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Mitigating plastic pollution at sea: Natural seawater degradation of a sustainable PBS/PBAT marine rope

Le Gué Louis [1, 2, *], Davies Peter [1], Arhant Mael [1], Vincent Benoit [2], Tanguy Erwan [3]

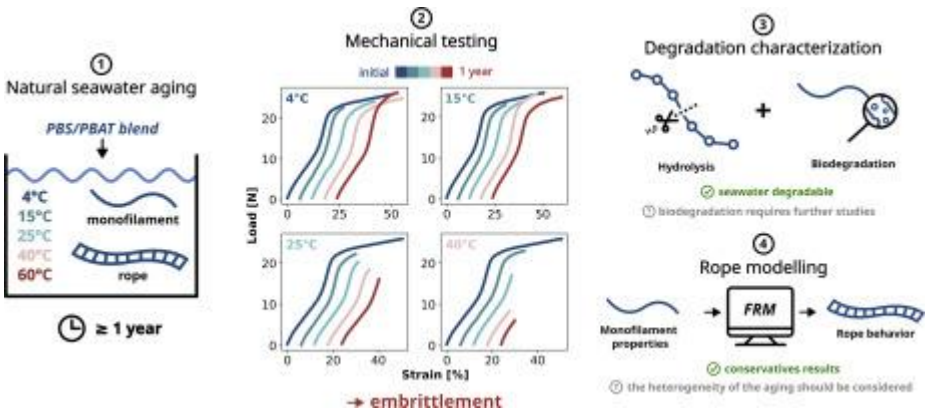
[1] Ifremer RDT, Research and Technology Development Unit, 1625 route de Sainte-Anne, Plouzané, 29280, France
[2] DECOD (Ecosystem Dynamics and Sustainability), IFREMER, INRAE, Institut Agro, Lorient, 56325, France
[3] Le Drezen, 12 rue de Kélareun, Le Guilvinec, 29730, France

* Corresponding author : Louis Le Gué, email address : louis.le.gue@ifremer.fr

Abstract :

This paper evaluates the use of a PBS/PBAT biodegradable rope to reduce the environmental impact of fishing gear lost at sea. The study aims to better understand the degradation mechanisms that the rope and its monofilaments may encounter due to the long term exposure to seawater. The monofilaments were immersed in natural seawater for up to 18 months, and rope samples were also immersed to study aging at a larger scale and evaluate the ability of a modelling tool to predict initial and aged states of the rope. At low temperatures, no loss of properties was observed for the monofilament and rope. However, at higher temperatures, biodegradation and hydrolysis processes were observed, leading to a faster loss of properties in the monofilament compared to the rope. The modelling tool provided conservative predictions due to severe mechanical test conditions of aged monofilament and a degradation gradient within the rope structure.

Graphical abstract



Highlights

► A rope made of braided PBS/PBAT monofilaments has been tested and aged. ► A PBS/PBAT rope could last at least 1 year and a half in seawater at 4 °C and 15 °C. ► Biodegradation and hydrolysis were observed for PBS/PBAT monofilaments at 25 °C. ► A numerical tool has been used to predict initial and aged properties of the rope.

Keywords : Plastic pollution, Biopolymer, Seawater aging, Polybutylene succinate, Rope structure, Numerical simulation

1. Introduction

Since awareness of plastic pollution in the oceans has increased, initiatives to reduce the use of single-use plastics, which are the most common type of waste found on the coast (Morales-Caselles et al., 2021), have been launched. However, even if no plastic entered via the coast or rivers, the problem of plastic pollution in our oceans would not be solved: more than 30% of the plastic waste in the open sea consists of synthetic ropes coming from ocean pathways (Morales-Caselles et al., 2021). Furthermore ropes used for fishing applications are the major source of entanglement for marine species (Johnson et al., 2005; Galgani et al., 2018), for example 83% of the population of the endangered *Eubalaena glacialis* had been entangled at least once (Knowlton et al., 2012). Entangled animals can die rapidly by drowning and sink, or be entangled for a long period and die slowly (Moore et al., 2006). Several ways to reduce the impact of ropes have been investigated in the past, such as enhancing the visibility of the gear to reduce the risk of contact

(Kraus et al., 2014), or limiting rope strength to increase the survival rate post-entanglement (Knowlton et al., 2016). But after a possible ghost fishing period, the gear disintegrates into particles less than 5 mm, known as microplastics (Wright et al., 2021). Microplastics thus produced will accumulate in the sediment (Van Cauwenberghe et al., 2013), be ingested by marine organisms (Wright et al., 2013), and affect a large number of species after entering the food chain by trophic transfers (Carbery et al., 2018).

Recently, the development of biodegradable polymer monofilaments has provided new ways to mitigate the environmental impact of derelict gear. Gear made of this kind of material could reduce the entanglement rate by limiting the accumulation of lost gear and facilitating the disentanglement process by the loss of properties. It could also tackle the microplastics pollution by being completely mineralized by the organisms present in the marine environment, and avoid the release of toxic chemicals by being additive free. However, such materials must strike a delicate balance, possessing the ability to maintain their mechanical strength for a sufficiently long period of time to be usable, while also having the capability to degrade or break down fast enough in order to minimize the impact of loss. Among biopolymers, polylactide (PLA) is the most common (European Bioplastics e.V., 2020). This bio-based polymer is processable into fibres (Puchalski et al., 2017; Le Gall et al., 2022) which could be braided into ropes (Furuike et al., 2015). However PLA does not degrade in seawater under natural conditions as shown by several authors (Deroiné, 2014; Bagheri et al., 2017; Huang et al., 2020), so it is not suitable for reducing the impact of current persistent materials. Polyhydroxyalkanoates (PHA) are microbial polyesters (Saito and Doi, 1994) known to be degraded by microorganisms living in seawater (Doi et al., 1990; Savenkova et al., 2000; Wang et al., 2004; Thellen et al., 2008; Numata et al., 2009; Volova et al., 2010; Deroiné et al., 2015; Dilkes-Hoffman et al., 2019). Nevertheless PHA fibres are very difficult to process due to a narrow window of processing temperatures (Luzier, 1992), which limits their industrial applications and explains why, at the time of writing, no PHA fibres are commercially available. In addition, according to the result of Dilkes-Hoffman et al. (2019), a PHA monofilament with a thickness of 0.3 mm would last less than a year. Considering their expensive production cost (Możejko-Ciesielska and Kiewisz, 2016), a rope or a net made of PHA would not be economically beneficial for users. In the absence of a law compelling the use of this type of material, such gear would not be used widely enough to address the problem of plastic pollution by lost gear. Chemically modified polymers with adjustable biodegradation rate are also in development (Martin et al., 2014; Samadi et al., 2019; Rheinberger et al., 2021), but are not commercially available as fibres at the time of writing. Polybutylene succinate (PBS) is a promising biopolymer which presents a low melting temperature, a good thermal stability, and suitable mechanical properties (Freyermouth, 2014). PBS is an aliphatic polyester produced through a two-step polymerization process, consisting of the esterification of succinic acid and 1,4-butanediol, followed by a transesterification (Xu and Guo, 2010; Sisti et al., 2016). Succinic acid is typically petroleum-derived, however it can also be biosourced through bacterial fermentation (Song and Lee, 2006). Similarly, 1,4-butanediol is primarily petroleum-sourced for industrial applications (De Munck,

1980; Harris et al., 1980), yet it can also be obtained from various biomass precursors such as the catalytic reduction of biosourced succinic acid, direct synthesis from biomass, or thermolysis of a PHA derived from biomass (Sisti et al., 2016). The marine ecotoxicity of PBS and bioplastics in general is a topic that is currently not well addressed in the literature. After a 28 day and 2 year observation of PBS buried in soil, Adhikari et al. (2016) found that the diversity of biomass was not affected by the degradation of PBS, while a reduction was observed in the aging of PA6,6. Based on these findings, PBS is a healthier alternative than the synthetic plastic materials currently in use such as PA6. According to a study by Zimmermann et al. (2020), the toxicity of commercial bioplastics, including PBS, was found to be primarily influenced by the additives used rather than the monomer itself and PBS was identified as the safest synthetic polymer among the bioplastics tested in the study. PBS biodegradation in the marine environment has been described as slow by Narancic et al. (2018) and Nakayama et al. (2019). The biodegradation of aliphatic polyester monofilaments was also investigated by Sekiguchi et al. (2011), who immersed them in the deep sea for one year. The study revealed that while PBS underwent degradation, it occurred at significantly slower rates compared to poly(ϵ-caprolactone) and poly(b-hydroxybutyrate/valerate). Poly(butylene adipate-co-tephtalate) is an aliphatic-aromatic co-polyester obtained by the poly-condensation of 1,4-butanediol, adipic acid and terephthalic acid (Jian et al., 2020). The properties of PBAT make it suitable for industrial use in various domains, including packaging, hygiene products, and biomedical fields (Ferreira et al., 2019). As for 1,4-butanediol and succinic acid, terephthalic acid is mainly petroleum-based but could be bio-based (Tachibana et al., 2015). PBAT is known to be compostable and biodegradable in soil environments (Müller et al., 2001). However, similar to PBS, its degradation in the marine environment has received limited attention and few studies have been conducted on this topic, but all the authors agree on the slow rate of degradation of PBAT in the marine environment (Kedzierski et al., 2018; Nakayama et al., 2019; De Monte et al., 2022; Delacuvellerie et al., 2023). PBAT's higher ductility compared to PBS makes it an ideal plasticizer for blending, resulting in a polymer blend with tailored properties (de Matos Costa et al., 2020). PBS/PBAT and PBSAT have already been used to manufacture less impacting fishing gear such as gillnets, traps and longlines (Seonghun et al., 2014; Kim et al., 2016; Grimaldo et al., 2018a, 2019; Seonghun et al., 2020; Grimaldo et al., 2020; Cerbule et al., 2022a,b). Authors agree that the slow degradation of monofilament can reduce the ghost fishing period in the event of a loss (Grimaldo et al., 2019, 2018b; Kim et al., 2018, 2019; Seonghun et al., 2020; Brakstad et al., 2022). PBS/PBAT blends are therefore suitable for the development of a new generation of less impacting marine ropes, but the conflicting specifications require a detailed understanding of the behaviour of this type of rope when used at sea for long periods. However, testing ropes requires significant resources and materials. The present study focuses first on the natural degradation of a PBS/PBAT monofilament immersed in seawater at temperatures from 4 to 60°C. Mechanical property degradation is then investigated and damage mechanisms are clarified. Data from these tests are then used to predict the aging of a braided rope, using the properties of the monofilament at both

initial and aged states.

2. Material and methods

2.1. Material

Two types of samples were studied: a braided rope with 8 strands each composed of 8 yarns with 21 monofilaments as shown in Figure 1, and the monofilament extracted from the rope. The monofilament was extruded, and the rope manufactured by Le Drezen (Le Guilvinec, France). The monofilament is colorless with a diameter of 0.35 mm, and obtained by extrusion and drawing of a PBS/PBAT blend. It has a density of 1.25 $g.cm^{-3}$ and a molecular weight by number of 25.6 $kg.mol^{-1}$ with a polydispersity of 4.8. The dry glass transition temperature of this polymer is 70°C and the melt temperature is 117°C with a melting enthalpy of 60 $J.g^{-1}$.

For comparison purposes, a monofilament extracted from a commercial high density polyethylene (HDPE) twine was also tested. Table 1 summarizes the mean properties of both monofilaments obtained by testing 20 monofilaments for each material.

2.2. Natural seawater aging

The samples were immersed in natural renewed seawater from the Brest estuary maintained at several temperatures. Monofilament samples were aged at 4°C, 15°C, 25°C, 40°C and 60°C for up to 18 months and removed regularly, every month over the first year, for characterization. Rope samples were spliced then immersed at 15°C and 40°C and removed for testing according to the results obtained on the monofilaments.

2.3. Gel permeation chromatography (GPC)

After dissolving the samples in a TCM chloroform solution for 24 hours, Steric Exclusion Chromatography (SEC) was performed at 30°C, with an injection volume of 100 μL, a flow rate of 1.0 $mL.min^{-1}$ an Agilent-DRI refractive index detector and three columns: a PS/DVB Agilent 5 μm precolumn, and two Agilent Mixed-C 5 μm columns. Calibration was performed with chloroform as well and polystyrene standards.

2.4. SEM observations

Surface observations on pristine and aged samples were obtained by Scanning Electron Microscopy (SEM) using FEI Quanta 200 equipment. Samples were coated with a 60% gold and 40% palladium coating before being placed in the microscope.

2.5. Mechanical testing

Mechanical testing of monofilament samples was carried out in tension with an Instron 10 kN capacity test machine equipped with a 50 N load cell and pneumatic yarn grips. The displacement rate was 50 $mm.min^{-1}$ and the strain was obtained by using two cameras to follow two markers on the monofilament. 20 tests were performed for the monofilament at the initial state, then for aged samples at least 3 samples were tested for each condition of immersion time and temperature. All the tests were conducted in a laboratory maintained at 21°C and 50% relative humidity.

A servo-hydraulic test machine equipped with a 300 kN AEP TC4 load cell was used to test the rope samples. For the test of the rope sample at the initial state, the strain was measured using cameras following markers shown on Figure 2. For aged samples, a 250 mm wire transducer was used to measure strain in the central section in order to determine initial stiffness. The initial and aged samples stiffness were determined by calculating the slope between 1 and 5 kN. For each condition, a 5-meter-long sample with eye splices at both ends was tested with a free length of approximately 2 meters between splices. Spliced samples were connected to the machine using shackles.

2.6. Mechanical modelling

The software Fibre Rope Modeller (FRM) developed by Tension Technology International (TTI) was used to model the rope. FRM allows the prediction of the mechanical properties of a rope based on the properties of the individual fibers or yarn and the rope construction (Banfield et al., 2001). This hierarchical model calculates the strain energy at each level and uses the virtual work principle to determine the rope response in tension and torsion. This software was used here to predict the properties of both the initial and aged states of the rope.

3. Results

3.1. Initial characterization of the monofilament and comparison with a commercial HDPE

Tensile test curves obtained for the PBS/PBAT blend and the HDPE are shown on Figure 3 and the mechanical properties determined from these curves are presented in the Table 1. With a Young's modulus of 0.79 GPa and a stress at break of 261 MPa the PBS/PBAT monofilament properties are below those of the HDPE, which exhibits a Young's modulus and a stress at break respectively of 1.90 GPa and 368 MPa.

3.2. Long term property changes of a PBS/PBAT monofilament immersed in seawater

3.2.1. Mechanical property changes

Every month at least three samples of the PBS based monofilament were retrieved from the seawater tanks and mechanically tested to study the changes in mechanical properties of the material for different

immersion times and temperatures. Three samples of the HDPE monofilament were also retrieved after 6 and 12 months of immersion. Figure 4 shows the tensile mechanical response of the PBS/PBAT monofilament at different immersion times and temperatures. An origin offset on each of the curve has been applied for clarity. Figure 5 summarizes the variation of the load at break with the immersion time for both materials where the error bars represent the scatter (minimum and maximum values) and the grey area represents the initial variability observed in Figure 3. The PBS/PBAT monofilament showed no significant changes in behavior or loss of load at break after being immersed for 18 months at temperatures of 4°C and 15°C. At 25°C the PBS/PBAT monofilament gradually lost its mechanical properties as seen in Figure 4 until it reached a breaking strength 38% lower than in the initial state. At the same temperature the HDPE monofilament showed no loss after 1 year, as depicted in Figure 6, which presents the tensile curves for both monofilaments after 1 year of immersion at 25°C. After 6 months at 40°C, the samples became brittle and began to break near the tensile clamps. A loss of strength of 74% was observed after 12 months at 40°C. After 4 months at 60°C, the PBS/PBAT monofilament became so brittle that it was no longer strong enough to be handled and mounted on the test machine. From 4°C to 60°C, the HDPE monofilament showed no loss of properties and even a slight increase.

3.2.2. Surface characterization by SEM

Figure 7 shows the surface changes samples during immersion in natural seawater. At 4°C and 15°C, no surface modification was observed, and the surfaces appear to be as new as the initial samples. For the samples at 25°C, as early as 3 months holes started to appear on the surface, and these became larger and deeper with time, leading to the surface aspect seen on the Figure 7 (d) after 18 months of immersion. To further understand the cause of the surface degradation, PBS/PBAT samples were immersed in deionized and sterilized water for 6 months. The difference in surface morphology between 6 months in renewed natural seawater and 6 months in deionized and sterilized water is shown in Figure 8. No surface erosion was observed on the sample immersed in deionized and sterilized water, whereas the surface of the sample immersed in natural seawater was severely damaged. After 12 months at 40°C, small cracks are visible on the surface of the monofilament and a strip looks as if it has been peeled off. The sample observed after 3 months of immersion at 60°C exhibited lengthwise cracks, which were evenly distributed across the surface of the monofilament. Additionally, in some areas, the surface of the filament was observed to peel off.

3.2.3. PBS/PBAT monofilament hydrolysis monitored by steric exclusion chromatography

The molecular weights at different immersion temperatures are presented on Figure 9. No significant loss in the molecular weight was observed after 18 months at 4°C and 15°C. The molecular weight decrease from 123.6 $kg.mol^{-1}$ to 90.2 $kg.mol^{-1}$ after 18 months of immersion at 25°C. At 40°C the molecular weight decreases faster and is 36.1 $kg.mol^{-1}$ after 1 year of immersion. The decrease is even faster at 60°C and the

molecular weight falls to 16.9 $kg.mol^{-1}$ after 3 months.

3.3. Initial and long term properties of the PBS/PBAT rope

3.3.1. Initial characterization

Figure 11 presents the tensile/strain curves of tests on three ropes in the initial state. The initial stiffness measured between 1 kN and 5 kN was between 0.69 and 1.01 kN with a mean value of 0.83 kN. A mean strain at break and mean load at break were reproducible and respectively 28.6 kN and 35.2% with failure always observed at the end of one splice.

3.3.2. Aged rope properties

Several rope samples were immersed in the same tanks as the monofilament samples at 15°C and 40°C to study the change in properties. At 15°C, one sample was removed and tested after 2, 4, 5, 9, and 12 months of immersion. At 40°C one sample was tested after 6 months of immersion and a second after 9 months. Figure 12 shows the residual strengths of the monofilament and the rope at 15°C and 40°C. No change in the load at break was observed for the rope immersed 1 year at 15°C. After 9 months at 40°C the rope broke at 17.1 kN, suggesting a loss of strength of 60%.

4. Discussion

This study aimed to investigate the natural seawater degradation of a PBS/PBAT marine rope, providing insights into its performance during service and potential loss scenarios. The monofilament was first mechanically tested and compared with a commercial HDPE used in the fishing industry. The S-shaped curves obtained for the PBS/PBAT monofilament are typical of PBS monofilaments as seen in published studies (Kim et al., 2016, 2019; Grimaldo et al., 2020), with an increase in stiffness due to a strain induced crystallization as explained by Ichikawa et al. (1994). The overall properties of the PBS/PBAT monofilament are below those of HDPE, but Deroiné et al. (2019) showed that it was possible to greatly improve Young's modulus and stress at break of PBS monofilaments by optimising the drawing process. However, both monofilaments have similar loads and strains at break: 25.1 N and 34.5% respectively for the PBS/PBAT blend, and 21.4 N and 40.5% respectively for the HDPE, so the PBS/PBAT monofilament could already be considered as a substitute of HDPE in applications where the use of a slightly thicker monofilament is possible. PBS and PBAT are known for their biodegradability in soil and compost (Ahn et al., 2001; Tserki et al., 2006; Zhao et al., 2005), but their degradation in seawater is slower and less studied (Narancic et al., 2018). The monofilament may still lose its initial properties when exposed to a natural environment like seawater, so it was important to study these changes to determine if it can be used for marine applications such as fishing or aquaculture gear. Knowledge of the lifetime is also essential for Life Cycle Analysis (LCA),

in order to check the environmental benefits of a material change. The next step was therefore the study of seawater aged specimens.

The PBS/PBAT monofilament was immersed in renewed natural seawater tanks at different temperatures alongside a commercial HDPE monofilament for comparison purpose. The loads at break of both monofilaments were monitored as an indicator of physical degradation. The HDPE monofilament's ability to retain its original properties after a 1-year immersion in seawater, regardless of temperature, explains its persistence in the marine environment and the potential threat it poses if discarded as a rope or fishing gear. The absence of property loss for the PBS/PBAT blend at 4°C and 15°C indicates that fishing gear made from this monofilament would have adequate durability for use in temperate waters, but also that it could persist in the environment and be a threat for at least 18 months if it is lost and sinks to low temperature regions of the ocean. On the other hand, the loss of properties in the PBS/PBAT monofilament at 25°C is an indicator of the polymer's degradation in the marine environment, and fishing gear made from this filament would be less dangerous in case of loss. The rapid degradation of the breaking load at 40°C and 60°C indicates that the PBS/PBAT monofilament is much more susceptible to the marine environment and less stable than the HDPE monofilament. A detailed understanding of these degradations is therefore necessary, both to ensure that it does not lead to the formation of microplastics and also to account for this degradation in the design phase of the gear.

With regard to the loss of properties at 25°C, 40°C, and 60°C, various techniques have been used to identify the degradation mechanisms of the polymer. The surface morphology was first examined using a scanning electron microscope. No significant changes were observed at 4°C and 15°C which is consistent with the stability of the mechanical properties when immersed in seawater at these temperatures. The surface erosion pattern seen after 18 months at 25°C on Figure 7 was already observed on a PBSAT monofilament by Kim et al. (2016) in a natural environment at lower temperatures, after a longer time period of 2 years, and described to be a result from a biodegradation process. Surface erosion has also been observed on pure PBAT samples immersed in seawater for a 1 year period (Kedzierski et al., 2018). No surface erosion was seen after 6 months in sterilized water while holes were presents after the same period and at the same temperature in the natural seawater tank as shown by Figure 8. The difference in erosion rates highlights the role of microorganisms present in natural seawater, which are absent in sterilized water. The observed surface degradation can be considered as an initial stage in a depolymerization process, triggered by enzymatically catalyzed hydrolysis, as described by Müller et al. (2001). This process could generate microbial assimilable intermediates. However, surface damage is not sufficient evidence to determine the overall assimilation of a polymer by microorganisms as Zettler et al. (2013) observed it on conventional plastics. Additionally, the absence of holes at lower temperatures indicates that further studies are necessary to fully understand the kinetics of this degradation. After 1 year at 40°C, no degradation justifying a 70% loss of properties was observed using the SEM. Nevertheless, the absence of holes at this temperature indicates that the

degradation is abiotic. For the sample immersed for 3 months at 60°C, lengthwise cracks were visible on the surface, corresponding to the material embrittlement as noted after the mechanical testing presented on Figure 4. As the surface morphologies were very different for the three temperatures where a significant loss of properties was measured, different degradation processes may be involved. Steric exclusion chromatography has been performed to further understand the loss of properties observed at the different temperatures. This technique provides information on the distribution in length of polymer chains within each sample. Polyester polymers like PBS and PBAT are known to be degraded by water by a chain scission process at the ester bonds (Bellenger et al., 1995; Deshoulles et al., 2022). The aim of using this method was to check whether the polymer chains were reducing in size during aging, and thus to confirm whether hydrolysis was one of the processes leading to the loss of properties of the samples at 25°C, 40°C, and 60°C. The absence of loss of molecular weight after 18 months at 4°C and 15°C on the Figure 9 correlates with the stability of the mechanical properties at these two temperatures as seen on the Figures 4 and 5. A significant reduction in polymer chain length was observed after 18 months at 25°C, indicating that hydrolysis is taking place and affecting the properties of the monofilament, in addition to surface erosion. At 40°C, the loss of molecular weight provides evidence of material degradation that was not visible through SEM observations alone. The decrease of molecular weight at 60°C could be considered as the potential cause of the visible cracks observed in the SEM photographs and the rapid loss of material properties visible on Figure 5. The decrease in molecular weight matches the temperature dependant loss of mechanical properties, so hydrolysis can be retained as one of the degradation processes taking place during the aging of the samples in seawater. Figure 10 presents the load at break versus the molecular weight and shows that a relation exists between these two properties. The data points obtained at 25°C are below the linear regression and yet they are still linear, which could be related to a lowering of the load at break introduced by the surface erosion seen on the SEM observations. The presence of multiple degradation processes at the same time does not allow a simple prediction of the lifespan of this polymer as done for other polymers in the literature (El-Mazry et al., 2012; Deshoulles et al., 2021; Dilkes-Hoffman et al., 2019). Modelling the loss of properties of biodegradable polymers at natural temperatures requires the separation of biotic and abiotic factors as shown by Deroiné (Deroiné, 2014).

The influence of the observed degradation processes has been investigated on the entire rope to determine whether the aging of the rope structure can be predicted from the loss of the monofilament's properties. The same methodology as for the monofilament has been used: initial characterization followed by monitoring the mechanical properties in natural seawater maintained at 15°C and 40°C.

Three samples has been tested for the initial state characterization. A similar mean strain at break to the monofilament, 35.2%, is obtained, with a strain-induced increase of the stiffness recorded at similar strains. If the rope were constructed ideally with no influence on the load distribution and each monofilament carrying an equal load, the load at break would be 33.4 kN, given that the rope is made of 1344 monofilaments.

However, the sample's load at break was measured to be 28.6 kN, which is 14% lower than the ideal case and expected due to the influence of rope construction and load introduction (splices) on the load distribution. Failure always occurred at the end of one of the splices, which is common for spliced ropes (Milne and McLaren, 2006). The braided structure of the rope resulted in a specific modulus that was 18% lower than that of the monofilament due to the construction angles of the rope. While the strain at break and load at break were reproducible between samples, a significant variability in stiffness was observed, which could be linked to manual splicing. The comparison between the properties of the rope and the monofilament suggests that this material is appropriate for producing twisted ropes.

After initial characterization, rope samples were immersed in natural seawater for a period up to 1 year at 15°C, and 9 months at 40°C. The absence of load loss in the rope sample after one year of immersion at 15°C seen on Figure 12 is consistent with the results obtained for the monofilament. At 40°C, the onset of property loss for the rope is delayed compared to the monofilament; however, once initiated, the rate of degradation appears to be similar, as the slopes are comparable. The delay observed at this temperature could be cause by two phenomena : (i) the monofilament testing is more severe, with the tensile test clamps causing lower break loads than the splices, (ii) the water diffusion is slower in the rope and the hydrolysis observed on Figure 9 is not homogeneous between all monofilaments.

In order to use this type of new monofilament in a net twine or rope it is necessary to account for the changes in properties with time at the design phase. This requires the use of a model which can integrate material property changes and analyze their influence on the structure. In the fishing industry, that structure is often in the form of a braid, whether net twine or larger braided ropes. Finite element modelling may be used, particularly if the full net structure including knots is to be studied, but here the focus is at the rope level. FRM, a modelling tool developed to predict rope properties, is therefore more appropriate. It has been used successfully for previous studies on large marine ropes (Davies et al., 2006) and can predict tensile properties and tension-twist coupling. The input data are the sub-element properties (the monofilament load-strain plots here) and their geometry within the rope structure.

The load-strain properties of the monofilaments (Figure 3) were used to estimate the initial unaged rope properties. The input data are normalized with respect to break load and strain and modelled using a polynomial fit as depicted by Figure 13. Given the highly non-linear behaviour a 6th degree polynomial fit was required for unaged specimens.

As there was some variability in monofilament properties the two extreme curves (on Figure 3) were also examined. The rope model offers two options, hard and soft constructions. The latter is usually applied to multifilament yarns, which can deform under loading; the monofilaments show higher transverse rigidity and a hard option was chosen. The numbers and orientations of the filaments are then entered and the model provides a load-strain plot for the unaged rope for each set of monofilament properties, Figure 14.

The predicted break loads, between 23 and 28.6 kN, are quite close to the measured unaged rope values

as shown in Table 2. The strains at break are also similar, but the overall behavior of the model is less linear than the rope due to the high order polynomials used to fit the monofilament curves. These results indicate that the model provides a satisfactory prediction of braided rope properties, so it was then applied to the aged ropes. After aging at 15°C there was no drop in measured monofilament properties even after 12 months in seawater, so only the 40°C condition is described here.

The same method as for the initial state has been used to predict the rope properties after aging from the aged monofilament load-strain curves and polynomial fits. Once again load at break and initial stiffness values were measured, and these are given in Table 2, which summarizes the model results. Figure 15 shows the prediction of aging of the rope alongside the change in properties for the monofilament and the rope.

For the unaged samples the prediction based on the mean monofilament properties is within 10% of the measured value; when the maximum measured break load is used the prediction is even closer. For the samples after immersion, the model tends to overestimate the effect of aging on failure properties, providing a conservative break load value. This is an interesting result. The model assumption is that all the monofilaments degrade to the same extent as an individual monofilament exposed to the same aging conditions. However, monofilaments within a strand will be more or less protected from degradation due to the limited access of bacteria to the interior of the rope construction. For smaller ropes or net twines, the prediction may be closer to measured values.

5. Conclusion

This study investigated the potential use of a PBS/PBAT blend to mitigate the environmental impact of lost marine ropes. Although the PBS/PBAT monofilament had lower properties than HDPE, this could be compensated by increasing the diameter. Both types of monofilament were aged in natural seawater at various temperatures for at least one year. The HDPE monofilament showed no loss of mechanical strength, whereas the PBS/PBAT monofilament experienced degradation via hydrolysis and biodegradation at 25°C, 40°C, and 60°C. While PBS/PBAT monofilament may be a safer option due to its lower persistence in the marine environment, further research is needed to decouple the degradation mechanisms, enhance understanding of their kinetics, and develop models for predicting the lifespan of such materials.

Additionally, the rope made from this PBS/PBAT monofilament was immersed in the same conditions to evaluate aging within a complex arrangement of monofilaments and determine if the loss of properties could be predicted from the monofilament data using the FRM modelling tool. The rope's loss of properties was slower than that of the monofilament, and while the initial correlation was good, the modelling tool predicted a faster loss of properties. The conservative results may be due to a more severe mechanical test conditions for the aged monofilament or a degradation gradient within the rope structure. Nonetheless, the FRM provided an effective approach to assess initial rope properties and provide a conservative prediction

of aging states.

This study provides seawater aging data for a biodegradable rope that could help reduce the environmental impact of synthetic ropes at sea. However, it should be noted that short-term impact cannot be completely avoided (Wilcox and Hardesty, 2016), and this material should be used in conjunction with existing solutions to produce safer ropes for marine wildlife and to help reduce open sea plastic pollution. Overall, the use of biodegradable rope such as the one evaluated in this study shows promise in addressing the issue of plastic pollution in the world's oceans and represents an important step towards sustainable marine practices.

CRediT authorship contribution statement

Louis Le Gué: Conceptualization, data gathering and investigation, formal analysis, visualization, writing – original draft, writing - review and editing.

Peter Davies: Conceptualization, data gathering and investigation, formal analysis, writing – original draft, writing - review and editing.

Mael Arhant: Conceptualization, investigation, formal analysis, writing - review and editing.

Benoit Vincent: Conceptualization, investigation, writing - review and editing.

Erwan Tanguy: Conceptualization, investigation, writing - review and 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.

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Property	PBS/PBAT	HDPE
Density [$g.cm^{-3}$]	1.25	0.95
Diameter [mm]	0.35	0.28
Tex [$g.km^{-1}$]	121.7	54.6
Young's Modulus [GPa]	0.79	1.90
Load at break [N]	25.1	21.4
Stress at break [MPa]	261	368
Strain at break [%]	34.5	40.5

Table 1: Properties of the PBS/PBAT blend and the commercial HDPE.

Condition	Initial stiffness [kN]	Break load [kN]	
	Experimental (Min-Max)	Experimental (Min-Max)	Model (Min-Max)
Unaged	0.83 (0.69 - 1.01)	28.6 (28.5 - 28.7)	26.3 (23.1 - 28.9)
15°C, 12 months	0.69	29.1	25.3 (23.9 - 26.0)
40°C, 6 months	0.64	25.4	17.4 (16.2 - 19.4)
40°C, 9 months	0.64	17.0	10.6 (8.1 - 12.7)

Table 2: Summary of main rope model results and predictions.

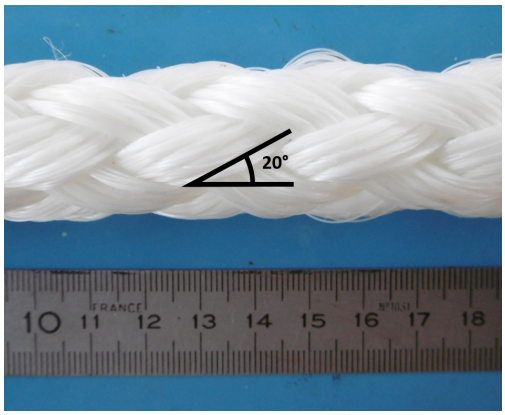

Figure 1: Close up view of the rope construction.

Figure 2: Rope tensile testing set-up equipped with cameras for strain measurements.

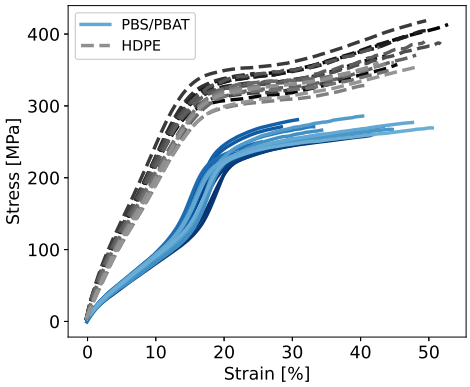

Figure 3: Tensile test curves at the initial state for the PBS/PBAT blend and HDPE.

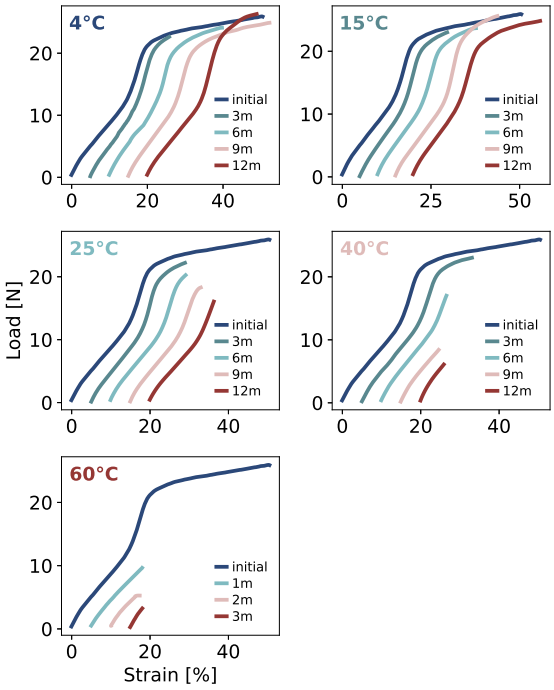

Figure 4: Change in the tensile test curve with aging at different temperatures.

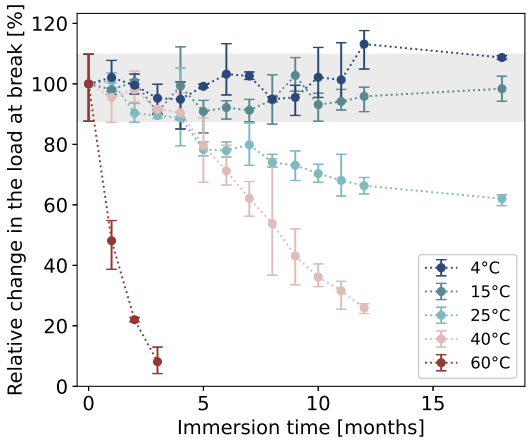

Figure 5: Load at break loss depending on the immersion time at different temperatures.

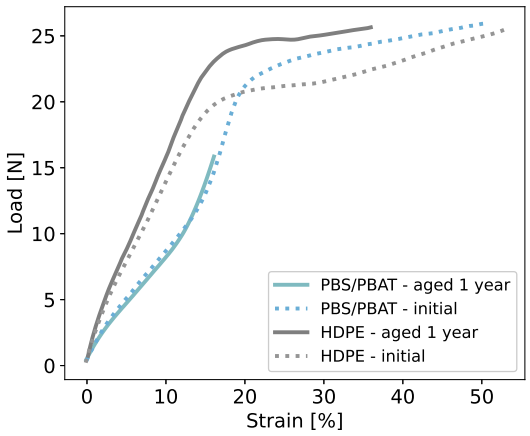

Figure 6: Tensile test curves after 1 year immersed at 25°C for the PBS/PBAT blend and HDPE.

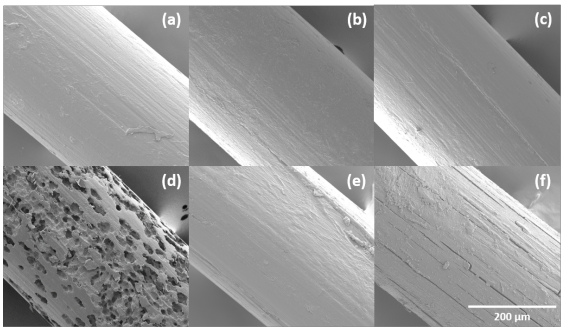

Figure 7: Surface observations for different immersion times and temperatures : (a) initial sample (b) after 18 months at 4°C, (c) after 18 months at 15°C, (d) after 18 months at 25°C, (e) after 12 months at 40°C, (f) after 3 months at 60°C.

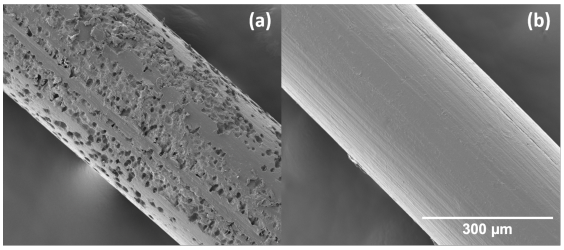

Figure 8: Surface observations for PBS/PBAT monofilaments immersed 6 months in (a) natural seawater and (b) deionized and sterilized water.

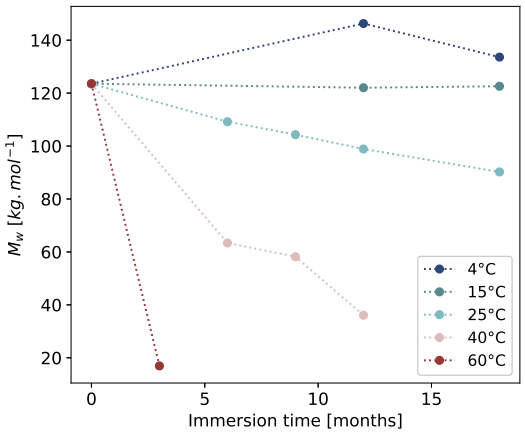

Figure 9: Mw change depending on the immersion time.

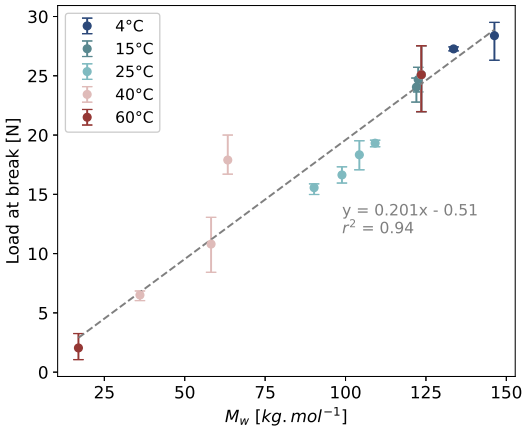

Figure 10: Load at break versus molecular weight M_w.

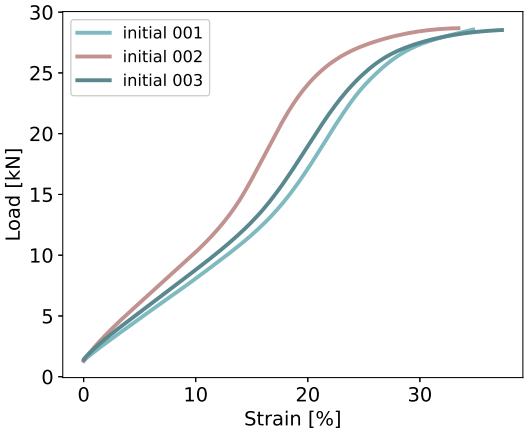

Figure 11: Tensile test curves of 3 rope samples before aging.

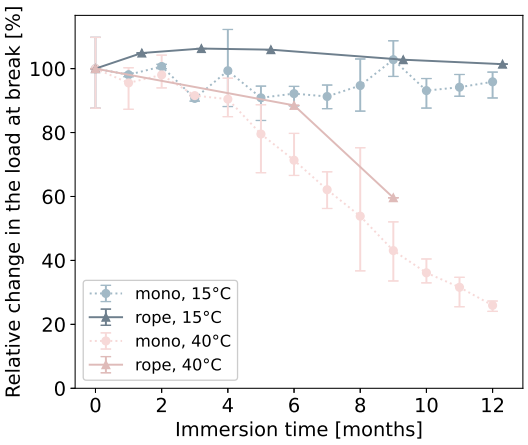

Figure 12: Load at break change for monofilament and rope at 15°C and 40°C.

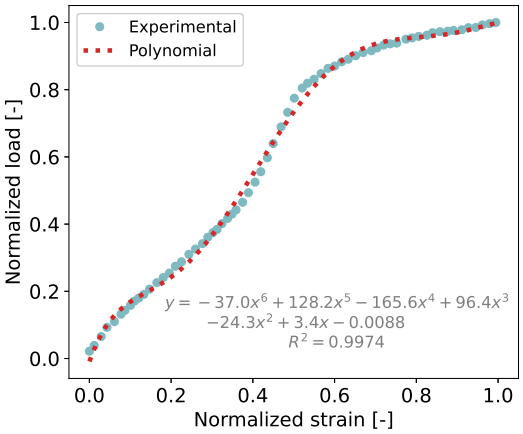

Figure 13: Example of monofilament input mean data for FRM.

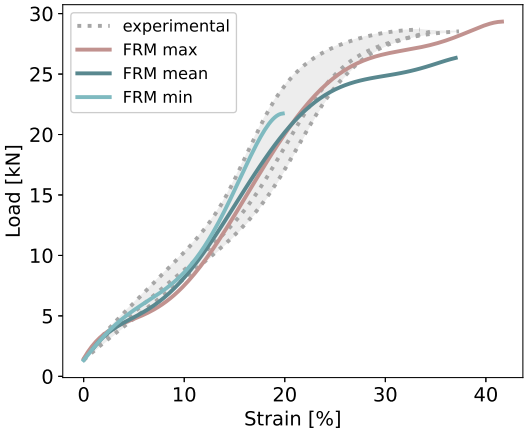

Figure 14: Predicted load-strain behaviour, unaged rope.

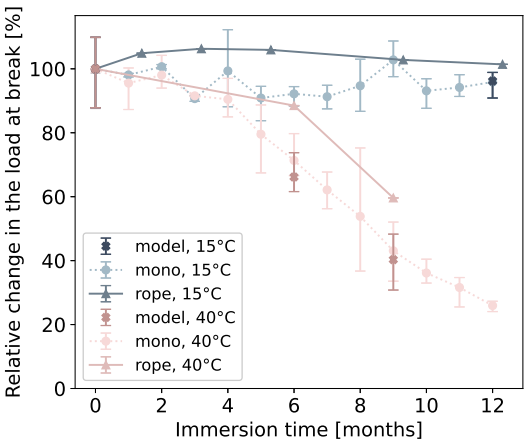

Figure 15: Load at break estimations predicted by the model alongside load at break for monofilament and rope at 15°C and 40°C.

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