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Degradation of plastic materials in the marine environment: A mussel farm as a case study for the development of alternative mussel nets

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ABSTRACT

Currently, mussel farming uses of traditional plastic nets that accumulate on beaches and on the seabed in the event of breakage and accidental dispersion, contributing to the marine litter issue. An attempt is being made to replace the polypropylene nets with alternative materials to make the aquaculture full production cycle more sustainable. However, alternative materials need to be characterised both functionally and environmentally. This article describes a characterisation study in which plastic materials were exposed for approximately three years to the marine environment in a bay dedicated to mussel farming to provide data on the degradation behaviour of the selected polymers for eco-design purposes. Samples of the different materials, in the form of 3-mm thick dumbbells, were placed on the seabed at a depth of 12 m and in the water column at 2 m below the sea surface. At different time periods (after 6, 15, 24, 32 months), the samples were recovered, their mass and thickness were measured, and the mechanical properties were characterised. The results lead to the identification of some materials as sufficiently resistant to deterioration and therefore possible candidates for the application. Other materials generally used to make bags and films showed a very fast degradation and therefore do not seem to meet the performance requirements for mussel farming. The methodology used in this study seems suitable for conducting long-term exposure tests on locations of interest and collecting specific data for eco-design purposes before the application of the product on the markets.

1. Introduction

Aquaculture grows faster than other major food production sectors and it is considered a good opportunity to mitigate the huge environmental and social impacts of terrestrial food production systems and the overexploitation of fish stocks and natural resources (Stevens et al., 2018). Aquaculture production of filter-feeding invertebrate species, such as bivalves, is expected to develop in Africa, Latin and South America, and the peri-Arctic Nations. This is due to its potential to improve national food security and nutrition in those regions through species diversification (Suplicy, 2020). Up to the seventies, mussels were farmed using natural three-strand ropes knitted by mussel farmers and made of esparto grass (*Stipa tenacissima*; *Magnoliophyta*, *Cyperales* sp.) in Southern Europe (Menzel, 2018). After the ‘70s, esparto ropes were replaced by socks made of polypropylene (PP) tubular nets worldwide, which brought many advantages to the farming operations and economics (Petrocelli et al., 2021). Nonetheless, PP is a type of polyolefin that is widely recognised for its resistance to biodegradation (Glaser, 2019; Celso Luis de Carvalho and Derval dos Santos Rosa, 2016). In the event of dispersal, such as through ruptures or accidental losses, which are becoming more common due to recurrent extreme weather events due to climate change, the PP socks do not break down in the environment and instead accumulate as debris on beaches or settle on the seabed, giving rise to numerous concerns and becoming a significant contributor to marine litter, particularly in the Mediterranean Sea (Fortibuoni et al., 2021; Vlachogianni et al., 2018; Pasquini et al., 2016).

To address the issue of aquaculture and fishing activities as a source of marine litter, various management strategies have been implemented to prioritise the reduction of plastic waste, including the use of alternative materials such as biodegradable and bio-based materials to replace traditional plastic-based products (Arantzamendi et al., 2023). For example, European Regulation (EU) 2017/2107 requires that when designing fish-aggregating devices (FADs), biodegradable materials shall, if possible, be prioritised with a view to phasing out

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non-biodegradable FADs (European Parliament and Council of the European Union, 2017). In the fish farming sector, there is a pressing demand to cultivate using more sustainable solutions, encompassing the three pillars of sustainability: environmental, social, and economic (Purvis et al., 2019). The best solution would be to use, on the one hand, biopolymers, that can be converted into nets with already well-tested industrial processes such as melt spinning (Temesgen et al., 2021) and, on the other hand, intrinsically biodegradable materials that do not end-up in the environment. Biodegradable and compostable materials are a promising solution in mussel farming because some of them can be processed using the same equipment applied with PP, making industrialisation relatively simple (Nitsch et al., 2021; Pavia et al., 2023), their use for farmers almost identical to the conventional PP sock and facilitating their disposal after their use. In practice, this means finding a balance between mechanical resistance (the socks must resist for the entire cultivation time), cost (the socks must not interfere with the current economics of the business) and environment (the socks must show intrinsic biodegradability in marine environment and be compostable after their disposal to make the entire process circular) (Degli Innocenti and Breton, 2020). After a long time at sea for mussel farming, conventional PP mussel socks are generally covered by biofouling, including mucilage and algae, etc. And for this reason they are not easily recyclable through traditional systems (e.g. mechanical recycling). However, if the gears are compostable, after use they can be collected and sent to composting plants for organic recycling (Folino et al., 2020). These measures promote a more sustainable and eco-friendly approach to gear management, helping to protect marine ecosystems and reduce overall environmental harm. In the event of accidental dispersion in the sea, biopolymer gears can undergo a natural biodegradation process facilitated by their intrinsic biodegradability (Degli Innocenti and Breton, 2020) and the presence of microorganisms (Degli Innocenti et al., 2023).

In a pilot study, Petrocelli et al. substituted plastic materials with tubular nets made of natural fibres (hemp and sisal) (Petrocelli et al., 2021). The net resistance to sea immersion as well as their mechanical and top load resistance was first assessed as well as the ability of mussels to settle and develop. The net resistance to sea immersion and as well as their mechanical and top load resistance was first assessed, as was as well as the ability of mussels to settle and develop. The results show that sisal nets were suitable for settlement and growth of both nets made of sisal were suitable for settlement and growth both for juvenile and adult mussels, with results comparable with those obtained with traditional plastic nets, despite the fact that they despite they were not sustainable from an economic point of view.

The current challenge is to identify plastic materials that are intrinsically biodegradable and maintain the performance and durability of socks during the time needed for farming operations and to maintain technological and economical sustainability (Curto et al., 2021).

Laboratory, mesocosm, and field methodologies can be used to expose the materials under study to microorganisms and marine environments (Lott et al., 2020, 2021) and verify their degradation. The International Standard Organisation (ISO) has developed a test method for the determining the degradation of plastic materials exposed to marine environmental matrices under laboratory conditions (ISO/TC 61/SC 14 Environmental aspects, 2021) and real field conditions (ISO/TC 61/SC 14 Environmental aspects, 2020). In addition, a standard test method was developed to evaluate the simultaneous effect of solar irradiation and permanence at sea in plastic floating devices (ISO/TC 61/SC 6 Ageing and chemical and environmental resistance, 2018). The different approaches have pros and cons. Laboratory tests, where environmental conditions are controlled and repeatable, are more easily standardised and offer reproducible results. That is, using the same standard conditions, the results obtained in a laboratory can be more easily reproduced in any laboratory worldwide. This is of great benefit for certification and claim verification purposes. On the other hand, the conditions in the laboratory are predetermined; therefore, laboratory tests only simulate natural conditions without considering the simultaneous environmental variables occurring in a natural ecosystem and synergistically acting on materials.

. Conversely, the results obtained in field tests are by definition very little reproducible because the multiple conditions, climatic, seasonality, etc., cross in a multifactorial matrix. However, when the field test is carried out in the location where the applications of interest are actually used, the results are very relevant.

This article describes a research activity carried out to characterize materials for making socks for mussel farming by evaluating the different rates of degradation in a long-term field experiment. This activity is part of a larger research eco-design project that includes the study of the performance of socks made of biodegradable materials compared with conventional plastic socks and studies to verify any ecotoxicological effect on mussels. The aim of this research was to test, over time (more than 30 months), the physical performance and degradation characteristics of five biodegradable commercial plastic materials and polyethylene (PE), as a negative control, exposed in the water-column and seabed in a marine area with a large mussel farm. The biodegradable materials were: poly (ε-caprolactone) (PCL) currently used in biomedical applications; Mater-Bi EF04P, a plastic material mainly applied in agricultural applications (i.e. mulch films); Mater-Bi HF03V, a plastic material mainly used for bag production; and Mater-Bi KF02B and Mater-Bi EF51L, both suitable for different conversion techniques (e.g. net extrusion) and thus candidates for producing nets.

The management of this field test activity is obviously much more burdensome than tests conducted in the laboratory under controlled conditions. However, we tested the performance and degradability of the target polymers in the specific environment in which these materials could be used and we suggest the best material for the production of the new mussel socks for their subsequent use in mussel farming.

2. Materials and methods

2.1. Tested materials

Six plastic materials were tested. The materials were thermoformed by injection moulding into “dumbbells-like” samples, according to ASTM D638-14 (ASTM International, 2021) Standard Test Method for the Tensile Properties of Plastics (moulded specimen Type I). The standard dimensions of the samples are shown in Fig. S1.

As a negative control, polyethylene (PE) was used (Lupolen, Lyondell Basell). PE is a conventional fossil-based polyolefin known to be recalcitrant to biodegradation and prone to the formation of persistent microplastics in the event of discharge in the environment (Degli Innocenti et al., 2022). PE was used instead of PP (the material most often used to make socks) for practical reasons of availability of materials at the time of starting the trial. PE and PP are both polyolefins and are considered non-biodegradable (Arutchelvi et al., 2008). Therefore, for the purposes of this article, they can be considered interchangeable as negative control materials.

Five biodegradable commercial plastic materials were tested to verify their degradation characteristics and potential for use in socks for mussel farming. All materials comply with the standard EN 13432, which defines requirements for packaging recoverable by organic recycling (CEN/TC 261, 2000).

Poly (ε-caprolactone) (PCL) (Capa™ 6800, Perstorp, SE) is an aliphatic fossil-based polyester well known to be biodegradable (Goldberg, 1995) and used in several medical applications (Azimi et al., 2014). This material was chosen because it is a polyester that is considered to be biodegradable.

Mater-Bi EF04P is a plastic material produced by Novamont mainly applied in agricultural applications (e.g. mulch films). This material complies with the European standard EN 17033 (CEN/TC 261, 2018) and exhibit biodegradation rates similar to natural reference materials when exposed to soil samples (CEN/TC 261, 2000; Tosin et al., 2020). This material was chosen because it has been proven to be resistant in agricultural applications, including prolonged exposure to soil and weathering, and it was assumed that it would be similarly resistant in marine applications.

Mater-Bi HF03V is a plastic material produced by Novamont and is mainly used for film applications (bags). Furthermore, this material is intrinsically biodegradable when exposed to microorganisms under mesophilic conditions, and it has been extensively studied in other areas and environmental contexts and is therefore useful as a reference (Pischedda et al., 2019; Tosin et al., 2019; Eich et al., 2021).

Both Mater-Bi EF04P and Mater-Bi HF03V are made of biodegradable polyesters, starch, and a plasticiser.

Mater-Bi KF02B and Mater-Bi EF51L are polyester-based materials without starch. Both materials were assessed for biodegradability at 28 °C and showed intrinsic biodegradability when exposed to microorganisms under mesophilic conditions. Mater-Bi KF02B is certified “OK Compost Home” (TUV Austria), and certification for home compostability of Mater-Bi EF51L is pending. These two materials were chosen because they can be made into filaments and appear to be suitable for netting.All polyesters used in the Mater-Bi grades are made with monomers that biodegrade in soil (Siotto et al., 2011).

2.2. Sample characterisation

Before and after environmental exposure, dumbbell-shaped samples were characterised for their tensile properties (tensile force at break, elongation at break and Young modulus), thickness, and weight. The initial characteristics of the tested material were determined on four dumbbells for each polymer, and the values are expressed as averages Table 1.

Before measurement, samples were conditioned in a controlled atmosphere of 23 ± 2 °C and 50 ± 10 % relative humidity (R.H.) until a constant weight was reached according to ISO 291:2008 (ISO/TC 61/SC 6 Ageing and chemical and environmental resistance, 2008).

Each dumbbell was weighed using a technical balance (Sartorius LC2200P) with a precision of 0.01 g, and the thickness was evaluated using a ±0.01 mm precision calliper (Mitutoyo-Co, Tokyo, Japan). Thickness was measured a three equidistant points along the length of the narrow section (see Fig. S1) of each dumbbell and expressed as an average.

Tensile properties were assessed following ASTM D638-14 (ASTM International, 2021), using a dynamometer Instron Machine (Model 5500 R), equipped with a load cell of 5 kN capacity and a testing speed (V0) of 50 mm/min, and a dynamic extensometer Cat.No. 2620-601 serial No. 1247 (GL = 50 mm).

The tensile force, defined as the maximum tensile force sustained by the specimen during a tension test (while tensile force at break is the stress needed to break the sample), is given in N.

Elongation at break is a measure of the percentage change in length in the material before the fracture. The modulus of elasticity, or Young’s modulus, is defined as the ratio of stress (σ) to strain (ε) in the linear elastic region (i.e., $E = \Delta\sigma/\Delta\varepsilon$) and is a measure of the stiffness of the material.

The surface area of the dumbbells was calculated from the dimensions shown in Fig. S1 and Table S1. The volume is determined by multiplying the surface by the thickness.

The decay of the tensile properties decay was expressed as the percentage decay of the initial tensile force at break.

2.3. Field testing

2.3.1. Test system setup

The dumbbell-shaped samples were placed inside commercial oyster farming net pouches made of HDPE with a mesh size of 6 mm. In each pouch, six groups formed by six dumbbells of each material were placed, for 36 dumbbells/pouch (Fig. 1). Dumbbells were fixed to the net pouch at an equal distance of approximately 1 cm from each other, using two non-biodegradable PP plastic bands. The dumbbells of each material were placed in a specific sequence to ensure their permanent identification during the exposure time (see Fig. 1).

2.4. Field experiment

The field experiment was conducted from March 2019 to November 2021 in a mussel farm located in the Gulf of La Spezia (Lat. 44.0781° N, Lon. 9.8709° E) and managed by Cooperativa dei Mitilicoltori Spezzini (cooperative of mussel farmers of La Spezia, Italy). Waters for mussel farming in the study area are classified as Type B (max 4.600 *E. coli*/100 g), according to EU Reg. 854/2004.

Hydrographic and current characterisation in the Gulf of La Spezia underlines that its circulation is the result of the interaction of large-scale coastal circulation from its external boundary and the estuarine circulation present in the dam interior, where a slow current is produced (where the mussel farm is present, and the experiment was deployed). The interior residence time of water varies from 5 days to approximately three weeks (Gasparini et al., 2009).

The trend of the environmental conditions during the experiment time period were retrieved from the monitoring of water physico-chemical parameters carried out approximately 6 times/year by ARPAL (Agenzia Regionale per la Protezione dell’Ambiente Ligure, freely available: https://ambientepub.regione.liguria.it).

Four pouches were placed in the water column and four on the sandy sediment at the interface between seawater and the seabed (for simplicity referred to below as “seabed”) to study the degradation behaviour of materials under two different conditions in which mussels socks can be found, i.e. in seawater simulating the environment exposure of socks during their use and on the seabed (interface between sandy sediment bed and water column) where socks can sink, accumulate, and undergo to degradation in the event of accidental dispersion.

Table 1

Average characteristics of the test materials in the form of standard dumbbell-shaped test specimens (at Time 0).

Test Material	Type of material	Thickness (mm)	Weight (g)	Density (g/cm^{-3})	Tensile force at break (N)	Elongation at break (%)	Young modulus (MPa)
Mater-Bi HF03V	Starch-based plastic	3.14 ± 0.03	10.80 ± 0.04	1.28	513,1[a]	>800	232,5[a]
Mater-Bi EF04P	Starch-based plastic	3.13 ± 0.02	10.52 ± 0.05	1.27	567,9[a]	>800	218,7[a]
Mater-Bi KF02B	Polyester-based plastic	3.12 ± 0.04	9.68 ± 0.01	1.18	454,6	101,5	467,4
Mater-Bi EF51L	Polyester-based plastic	3.10 ± 0.07	10.10 ± 0.06	1.23	770,4[a]	>800	478,2[a]
Poly (ε-caprolactone) (PCL)	Polyester	3.13 ± 0.01	9.25 ± 0.07	1.14	783,9[a]	>800	459,7[a]
Polyethylene (PE)	polyolefin	3.12 ± 0.03	7.28 ± 0.04	0.94	529,4	124,1	382,9

[a] Value determined at the endpoint (elongation = 800%) and not at break. Force does not increase as strain increases.

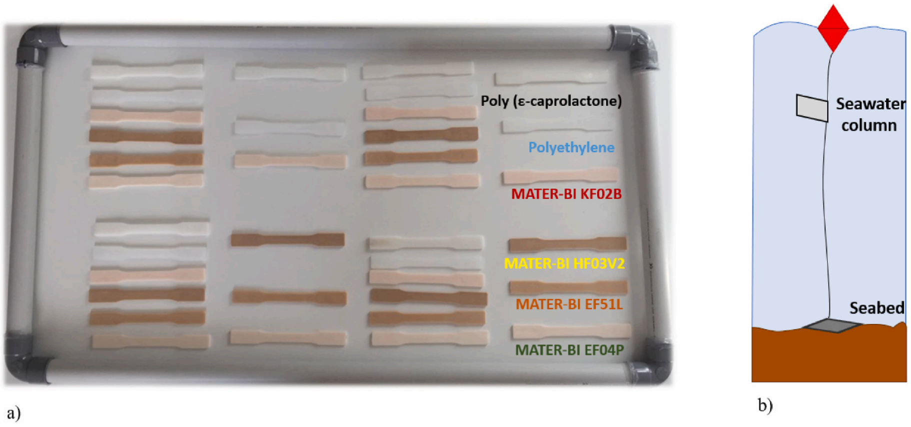

Fig. 1. A) Plastic samples positioned in the net pouch used for oyster farming. The samples of the different materials were positioned in six groups following the same order (as indicated in the group at the right end); b) Disposition of the pouch with samples at the bottom of the sea and in the water column along a rope indicated by a float. In total, four pouches were positioned at the bottom of the sea and 4 pouches were positioned in the water column. Each pouch contained 6 samples of each material.

The pouches were exposed to the water column at a depth of 2 m with the aid of buoys, whereas the pouches at the seabed were maintained adherent to the sandy sediment with sand ballast at a depth of 12 m (Fig. 1). At each sampling time: 184 days (about 6 months), 465 days (about 15 months), 738 days (about 24 months), and 970 days (about 32 months), one pouch was collected from the water column and one from the seabed and dumbbell samples recovered for laboratory analysis. Samples were maintained at 4 °C until their cleaning, characterisation and analysis.

2.5. Sample analysis

The degradation of the samples over time was assessed by measuring the mass loss, thickness loss, and decay of the tensile properties of the dumbbell-shaped samples to estimate the degradation of each material.

For each sampling time, two pouches were recovered (one from the water column and one from the seabed), and the dumbbell-shaped samples were extracted from the pouches for analysis. Four samples of each material were analysed and two were stored for further possible analysis.

The dumbbells exposed and retrieved from the marine environment were first soaked in freshwater for 10 min, rinsed in distilled water, and then gently cleaned with a soft sponge to remove sea salt, biofilm, and sediment particles adhered to their surface. Before measurement, the samples were conditioned at controlled atmosphere of 23 ± 2 °C and 50 ± 10 % R.H. until a constant weight was reached and characterised as reported in section 2.2.

2.6. Statistical analysis

The statistical analysis of data in this study employed the functionality provided by Microsoft Excel. Specifically, the standard error of means was calculated using Excel's statistical functions. In addition, regression analyses were conducted using the relevant statistical tools within the Excel software suite. The application of these analytical procedures facilitated the quantitative evaluation of the data and the derivation of pertinent statistical measures.

3. Results

Two pouches (one from the seabed and one from the water column), each containing the six different plastic types in six samples, were retrieved after 184 days (about 6 months), 465 days (about 15 months), 738 days (about 24 months), and 970 days (about 32 months). No pouches were lost or damaged.

Concerning the environmental conditions, during the experiment seasonal variations were observed for temperature, dissolved oxygen, and pH, with slight differences between the sampling site at depth of 2 m and 11 m of depth, where the water column and seabed pouches were placed (Table S2, Fig. S2). Salinity, instead, varied most between the two depths on a seasonal basis (Table S2, Fig. S2), mainly due to the effects of the rainy season on the upper layer of the sea during winter.

A rich fouling development on the dumbbell surface was observed by visual analysis as early as 6 months (Fig. 2), without macroscopic differences in colonisation between different materials (in terms of variety and abundance of phenotypes). Comparing the two exposure locations (seabed and water column), a clear difference in colonisation was observed as exposure time increased. In the water column, there was greater and growing colonisation by micro- and macroinvertebrates over time. In contrast, a progressive decrease of macrofouling was observed on the dumbbells exposed to the seabed from month 15 onward, until its total disappearance after month 24 and 32, likely due to the progressive accumulation of sandy sediment on the pouches.

3.1. Visual analysis of the samples

The pouches were brought to the laboratory for dumbbell recovery. Photos of the cleaned samples at each sampling time are shown in Figs. S3 and S4 of the Supplementary Materials. Clear signs of alteration/degradation on their surfaces were observed, such as colour changes and roughness, as early as six months of exposure. With increasing exposure time at sea, a gradual increase in degradation, such as cracks, cavities, roughness and an increased flexibility or fragility, was observed to a different extent depending on the test material and exposure position. In some cases, the samples were missing some parts and some samples completely disappeared at the time of sampling. The samples were bordered by a non-biodegradable plastic net with a 6 mm opening. The net remained intact during the test. Therefore, it cannot be excluded that the missing pieces and the missing samples broke into fragments smaller than 6 mm that escaped from the pouch. It should be noticed that no particles slightly larger than 6 mm, which could be an intermediate stage of degradation before leaving the holes in the pouches, were found. In any case, in this experiment, the mass is missing from the 6 mm mesh is considered to be degraded.

The greatest degradation was found for Mater-Bi HF03V and Mater-Bi EF04P, which showed evident colour change, cracks and increased flexibility, particularly after 15 months of exposure in the water column. Moreover, some dumbbells partially disintegrated. In the pouches exposed to the water column, partially disintegrated Mater-Bi HF03V dumbbells were recovered after 24 (3 replicates) and 32 (2 replicates)

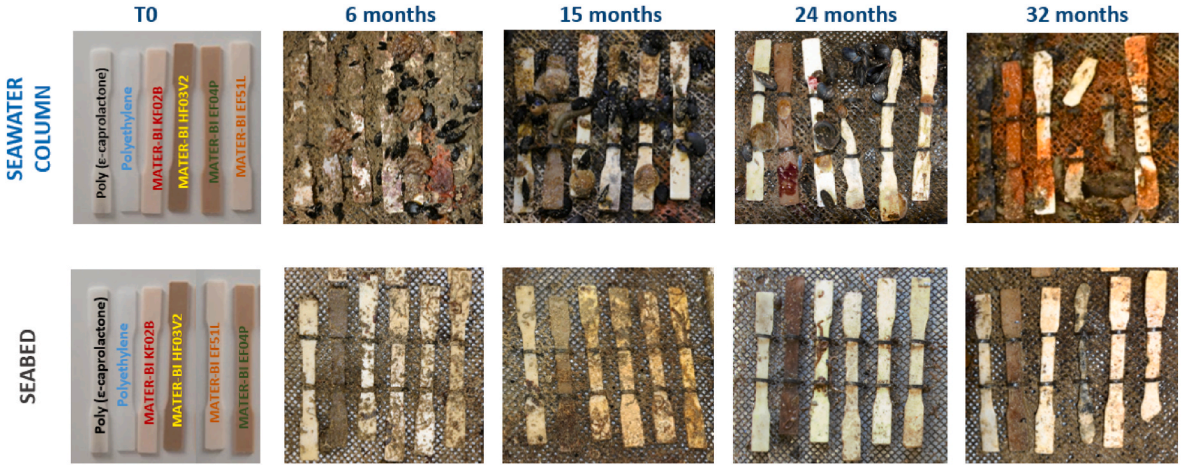

Fig. 2. Dumbbells exposed in the water column and at the seabed (water/sediment interface) taken at different time intervals from 0 to 32 months. The samples are arranged in the following order (from left to right): PCL, PE, Mater-Bi KF02B, Mater-Bi HF03V, Mater-Bi EF04P, and Mater-Bi EF51L (in the water column); PCL, PE, Mater-Bi KF02B, Mater-Bi HF03V, Mater-Bi EF51L, and Mater-Bi EF04P (in the seabed).

months, and 3 partially disintegrated Mater-Bi EF04P dumbbells were recovered after 32 months. Regarding the seabed, at month 32, one of six dumbbells of both materials was not whole. PCL dumbbells showed an initial slight surface roughness in the first sampling (6 months) and then diffuse cavities on the surface and a progressive thinning as the exposure time continued, to a greater extent on samples placed on the seabed.

Dumbbells of Mater-Bi KF02B and Mater-Bi EF51L did not show substantial signs of degradation in the first 15 months of incubation (465 days), except for a slight colour alteration. Subsequently, increasing roughness and fragility were noticed on the KF02B sample.The PE dumbbells remained almost unaltered up to the end of the trial (32 months).

3.2. Thickness loss

The thicknesses of the samples exposed to the water column and seabed are reported in Table S3 and plotted in Fig. 3 (top) and in Table S4 and plotted in Fig. 3 (bottom), respectively.

The samples left in the water column showed a latency phase, i.e., the thickness of all samples remained unchanged for the first year and a half. After this lag phase, the materials behaved in different ways that are ranked in three arbitrary classes based on the erosion level found at the end of the trial: low thickness loss, i.e., less than 10% (Mater-Bi KF02B and Mater-Bi EF51L), intermediate thickness loss, i.e., less than 33% (PCL and Mater-Bi EF04P), and high thickness loss, i.e., higher than 33% (Mater -bi HF03V). The high variability recorded for Mater-Bi HF03V and EF04P is due to the partial or total disintegration of some replicates during the last sampling times. PE did not show any substantial variation.

The samples exposed to the seabed showed similar behaviour with the following exceptions. Mater-Bi HF03V and Mater-Bi EF04P showed lower erosion in the seabed than in the water column, whereas, PCL had a relevant increase in erosion.

3.3. Mass loss

The dumbbells retrieved at different time intervals from the water column and seabed were also weighed.

The masses are shown in Table S5 (water column) and S6 (seabed). The normalised values are shown in Fig. 4. The ranking in the water column is as follow: low mass loss, i.e., less than ca. 10% (Mater-Bi KF02B and Mater-Bi EF51L), intermediate mass loss, i.e., less than 50% (PCL) and high mass loss, i.e., higher than 50% (Mater-Bi EF04P and Mater -Bi HF03V). The ranking in the seabed is the following: intermediate mass loss, i.e., less than ca. 50% (Mater-Bi KF02B, Mater-Bi EF51L, Mater-Bi EF04P, Mater -Bi HF03V) and high mass loss, i.e., higher than 50% (PCL).

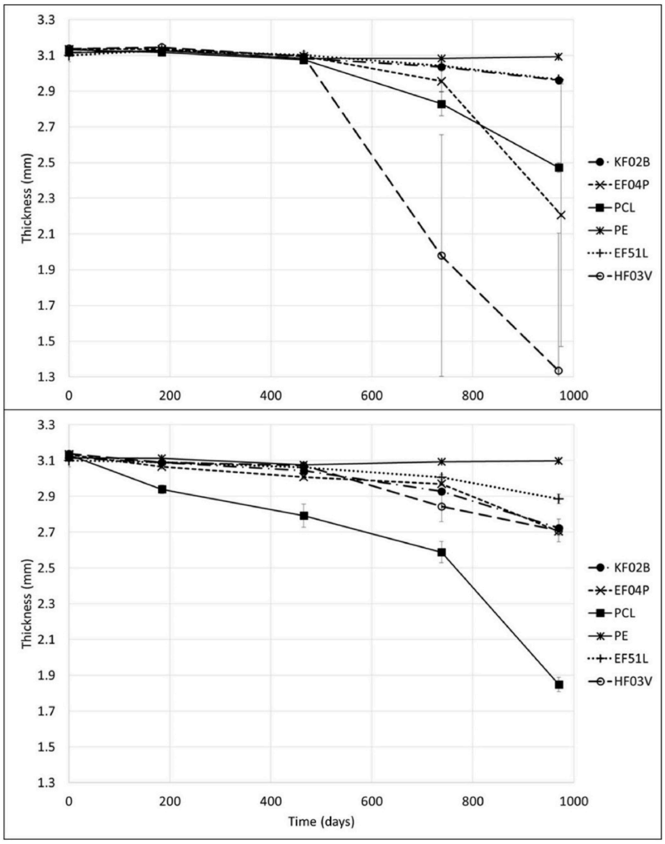

Fig. 3. Thickness of dumbbell-shaped samples for each polymer exposed to the water column (top) and seabed (bottom) for different times. The standard error of the mean is indicated by the bars. The bar is displayed only if the value is greater than the symbol size.

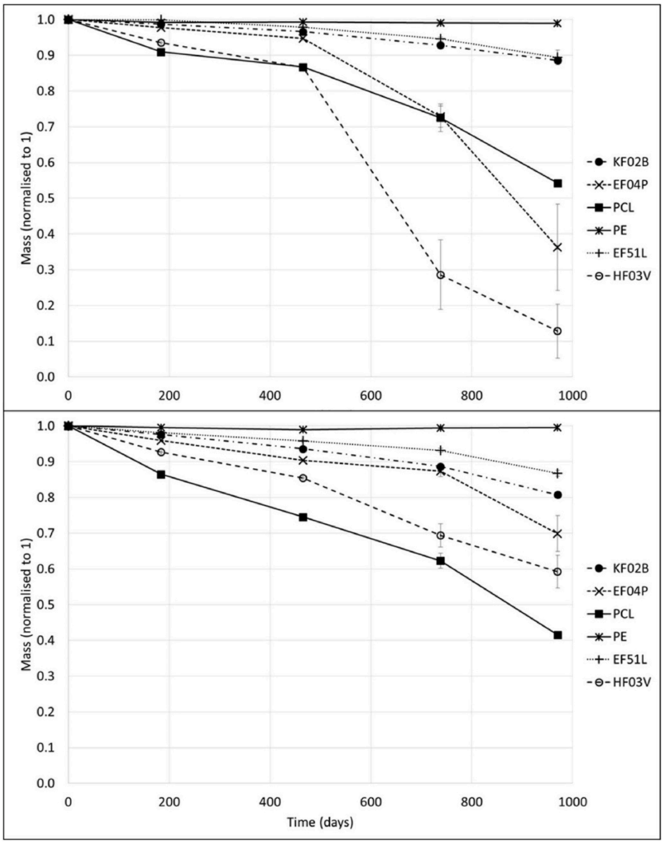

Fig. 4. Mass loss of samples of each polymer exposed to the water column (top) and the seabed (bottom) for different times. To facilitate comparison, the values are normalised to 1 (mass at time = 0). The masses of the samples at time 0 are shown in Table 1. The standard error of the mean is indicated by the bars. The bar is displayed only if the value is greater than the symbol size.

3.4. Regression analysis

3.4.1. Erosion

The erosion, i.e., thickness loss of a single surface, was determined as the difference between the initial thickness and the thickness at each sampling time divided by two (see Tables S7 and S8).

We carried out a linear regression considering only the values from the 3rd sampling onwards (465, 738 and 970 days), i.e., when the biodegradation process is expected to have stabilised after the first lag period, which involved all the materials at a major or minor measure.

The applied regression model is

$$y = k \times x + a$$

where y is the erosion (mm), x the time (days), k is the slope and a the intercept with the y axis. The regression curves lines are plotted in Fig. S5 (seabed) and S6 (water column).

Due to the way they were constructed (excluding the first samplings), the regression lines do not go from time zero; in fact, the biodegradation did not start at time zero but after a period of lag. We determine this period as the value of x where the regression line intercepts the ordinate axis (i.e. when y = 0) as follows:

$$lag\ time = \frac{-a}{k}$$

The time required to halve the diameter of a 1 mm diameter string (the typical size used in mussel socks), i.e., to get the radius eroded from 0.5 to 0.25 mm is called Erosion Time 50 (ET50) and is determined as the time predicted by applying the regression equation (x = y/k) with the addition of the lag time:

$$ET_{50} = \frac{0.25}{k} + lag\ time$$

The regression analysis and ET50 values for a 1 mm string exposed to the seabed and water column are shown in Table 2 and Table 3, respectively.

It is interesting to note that the ET50 values are higher in the water column than in the seabed (see Table 4), with the exception of Mater-Bi EF04P and Mater-Bi HF03V (both starch-based materials). This suggests that degradation of polyesters is more active in the seabed than in the water column, whereas the starch-based materials seem more susceptible to degradation when exposed to the water column.

3.4.2. Erosion compared with mass loss

The thickness loss was compared with the mass loss data. For this purpose, the thickness loss values were converted into mass loss values. In practice, for each sample, the value of thickness loss was subtracted from the original dimensions of the samples (Fig. S2 and Table S2) to obtain the overall volume of the object. The volume was then multiplied by the density (Table 1) thus obtaining the estimated mass based on the dimensions of each material (Tables S9 and S10). The estimated mass vs. measured mass are plotted in Fig. 5.

It is interesting to note that, in all cases, the initial good convergence between the measured mass and the mass derived from the thickness tends to deviate with a rather constant bias, creating a growing gap between the two values. In other words, the material loss due to degradation is found to be greater when determined by weight measurement than when determined by thickness measurement.

3.5. Tensile properties decay

The tensile properties of the test materials in dumbbell shape, i.e., tensile force at break and, elongation at break, were assessed.

The values are shown in Tables S11 and S12 of the supplementary material. The tensile properties measured on the samples at different sampling time are shown in Figs. 6 and 7. For Mater-Bi HF03V, EF04P, and KF02B dumbbells, measurements are reported only up to month 15 because in subsequent sampling specimens were not suitable for characterisation as they shattered upon insertion inside the clamp and/or strain gauge.

All samples, except PE, showed a progressive reduction in tensile force over 32 months of exposure. Such reduction was visible, already, after 6 months and was of variable intensity depending on the test material, independently from the exposure position.

After 6 months, the force of Mater-Bi HF03V was approximately 36% and 64% of the initial one in the water column and in the seabed, respectively, and approximately 39–41% for Mater-Bi EF04P in both positions. The force finally reached a value between 18 and 37% after 15 months (last determinable measurement for these samples).

The tensile force of Mater-Bi KF02B remained almost unchanged until month 15, after which the specimens were no longer suitable for characterisation.

Table 2
Regression analysis of erosion of samples exposed to the seabed and estimation of the ET50 for a 1 mm string made with different biodegradable materials.

Material	a	k (mm/ day)	R2	lag phase (days) (-a)/k	Days to achieve 0.25 mm erosion[a] (0.25/k)	ET 50 (days)
KF02B	−0.1154	0.0003	0.95	385	833	1218
EF04P	−0.0937	0.0003	0.81	312	833	1146
PCL	−0.3022	0.0009	0.87	336	278	614
EF51L	−0.0636	0.0002	0.92	318	1250	1568
HF03V	−0.1262	0.0004	0.99	316	625	941

[a] Without lag phase.

Table 3
Regression analysis of erosion of samples of each polymer exposed to the water column and estimation of the ET50 for a 1 mm string made with different biodegradable materials.

Material	a	k (mm/day)	R2	lag phase (days) (-a)/k	Days to achieve 0.25 mm erosion[a] (0.25/k)	ET 50 (days)
KF02B	−0.0384	0.0001	0.95	384	2500	2884
EF04P	−0.4384	0.0009	0.83	487	278	765
PCL	−0.266	0.0006	0.98	443	417	860
EF51L	−0.0612	0.0001	0.99	612	2500	3112
HF03V	−0.765	0.0018	0.99	425	139	564

[a] Without lag phase.

Table 4
ET50 water column/seabed ratios for each polymer.

Material	ET50		
	water column	seabed	Ratio water column/seabed
KF02B	2884	1218	2.4
EF04P	765	1146	0.7
PCL	860	614	1.4
EF51L	3112	1568	2
HF03V	564	941	0.6

Mater-Bi EF51L and PCL showed a decay in tensile force with an almost identical trend over time, retaining approximately 80–90% of the initial force in the first 6 months and approximately 50% after 32 months.

The force of PE dumbbells in 32 months remained within 95% on average.

Elongation at break of Mater-Bi HF03V, EF04P, and KF02B samples was drastically reduced in the first 6 months in both positions and reached an average a value of 90–100% after 15 months. Elongation reduction of Mater-Bi EF51L was first higher in specimens exposed to the seabed (39% vs 67% of the initial value of seabed and water column samples, respectively, in the first 6 months); subsequently, the reduction was comparable between samples from the two positions, reaching a value of about 0% of the initial one after 32 months.

No evident reduction in elongation was assessed for PCL dumbbells, and a slightly variation was observed for PE (>97% of the initial values).

4. Discussion

The aim of this work was to determine the tendency to physical degradation and the decay of the mechanical properties of different plastic materials exposed in the marine environment for use in the production of alternative mussel socks and to reduce plastic litter derived from aquaculture facilities. As mentioned, a material used in a mussel sock is expected not only to resist well during its use (i.e. behave as much as possible like a non-biodegradable conventional plastic) and to be composted in specific facilities after the end of the mussel farming cycle, but also to degrade in the marine environment in case of accidental loss. Therefore, the objective of this work was twofold: on the one hand, to understand whether the resistance of biodegradable materials to environmental ageing is sufficient for their use in mussel socks; on the

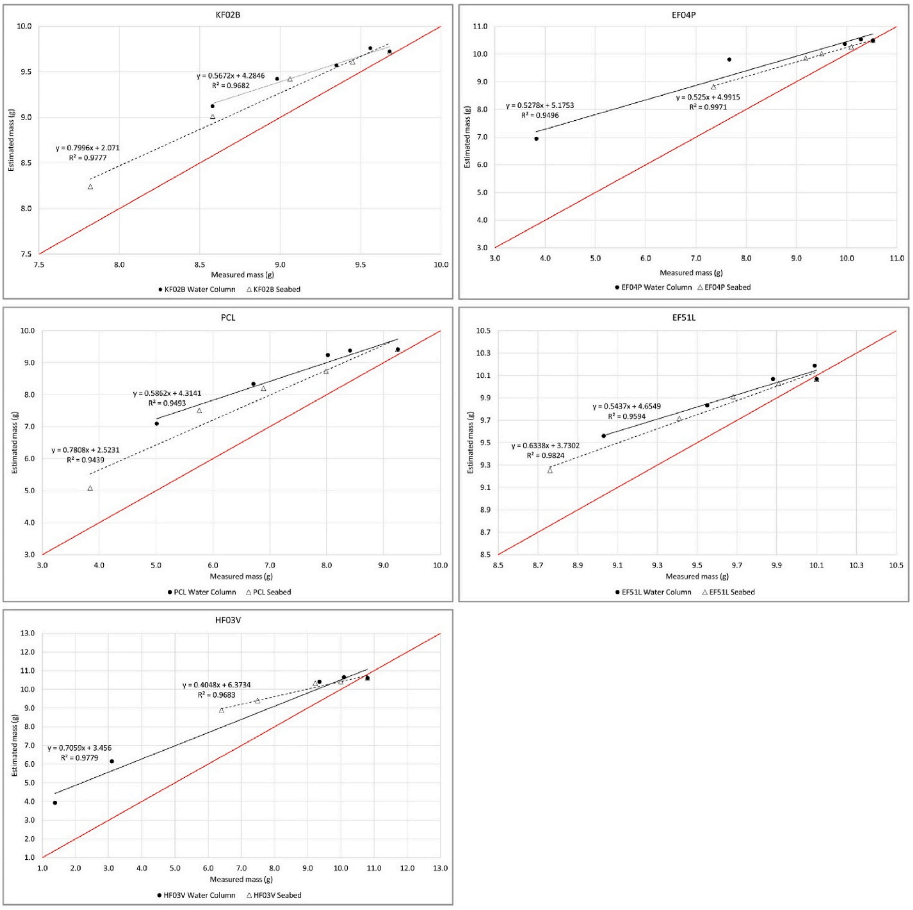

Fig. 5. Comparison of the measured mass with the mass estimated from the erosion data of each polymer exposed to the water column (solid line) and seabed (dashed line). The red diagonal indicates the line where the points would have to lie if the measured and estimated data were fully congruent. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

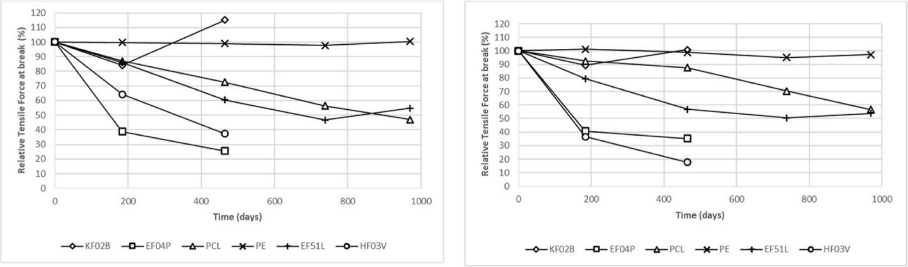

Fig. 6. Tensile force at break (N) of dumbbells exposed in the seabed (figure to the left) and in the water column (figure to the right). Each point is the mean of four replicates. To facilitate comparison, the values are normalised to 100 (tensile force at time = 0). The tensile force of the samples at time 0 are shown in Table 1.

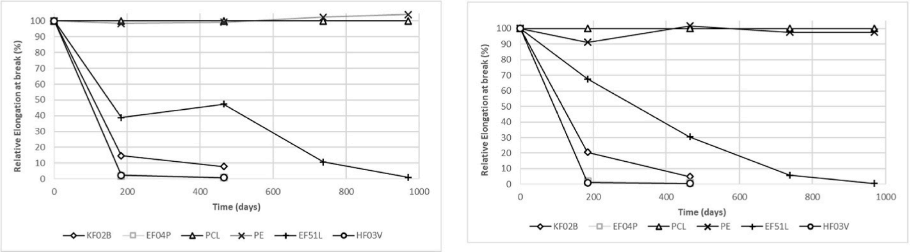

Fig. 7. Elongation at break (%) of dumbbells exposed in the seabed (figure to the left) and in the water column (figure to the right). Each point is the mean of four replicates. To facilitate comparison, the values are normalised to 100 (tensile force at time = 0). The tensile force of the samples at time 0 are shown in Table 1.

other hand, to understand if in the event of accidental dispersion, the materials tend to degrade (i.e., to disappear) substantially faster than current stockings.

A long-term field trial was conducted for this purpose. Field trials are not replicable compared with standardised laboratory tests conducted under controlled conditions. However, the field was carried out in a marine area strongly interested by mussel farming, which is precisely the final application objective of the research project. Therefore, the results obtained in this area are very significant because they were obtained in the specific habitat where mussel socks will be used and where they will accumulate in the event of accidental dispersion.

The samples used were very thick, much thicker than the typical mussel net thread (1 mm). The aim was to avoid the risk of losing the samples during the experiment and to measure the decay rates of the parameters of interest over long periods of time. This would not have been possible with thin netting. However, in this way, it was possible to derive the kinetic parameters of interest and apply them to the specific case of the mussel sock.

The samples were exposed in two positions relevant to the life cycle of the socks: in the water column and in the seabed. The socks perform their function while suspended in the water column. Therefore, it is important to understand the course of ageing under these conditions. At the end of the cycle, the socks are collected and disposed of on land. However, in case of breakage, the socks tend to sink due to biofouling and accumulate on the seabed, as also revealed by several studies on marine litter on the seafloor in the Mediterranean Sea, particularly in the proximity of mussel farms (Pasanisi et al., 2023; Fortibuoni et al., 2019). Consequently, it is important to study the degradation that occurs on marine sediments where lost socks accumulate. The sample exposure system applied in this trial proved to be adequate for the purpose of the study. In fact, there were no pouch losses due to anchor breakage in almost three years of exposure, and it was possible to properly collect the dumbbells at different time periods for subsequent laboratory analysis.

All the tested materials (but PE) were compostable, i.e., they were compliant with the relevant standards on organic recycling (i.e. EN13432, EN 14995, ISO 17088, ISO, 18606). These standards require several characteristics to be demonstrated, including intrinsic biodegradability under composting conditions. This means that tests conducted by independent laboratories have shown that the materials mineralise by at least 90%, either absolutely or relative to cellulose, in less than six months. This is an important feature, because it makes the waste of the socks recoverable by composting, a recycling system particularly suitable for plastic waste closely mixed with organic residues (e.g. biofouling, algae, mucilage, etc.). Furthermore, all materials have been shown (in some cases they are certified) to be biodegradable when exposed to mesophilic microorganisms at ambient temperature under controlled conditions. Thus, they are susceptible to biodegradation both when exposed to high temperatures (i.e. composting) and lower temperatures. This means that in the event of fragmentation, the particles created have a short-lived life and therefore cannot be considered as microplastics from the point of view of their environmental problems (Degli Innocenti et al., 2022, 2023; Barbale et al., 2021).

The results on degradation, determined both as erosion and weight loss, and on the decay of the mechanical properties of the material tested, are relevant to predict their performance for commercial application (i.e. the mechanical and functional performance of the mussel socks in the water column that must resist without causing commercial losses to farmers) and the environmental behaviour (i.e. related to the ecological hazard due to the persistence of solid litter items released into the environment). For this purpose, the plastic materials were thermoformed as standard dumbbells (ASTM International, 2021), confirming their suitability to test the characteristics and properties of bio-based and biodegradable plastics (Yoksan et al., 2022). This choice proved to be suitable because most samples resisted until the end of the test, thus making it possible to measure the selected parameters for the entire period considered (0–32 months).

The results show in a concordant and unequivocal way that the PE samples remained unaffected during the trial in terms of visual appearance, weight, thickness, and mechanical properties. This polymer is confirmed to be very resistant to degradation. It is worth also taking into account that the samples used in this study were not supplemented with stabilizers, biocides or other additives sometimes used to counteract environmental degradation. Our results are in agreement with the widespread idea that PE is not biodegradable in the environment

(Albertsson and Karlsson, 1993), as it was demonstrated in a previous study conducted in laboratory seawater microcosm after more than 400 days of incubation (Gerritse et al., 2020). In fact, despite many decades of testing, it has not been possible to highlight a substantial biodegradation of this polymer even using very sophisticated systems and many different microbial inoculums (Albertsson and Karlsson, 1993). To conclude, PE demonstrates a resistance to degradation both from a positive point of view (for commercial activities) and from a negative point of view (high environmental persistence, with no signs of degradation). Conversely, on visual observation, the dumbbells of biodegradable materials showed clear signs of degradation on their surface (furrows, cuts, or roughness), with different extents according to material type during the 32-months trial. The following ranking (from the most intact to the most degraded) was established: Mater-Bi EF51L and KF02B > PCL > Mater-Bi EF04P and HF03V.

This ranking was somewhat confirmed by measuring the thickness (Fig. 3) and the mass (Fig. 4) of the samples exposed both to the water column and the seabed. In particular, Mater-Bi EF51L and KF02B appears to display higher durability. Mater-Bi HF03V, Mater-Bi EF04P, and PCL showed faster degradation (Figs. 3 and 4). HF03V and EF04P seemed to be more sensitive to exposure to the water column and somehow more resistant to the seabed, whereas PCL showed the opposite behaviour.

The rapid degradation of Mater-Bi HF03V was demonstrated in another experiment carried out in a mesocosm (Eich et al., 2021).

The time needed to obtain the degradation of a 1 mm plastic string (the typical size of the strings used in mussel socks) was predicted using regression parameters based on thickness loss (Tables 2–4). The time needed for a 1 mm string typically used in socks to lose 50% of its diameter is estimated to be from approximately 2 to 4 years in the seabed, whereas PE shows an absolute absence of degradation during the test (almost 3 years). We think the ET50 values are conservative. Comparison of thickness loss with mass loss indicates that mass loss is faster than thickness loss. The gap between thickness and mass tends to increase as the degradation of the samples increases. This is partly true because in some cases the samples lost entire pieces during exposure. This absence may not be calculated in the thickness measurement, but it always affects the weight measurement. Moreover, the results suggest that the apparent density of the samples decreases with time, perhaps because of superficial degradation that creates holes and cavities, maintaining the thickness with a loss of matter.

These values can be very convenient for classifying materials in terms of their resistance to degradation for eco-design purposes. However, these data were collected in a specific location and the number of replicates was limited. Thus, their use for predictive purposes in other environments should be confirmed with supplementary tests performed in the environment of interest.

The tensile force at break (i.e. the maximum stress that a plastic object can withstand while being stretched before breaking) of the Mater-Bi HF03V and Mater-Bi EF04P samples decreased rapidly already in the first period of exposure (6 months), both in the seabed and in the water column. The decay of PCL and Mater-Bi EF51L was slower and more progressive. The tensile force at break of Mater-Bi KF02B was almost constant until the samples were no longer suitable for testing.

The elongation at break (i.e. the ratio between the initial and final length of the plastic object before it breaks) of the Mater-Bi HF03V, Mater-Bi EF04P, and KF02B dropped rapidly in the first period of exposure (6 months), both in the seabed and in the water column. On the other hand, Mater-Bi EF51L maintained greater ductility (i.e. a capacity to undergo plastic deformation) for longer exposure times, especially in the water column. PCL showed a constant elongation at break over time, as if the polymer, although subject to considerable erosion, maintained a totally intact polymeric core. On the other hand, the tensile force at break of PCL changes because the dumbbells section shrinks over time and therefore decreases the total strength that can be sustained by the samples. Conversely, the other plastics show both a progressive erosion (loss of thickness) and degradation in the core of the sample, which increasingly loses the ability to stretch without breaking.

Our results, carried out in temperate waters (T min: 11.86 °C and T max: 27.20 °C, mean value: 18.42 ± 4.51 °C; see Table S2 and Fig. S2 for temperature trends over the experimental period), are in accordance with previous findings and studies performed in warmer waters. For examples, PCL exposed to water collected from Bohai Bay for one year showed various superficial depressions, decrease of mechanical strength, and reduction of weight by 29.8% compared with the initial weight (Lu et al., 2018). After 5 weeks of immersion in the water of Akabane Harbour, Aichi, Japan, the PCL specimens showed a complete loss of tensile strength, 0% elongation at break, a reduction in Young's modulus to approximately 50% of the initial value and a reduction in weight of approximately 34% of the initial weight. (Tsuji and Suzuyoshi, 2002). In another study, PCL was incubated in a buffer containing Tokyo Bay and Pacific Ocean seawater at 25 °C under aerobic conditions for 28 days. The observed BOD biodegradation of PCL varied between 56% and 79% (Suzuki et al., 2021).In addition, incubation of PCL in buffer containing seawater collected from Osaka Bay for 17 days at 27 °C under aerobic conditions resulted in BOD degradation of 14.5–40.9% (Nakayama et al., 2019). Furthermore PCL samples from Rausu, Toyama and Kume showed numerous pores and cracks on the surface after 12 months of exposure to deep seawater, resulting in a complete loss of tensile strength. (Sekiguchi et al., 2011).

Biodegradable polymers can undergo surface erosion or bulk erosion by hydrolysis (Burkersroda et al., 2002; Laycock et al., 2017). In our case study, we should consider that, in the marine natural environment, biotic and abiotic factors frequently act synergistically on biodegradable polymers in a complex scenario. Disintegration, erosion, biotic/abiotic hydrolysis, and enzymatic degradation can act and interplay together (Laycock et al., 2017). In addition, fungi and bacteria or other biological agents (algae, micro and macroinvertebrates) can also fragment the product, accelerating the ageing process (Kim et al., 2022), as demonstrated by the visual analysis of the dumbbells.

The mechanical properties of the samples exposed to the water column are relevant to the application of interest, i.e., mussel socks, which are suspended in water for months and must resist. Conversely, the decay of mechanical properties in the sediment is interesting for understanding the potential for degradation of socks once torn and lost at sea.

The materials generally used to make films and bags (Mater-Bi HF03V) or for agricultural applications (EF04P) showed rather fast degradation, as proven in other studies (Eich et al., 2021). Likewise, the mechanical properties also showed a fast decay, suggesting these materials not suitable for these purposes.

The materials based on polyesters (Mater-Bi KF02B and Mater-Bi EF51L) were the most resistant to degradation (both in terms of erosion and mass loss). It is interesting to note that the materials apparently showed faster degradation at the seabed. The subject is particularly interesting from the viewpoint of the application of these materials in socks for mussels. Indeed, when the socks are in use, they are suspended in the water column. In the case of dispersion, due to the density of the materials (which is greater than 1) and to the biofouling, they tend to settle on the seabed. The socks are therefore in the water column when in use, but sink to the seafloor when dispersed. Materials that are more resistant to biodegradation when suspended in the water column, but also biodegradable when immersed in the seabed, therefore appear to be suitable for use in terms of both performance and environmental requirements.

5. Conclusions

This study aimed to characterize the degradation of plastic materials when exposed to a marine environment. The ultimate goal is to develop plastic nets (called mussel socks) for mussel farming with more sustainable characteristics compared to the polyolefin materials currently used. These materials are highly efficient from a mechanical point of view, but very recalcitrant to biodegradation.

This persistence leads to accumulation in the coastal and marine environment when nets become accidently or deliberately dispersed during cultivation, resulting in serious potential environmental impacts. The principle of sustainability, which includes economic, social and environmental aspects, must be taken into account in the search for suitable replacement materials. Therefore, a sock that biodegrades very quickly but does not meet the performance requirements of the application is not suitable because it meets one of the sustainability requirements (the environmental one) but not the other two, namely the economic and social ones, since premature breakage can cause serious economic losses to farmers. According to our results, while polyethylene confirmed its high resistance to degradation after more than 30 months at sea, not all the biodegradable plastics tested in this study seem to be suitable for the production of mussel farming nets, since all of them showed degradation in the marine environment, but with different losses of mechanical properties.

Combining the degradation data with the mechanical characterisation of the tested materials, biodegradable polymer based on polyesters, in particular Mater-Bi EF51L, could be identified as the most promising candidates among the tested polymers.

Mater-Bi EF51L have the advantage of being compostable after use and can potentially meet the conflicting requirements of resistance during use and degradation in the event of accidental loss of mussel socks. All these properties are necessary for a sustainable substitution of the current socks and for the use of these polymers in other applications related to the marine environment and aquaculture/fishing gear.

CRediT authorship contribution statement

Matteo Baini: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Visualization, Writing – original draft, Writing – review & editing. **Maria Cristina Fossi:** Conceptualization, Data curation, Funding acquisition, Investigation, Resources, Supervision, Writing – original draft, Writing – review & editing. **Francesco Degli Innocenti:** Conceptualization, Data curation, Funding acquisition, Investigation, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing. **Selene Chinaglia:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Visualization, Writing – original draft, Writing – review & editing. **Maurizio Tosin:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Visualization, Writing – original draft, Writing – review & editing. **Marco Pecchiari:** Conceptualization, Data curation, Funding acquisition, Investigation, Project administration, Resources, Supervision, Writing – original draft, Writing – review & editing. **Cristina Panti:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – original draft, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2024.141825.

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