing. (A) Initial; (B) L1-Abio; (C) S1-780; (D) S2-1740.

Table 3

Measured values of porosity (μm^3) of the PHBV-Flax sample and increase with respect to Reference (%).

	L1-Abio	S1-780	S2-1740	Reference
Porosity μm^3	1.1	10.8	18.6	0.4
% increase compared to reference	184	2609	4558	-

4.1.2. PHBV

PHBV displays unambiguous evidence of biodeterioration at both in situ locations (S1-780, S2-1840). The observed surface degradation, mass loss, and the presence of biomass on the specimens are indicative of biological degradation. These observations have been previously documented in numerous other cases of biological degradation in marine environments (Deroiné et al., 2014a; Ohura et al., 1999; Omura et al., 2023, 2024). The measured physicochemical properties (molecular weights and fusion enthalpy) demonstrate relative stability, which

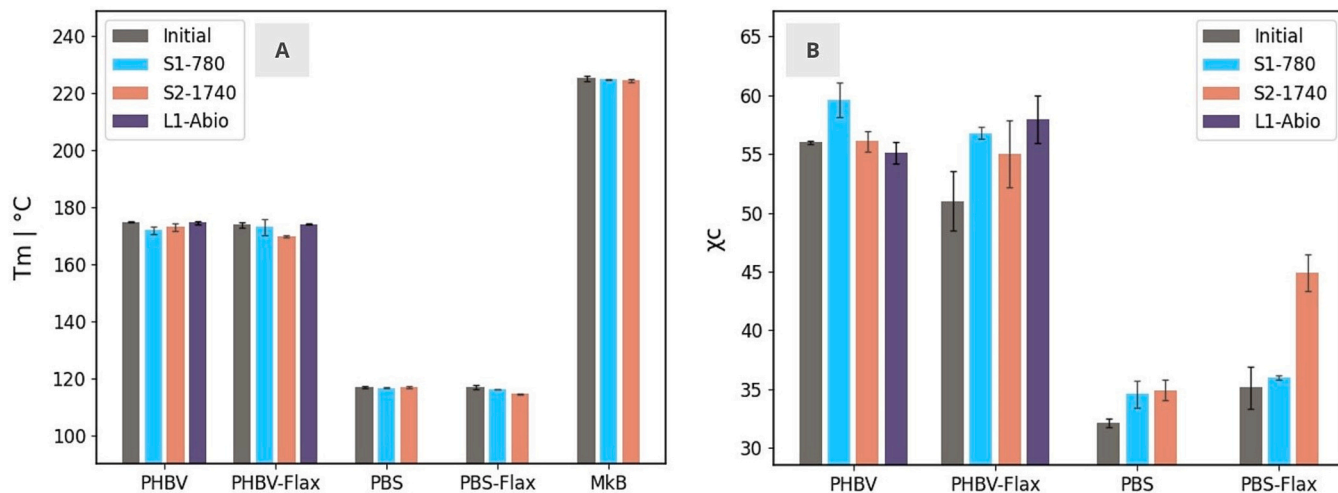


Fig. 6. (a) Melting temperature for each material for the different ageing conditions; (b) Degree of crystallinity during the first heating for each material for the different ageing conditions.

Table 4

Molecular weights measured by Gel Permeation Chromatography on PHBV specimens before and after ageing.

Site	Test number	Mw (10^3 g.mol^{-1})	Mn (10^3 g.mol^{-1})	PI
Reference	10	203 ± 8	28.5 ± 4	6.9 ± 1.5
S2-1740	4	210 ± 3	27.6 ± 0.7	7.6 ± 0.1
S1-780	1	217	27	8

aligns with the findings of other PHA biodegradation studies in marine environments (Deroiné et al., 2014a; Doi et al., 1990; Sashiwa et al., 2018). It is established that biofragmentation occurs at the surface, with the degradation products being rapidly assimilated and/or released into the biofilm. Therefore, these methods primarily reveal the properties of the remaining non-degraded material (Laycock et al., 2017). The stability of the mechanical properties, despite significant indications of biodeterioration, can also be attributed to the nature of the degradation process. The mechanical properties are susceptible to alteration only when the specimen's thickness is reduced to a level that exceeds a critical threshold, which is not met in the ageing performed in this study (Laycock et al., 2017). The loss of thickness and the substantial surface defects observed in this study are not sufficient to markedly impact the mechanical properties of the PHBV specimens.

4.1.3. Comparison with the other studies

The results obtained from weight measurements translate into degradation rates of the order of tens of microns per cm^2 per day for PHBV, PHBV-Flax, and PBS-Flax. PHBV-Flax is the most degraded material. Conversely, the reference material, Makroblend, and the PBS did not exhibit any indications of degradation (Fig. 7). These results are of a similar magnitude to those reported by Omura et al. (2024) under comparable ageing conditions (20.2 and $0 \text{ } \mu\text{g.cm}^{-2}.\text{day}^{-1}$ for injection-moulded samples of PHBV and PBS submerged at a depth of 900 m near a cold seep). These values fall within the lower range of those reported in studies on PHBV biodegradation in marine environments, as summarised by Dilkes-Hoffman et al. (2019) in their review: $40\text{--}90 \text{ } \mu\text{g.cm}^{-2}.\text{day}^{-1}$. This supports the observation made by Omura et al. (Omura et al., 2024) that deep-sea environments are less conducive to biodegradation than coastal marine environments. This is an unsurprising outcome given that these environments are predominantly oligotrophic, characterised by low temperatures and elevated pressures, which have been demonstrated to impede the activities of living organisms and their diversity (Chamley et al., 2024).

In contrast to the findings of the study conducted by Omura et al., which indicated that the degradation kinetics were strongly dependent

on the depth, the results obtained in this study demonstrate minimal to no differences in the degradation rate of the pure materials between the two sites. These findings suggest that pressure and temperature are not the primary factors influencing the degradation kinetics. It is therefore proposed that microbial community structure and activity are the primary controlling factors in this process. The enhanced degradation observed at S1-780 for PHBV-Flax samples, which is associated with the presence of a considerable number of nematodes in the biofilm, as well as an impression of greater diversity, lends support to this hypothesis (Fig. 1). Further microbiological studies are currently being performed on the collected samples to facilitate a comparison of the microbial communities present at the two sites and to provide support for or against this hypothesis.

4.2. Impact of the reinforcement with flax fibres

The results obtained for the flax fibre reinforced specimens (PHBV-Flax and PBS-Flax) demonstrate a more significant degradation compared to the pure material. The degradation rate increases significantly for both PHBV (S1-780: 20 to $65 \text{ } \mu\text{g.cm}^{-2}.\text{day}^{-1}$, S2-1740: 26 to $38 \text{ } \mu\text{g.cm}^{-2}.\text{day}^{-1}$) and PBS (0 to $15 \text{ } \mu\text{g.cm}^{-2}.\text{day}^{-1}$ in both sites), reaching a level of degradation that is comparable to that observed in coastal environments (Fig. 7) (Dilkes-Hoffman et al., 2019; Omura et al., 2023). Surface degradation is characterised by the appearance of deeper cracks (Fig. 2) and the presence of flax fibres induces internal degradation (Fig. 5). Together, these degradation mechanisms result in a more significant loss of mechanical properties (Fig. 4).

Flax fibres are highly hydrophilic, significantly enhancing the water absorption capacity of the composite material (Le Duigou et al., 2009; Ventura et al., 2017). This increase in water absorption can result in significant swelling within the material, which in turn induces mechanical constraints and structural evolutions such as matrix and fibre decohesion, an increase in porosity and the creation of micro-cracks (Lu et al., 2022; Pantaloni et al., 2022). Moreover, their biochemical composition, comprising a high proportion of cellulose and a low proportion of lignin, is conducive to biodegradation (Erdal and Hakkarainen, 2022; Kwon et al., 2021): SEM and tomography images suggest that they degrade more rapidly than the matrix, leaving visible voids both on the surface and within the volume (Figs. 2, 5), voids that are not observed in abiotic conditions. These two phenomena appear to indicate that the diffusion of microorganisms and secreted enzymes within the specimens is facilitated by the presence of flax fibres, which increases the contact area between biofilm and matrix.

The PBS-Flax specimens display surface degradation characteristics that are indicative of biological degradation (formation of holes) to a greater extent than the pure PBS specimens at S1-780 (Fig. S3 versus Fig. S2). The methodology employed in this study does not permit the calculation of the proportion of mass loss attributable to the PBS or flax components. However, the increased biomass and diversity observed on the specimens, as illustrated in Fig. 1, appear to create conditions conducive to attracting or enhancing the strains necessary for PBS biofragmentation. Further microbiological studies are required to substantiate this hypothesis, which may also explain the accelerated degradation kinetics observed in the PHBV-Flax specimens. The ageing in S2-1740 revealed no indications of an intensification of the degradation processes, thereby corroborating the hypothesis that the biodegradation of a flax-fibre composite in a particular environment is contingent upon the biodegradation of the matrix in this environment.

It can thus be concluded that the reinforcement of the material with flax fibres accelerates the degradation process. A variety of mechanisms have been proposed, to underpin this observation. First, the biodeterioration process is significantly accelerated by the increased water absorption, which creates internal degradation and formation of deep surface crevices that reduce the cohesion of the specimens. Second, the quantity and variety of biomass increase in the presence of flax fibres, which appears to accelerate the degradation process. Finally, these two

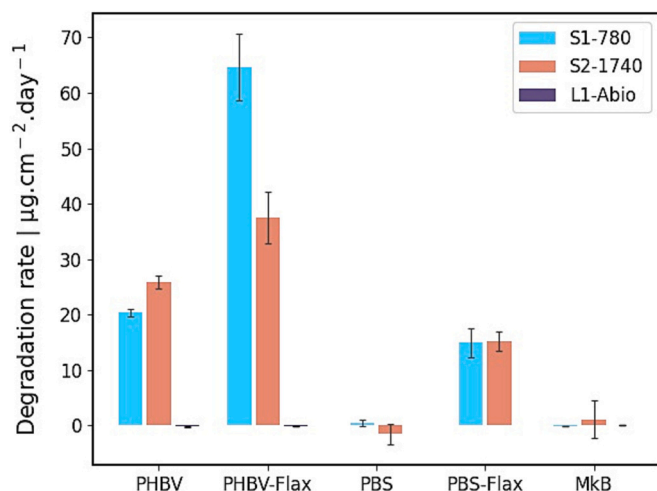


Fig. 7. Degradation rate of the studied materials after ageing.

previous factors are likely to enhance the biofragmentation and the bioassimilation by increasing the circulation of microorganisms and/or of extracellular enzymes within the material and extending the surface of contact between the biofilm and the matrix.

5. Conclusions

The results of this study indicate a significant biodeterioration of the PHBV, PHBV-Flax, and PBS-Flax specimens after one year in two deep-sea environments of the Atlantic Ocean. The incorporation of flax fibres was found to accelerate the degradation process. These findings support the hypothesis that PHBVs and their biocomposites could be viable materials for marine biodegradable applications, whereas PBS does not appear to be a suitable alternative.

It is important to emphasise that while the degradation mechanisms appear to be similar to those observed in coastal environments, where assimilation has been demonstrated, there is currently no evidence to confirm that the degradation products are assimilated in the deep sea. The methodology employed in this study or in the studies cited here above do not allow the characterisation of the fragmentation and more importantly of the assimilation of the materials under investigation. To address this knowledge gap, further research is required. The application of microbiological studies, including metatranscriptomics, proteomics, and metabolomics, in conjunction with the development of technical means to conduct *in situ* respirometric studies, may assist advances in this field of study and enable the quantification of these phenomena (Chamley et al., 2024). In the next few years, further investigations will be conducted on the degradation of samples of the same materials, subjected to prolonged ageing periods at the same sites with the application of additional methodologies. This should provide further insight into the biodegradation kinetics and processes in these environments. Given that deep-sea environments may represent the ultimate sink for plastics in the oceans, the advancement of such studies are essential to ensure the development of genuinely biodegradable substitutes that can be safely introduced to marine environments.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used DeepL Write in order to improve the readability and language of the manuscript. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the published article.

Funding sources

This work was supported by the Direction générale de l'armement (DGA), France.

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Alexandre Chamley: Writing – original draft, Investigation. **Christophe Baley:** Writing – review & editing. **Nicolas Gayet:** Investigation. **Jozée Sarrazin:** Investigation. **Sandra Fuchs:** Investigation. **Floriane Freyermouth:** Writing – review & editing. **Peter Davies:** Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Chamley Alexandre reports financial support was provided by General Directorate of Armaments. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in

this paper.

Acknowledgments

We thank all the members of the MOMARSAT and the CHEREEF missions, including scientific and marine crews of the research vessels that enabled the sampling of the materials studied in this study: RV Pourquoi Pas?, RV L'Atalante, RV Thalassa. In particular, we thank the chief scientists of the MOMARSAT and CHEREEF missions, namely Marjolaine MATABOS (MOMARSAT-2022/2023), Pierre-Marie SARADIN (MOMARSAT-2022) and Lenaïck MENOT (CHEREEF-2022/2023), for integrating our sampling within their already extensive operational programmes. We also thank Antoine Kervolen for processing the materials, Morgane Chalopin and Gaetan Burgaud for helping with sterilisation, and the Ifremer SMASH laboratory team for their help with characterisation and abiotic ageing. We also thank the Direction Générale de l'Armement (DGA) for their financial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2024.117230>.

Data availability

No data was used for the research described in the article.

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