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**A COMPARATIVE STUDY OF MECHANICAL PROPERTIES OF BIODEGRADABLE PBSAT
AND PA GILLNETS IN NORWEGIAN COASTAL WATERS**

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ABSTRACT

This paper presents a comparative study of mechanical properties of biodegradable PBSAT (polybutylene succinate co-adipate-co-terephthalate) and conventional polyamide (PA) gillnets used in Norwegian fisheries. Field tests were performed to simulate abandoned, lost, or otherwise discarded fishing gear. Changes in mechanical properties of PBSAT and PA nets in two Norwegian coastal environments were studied. Samples of biodegradable PBSAT gillnets and PA gillnets were placed inside modified lobster pots at four different locations: two outside the island Hitra in the middle of Norway and two outside Tromsø in the north of Norway. For each pot, seawater temperature was logged each hour, and net samples were retrieved for analyses at 3 to 9 months intervals.

Tensile strength testing was performed to determine and compare mechanical properties of biodegradable and PA monofilaments and gillnets. Comparative analyses were conducted, aimed at investigating the different behaviors of biodegradable material and conventional PA material, and the possible influence of seawater temperature on the degradation process of biodegradable PBSAT gillnets. Reduced tensile strength and elongation at break, and a slight increase in stiffness was observed for both PA and PBSAT monofilaments after the field trial at Hitra, indicating degradation of both polymer materials. After 25 months immersion in seawater, the PBSAT gillnets exhibited a significant reduction of tensile strength due to seawater exposure (35%), and the tensile

strength of PBSAT gillnets was then 26% lower than the average strength of the PA net samples.

NOMENCLATURE

ALDFG	Abandoned, lost, or otherwise discarded fishing gear
PA	Polyamide
PBS	Polybutylene succinate
PBAT	Polybutylene adipate-co-terephthalate
PBSAT	Polybutylene succinate co-adipate-co-terephthalate
t-test	Student's t-test
SEM	Scanning electron microscope

INTRODUCTION

When fishing nets are lost, abandoned or discarded at sea, they may continue to catch fish and other animals for a long period of time. This phenomenon is known as "ghost fishing" [1]. Lost fishing gears also cause a variety of harmful impacts to coral reefs and benthic fauna, and marine pollution may introduce synthetic (non-biodegradable) plastic materials into the marine food web. There are also economic consequences

due to marine species mortalities, replacement of lost gear, and diverse costs related to retrieving operations. Recognition of all these problems is nowadays demonstrated through the large number of international organizations and agreements that currently focus on reducing the effect of abandoned, lost, or otherwise discarded fishing gear (ALDFG). In addition to numerous national initiatives that have been implemented around the world to mitigate the ALDFG impact on the marine ecosystem [2]. To date, Norway is one of the few countries in the world that has a program for systematic annual retrieval of ALDFG from the most intensively fished areas [3–5]. Based on information provided by fishermen, the Norwegian Directorate of Fisheries carry out annual retrieval operations for reported lost fishing gear and deliver it on land to recycling [6, 2]. However, these operations are highly challenging because of the depth (500–1000 m) and strong currents in the areas, as well as uncertainties associated with the position of lost gear.

The development of fishing gears made of biodegradable plastic materials is considered as a potential solution to reduce "ghost fishing" and plastic pollution at sea caused by ALDFG [7–10]. In recent years, many studies have documented the mechanical properties, biodegradability, and fishing efficiency of colorless gillnets made of polybutylene succinate (PBS) resin blended with polybutylene adipate-co-terephthalate (PBAT) resin and polybutylene succinate co-adipate-co-terephthalate (PBSAT) resin [11–21]. In Norway, gillnets are among the most important commercial fishing methods for the coastal fleet, however colorless gillnets are not currently used. Norwegian fishermen prefer colored gillnets because they provide a better contrast with the sorting boards and make removal of fish from nets easier, and also because many fishermen believe that some colors have better catch efficiencies than others depending on the contrast with the seabed and surroundings.

In 2016 and 2017, a set of fishing trials were carried out to compare the relative fishing efficiency of colored gillnets made of a new biodegradable PBSAT resin (Patent EP3214133 A1) with conventional PA gillnets. This new biodegradable resin was designed for better coloring properties which does not give rise to problems such as reduced strength due to coloration [22]. The fishing trials covered two consecutive fishing seasons for cod (*Gadus morhua*) and saithe (*Pollachius virens*) in northern Norway. The corresponding catch rates were assessed in a previous study [23].

The present study focuses on the mechanical properties of ALDFG due to degradation of gillnet materials. Field tests were performed to simulate abandoned, lost, or otherwise discarded fishing gear. Changes in mechanical properties of PBSAT and PA nets in two Norwegian coastal environments were studied.

MATERIALS AND METHODS

Materials

Polybutylene succinate-co-adipate-co-terephthalate (PBSAT) resin is an aliphatic-aromatic co-polyester. According to the patent application, it is biodegradable, exhibits an excellent coloration effect and does not cause problems such as a decrease in strength due to coloration, as observed in PBS and PBAT resins [22]. Anti-oxidants and UV stabilizers are applied in production of monofilaments for gillnets and fishing lines.

Test samples

Gillnets and monofilaments of both PBSAT and PA (Polyamide) were applied in the experiments (Figure 1 and 2). Conventional nets and fishing lines of PA were included as reference (Vónin Refa gillnets and Sølvrøken sea fishing line). Monofilaments had a diameter of 0.7 mm, and gillnets had been produced by similar monofilaments and double knots. Mesh size was 200 mm for PBSAT nets, and 215 or 330 mm for PA nets.

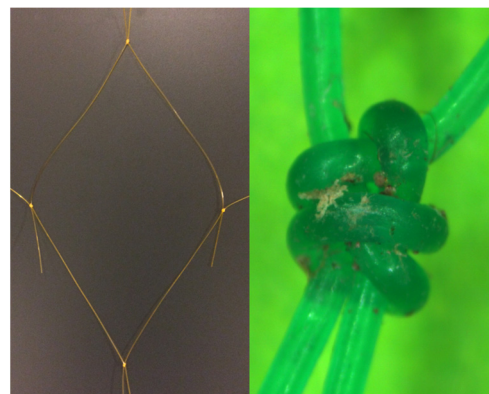


Figure 1. Gillnet made of double knotted monofilaments. Left: PA (new); Right: PBSAT (used).

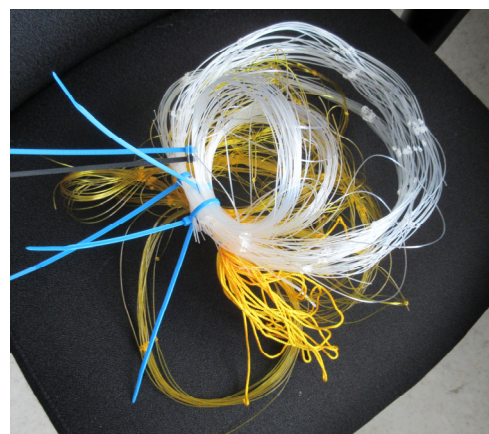


Figure 2. Set of test samples: Gillnets of PA (yellow) and PBSAT (white), and monofilaments of PA and PBSAT (both white).

Field test in coastal environment

Field tests were performed to assess changes in mechanical properties of biodegradable ALDFG PBSAT gillnets in Norwegian coastal environments. Test samples were attached inside modified lobster pots at four different locations: two outside the island Hitra in the middle of Norway (Figure 3) and two outside Tromsø in the north of Norway.

The PA gillnets deployed had a nominal mesh size of 330 mm at Hitra and 215 mm in Tromsø. In addition to gillnets, monofilament samples of PBSAT and PA were deployed at the two sites outside Hitra. The monofilaments may provide a more direct measure of material degradation, excluding the effect of knots [21]. All the conducted degradation tests are listed in Table 1 by the locations, deployed samples and durations.

The samples were deployed on May 30th, 2016 at the two sites outside Hitra and one month later at the two sites outside Tromsø. The pots containing the samples were placed at water depths of 35–50 m. For each pot, seawater temperature was logged each hour, and samples were retrieved for analyses at 3 to 9 months intervals.



Figure 3. Modified lobster pot with 8 sets of test samples (at Hitra).

Table 1. List of the conducted degradation tests in seawater.

	Location	Samples	Duration
Location 1	Hitra	gillnets and monofilaments	25 months
Location 2	Hitra	gillnets and monofilaments	25 months
Location 3	Tromsø	gillnets	15 months
Location 4	Tromsø	gillnets	6 months

Tensile testing of nets and monofilaments

Tensile testing was performed to determine and compare mechanical properties of PBSAT and PA gillnets and monofilaments before and after the field test. Both tensile strength, elongation at break and stiffness found from a force-elongation curve can be applied to assess degradation of mechanical properties. All measurements were performed in compliance with ISO 1806:2002 (gillnets) and ISO 1805:1973 (monofilaments), using a universal testing machine (H10KT, Tinius Olsen TMC, PA, USA) equipped with a load cell of 5000 N capacity.

Tensile properties of the gillnet samples were found by mesh strength tests, while monofilaments were tested using bollard grips. Initial mesh length of gillnets was found as the mesh opening at pretension. For monofilaments, the initial length of each sample was defined as the monofilament length between the clamps at pretension, which was approximately 450 mm. Pretension was applied as 2 N for gillnets and 1 N for monofilaments.

For gillnets, testing speed was adjusted according to the mesh size: 200 mm/min for gillnets with mesh size 200-215 mm, and 300 mm/min for mesh size of 330 mm. Testing speed for monofilaments was 400 mm/min between grips.

Tensile properties were measured and found based on at least 20 replicates for nets and at least 10 replicates for monofilaments.

Tensile testing was performed in wet condition, with samples that had been wetted for 48-72 hours in room tempered tap water. New samples were also tested in dry condition to consider the effect of water on tensile properties. In dry condition, the specimens were acclimated to the laboratory atmosphere for at least 48 hours.

Figure 4 shows an example of force-elongation curves obtained from tensile testing of PBSAT monofilaments after 25 months immersion in seawater (10 replicates). For each replicate, the tensile strength was determined as the peak of the force-elongation curve, and the corresponding elongation was taken as the elongation at break. For a set of samples, the tensile strength was determined as the average of all replicates, and polynomial fitting was performed to determine the average force-elongation curve.

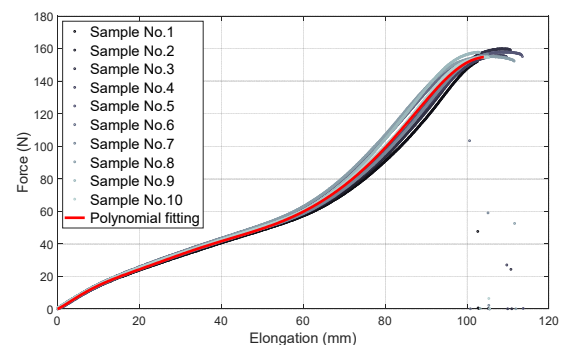


Figure 4. Polynomial fitting of the force-elongation curves obtained from tensile strength tests of the PBSAT monofilaments after 25 months immersion in seawater.

RESULTS AND DISCUSSION

Results from the field degradation tests are given as changes in strength and elongation of gillnet and monofilament samples. In addition, stiffness properties were assessed for a selected location (Location 1). Possible effect of temperature on degradation was assessed, and finally possible degradation mechanisms and observations were presented and discussed.

Changes in strength and elongation at break after field trial

After the field trial, most samples from Location 1 and 2 (Hitra) showed reduced strength and elongation at break, indicating degradation of the material (Table 2 and 3). The strength loss was up to 43% for the PBSAT net at Location 2. A contributing source of this strength loss is possibly mechanical damage due to crabs, which is discussed later. Reduction in elongation corresponds with reduction in strength. At Location 3 and 4, no significant changes in average strength have been found for PA and PBSAT gillnets after 6-15 months in sea. For the PA netting at Location 4, an increased average strength value was found after the field test. This may be explained by naturally varying properties of PA gillnets.

The results show that after 25 months of exposure to coastal seawater, PBSAT gillnets showed larger reduction in average strength and elongation than comparable PA nets. At location 3 and 4, no significant reduction in strength or elongation was found. Thus, there were no signs of degradation of the samples at Location 3 and 4.

Monofilaments showed reduced strength and elongation at break at approximately the same level as the gillnets, except the PBSAT monofilaments at Location 1, which had significantly less reduction in properties.

Tensile strength and elongation at break as a function of time is given for test samples at Location 1 in Figure 5-8. Data is given for "new" material, i.e. new specimens not subjected to degradation test in seawater, and material samples retrieved 3, 9, 16 and 25 months after being immersed in seawater. PA nets and monofilaments experienced reduced properties after 3 months in sea, after that, no significant changes were found throughout the total test duration of 25 months. After having been immersed in seawater for 3 months, the tensile strength of PA nets and monofilaments was reduced by 16% and 19% respectively.

When new (and wet), the measured tensile strength of PBSAT gillnets was 11% lower than for PA nets. After being immersed in seawater from 3 to 16 months, no significant difference in strength was found using a 95% confidence interval (Kolmogorov–Smirnov test, $P = 0.146$, > 0.05 ; t-test, $P = 0.065$, > 0.05). However, after 25 months immersion in seawater, the PBSAT gillnets exhibited a significant reduction of tensile strength due to seawater exposure (35%), and the tensile strength of PBSAT gillnets was then 26% lower than the average strength of the PA net samples.

When new (and wet), the measured tensile strength of PBSAT monofilaments was 23% lower than for PA monofilaments. After 3 months of submergence and throughout the test, the tensile strength of PBSAT and PA

monofilaments were at the same level (except at Location 2 after 25 months). No significant reduction was found from the 9th to 25th month in the 95% confidence interval (Kolmogorov–Smirnov test, $P = 0.241$, > 0.05 ; t-test, $P = 0.174$, > 0.05) for the PA monofilaments. The PBSAT monofilaments exhibited a slight strength reduction over time: reduced by 8% after having been immersed in seawater for 25 months.

Figure 7 compares the elongation at break of PA and PBSAT gillnets. When new (and wet), the elongation of PBSAT gillnets was 12% higher than PA. After 16 months in seawater, the elongation of PBSAT gillnets was still 14% higher than PA. The elongation of PBSAT gillnets showed a significant reduction (27%) after 25 months in seawater, and elongation at break was then at the same level as for PA gillnets.

Figure 8 compares the elongation at break of PA and PBSAT monofilaments. When new (and wet), the elongation of PBSAT monofilaments was 22% lower than PA, while no significant difference was found when they were immersed in seawater between 3 and 25 months. After having been immersed in seawater for 3 months, the elongation of PA monofilaments was reduced by 24%. No significant reduction was found from the 9th to 25th month in the 95% confidence interval (Kolmogorov–Smirnov test, $P = 0.678$, > 0.05 ; t-test, $P = 0.566$, > 0.05). The elongation of PBSAT monofilaments was on average reduced by 7% after having been immersed in seawater for 25 months.

Figures 9-12 compare changes in strength and elongation for PBSAT gillnets and monofilaments at Location 1 and 2. Results are given relative to new material in percentage. The degradation tests at the two different locations gave similar results during the first 16 months. During the last time period (16-25 months), some of the PBSAT samples at Location 2 showed larger reduction in tensile properties: Several of the individual strength tests of the gillnet and monofilament samples yielded relatively low strength and elongation. This was probably due to observed mechanical damage to the nets and monofilaments caused by crabs.

Table 2. Changes in measured average strength and elongation of gillnets after field test. Mean value / standard deviation [%].

	PA		PBSAT	
	Strength	Elongation	Strength	Elongation
Location 1	-22 / 8	-17 / 8	-35 / 7	-27 / 8
Location 2	-21 / 10	-15 / 9	-43 / 15	-37 / 17
Location 3	2 / 7	-9 / 6	-3 / 3	-6 / 3
Location 4	11 / 5	-2 / 4	0 / 4	-3 / 3

Table 3. Changes in measured average strength and elongation of monofilaments after field test. Mean value / standard deviation [%].

	PA		PBSAT	
	Strength	Elongation	Strength	Elongation
Location 1	-22 / 3	-26 / 8	-8 / 1	-7 / 2
Location 2	-35 / 12	-33 / 12	-34 / 15	-14 / 7

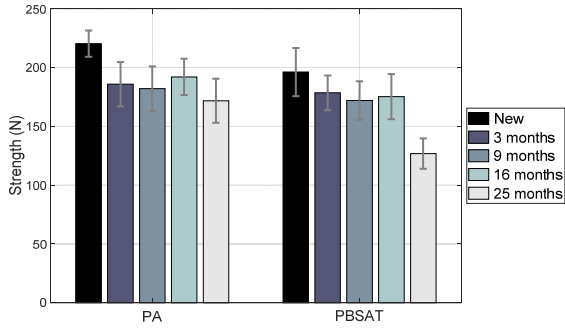


Figure 5. Tensile strength of PA and PBSAT gillnets at Location 1 as a function of time. Given as average value with standard deviation.

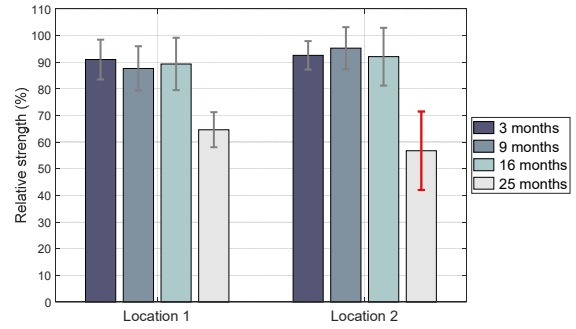


Figure 9. Relative tensile strength of PBSAT gillnets at Location 1 and 2. Given as average value with standard deviation.

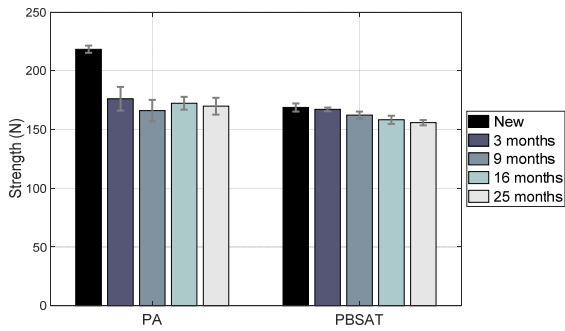


Figure 6. Tensile strength of PA and PBSAT monofilaments at Location 1 as a function of time. Given as average value with standard deviation.

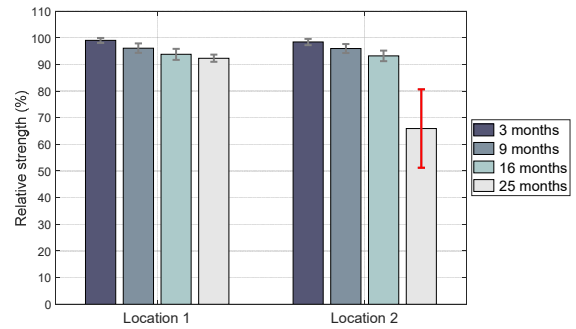


Figure 10. Relative tensile strength of PBSAT monofilaments at Location 1 and 2. Given as average value with standard deviation.

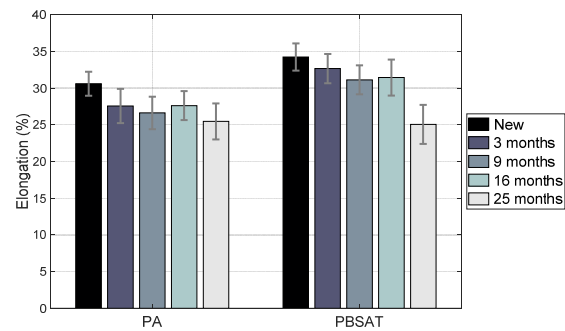


Figure 7. Elongation at break of PA and PBSAT gillnets at Location 1. Given as average value with standard deviation.

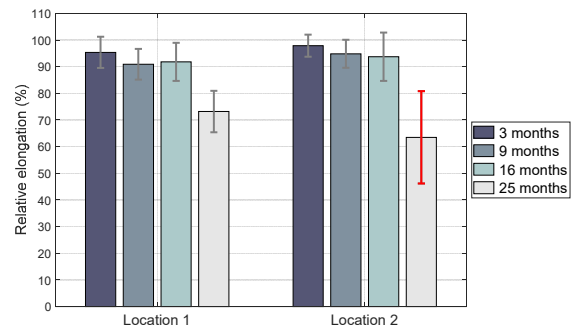


Figure 11. Relative elongation of PBSAT gillnets at Location 1 and 2. Given as average value with standard deviation.

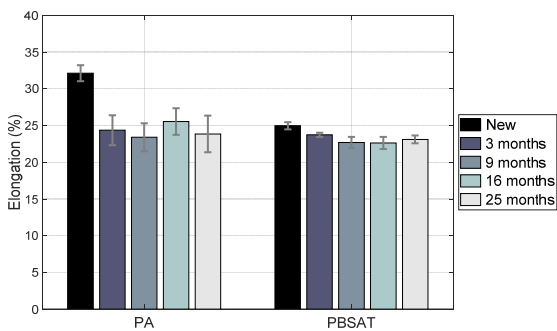


Figure 8. Elongation at break of PA and PBSAT monofilaments at Location 1. Given as average value with standard deviation.

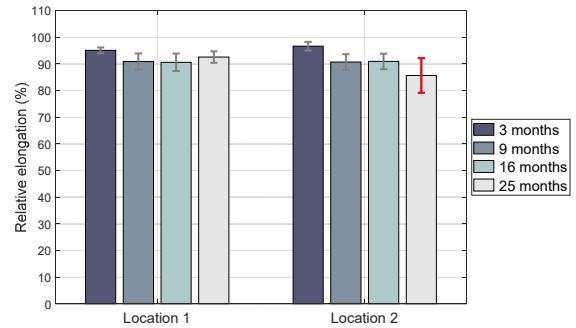


Figure 12. Relative elongation of PBSAT monofilaments at Location 1 and 2. Given as average value with standard deviation.

Tensile properties

Changed stiffness properties for the monofilaments may indicate degradation of the polymer material. Increased stiffness can be identified as an increased slope in a force-elongation curve from tensile testing of the materials and vice versa. Fitted force-elongation curves from tensile testing are shown for samples from Location 1 after 25 months of submergence in Figure 13-16. Elongation is given in percentage relative to the initial length of the samples. For comparison, curves are also given for new material, both in dry and wet conditions.

The gillnets have different tensile properties in dry and wet condition. This is due to different behaviors of the knots; the knots will tighten during the first part of a mesh strength test and will behave differently depending on their condition. PA will absorb water, which has a significant effect on tensile properties as stiffness at low elongation (Figure 15), also affecting the behavior of the knot. Wetting of new PA monofilaments reduced the average tensile strength by 19%. Properties of PBSAT monofilaments are not affected by wetting (Figure 16), however the knots slipped in dry state, resulting in reduced stiffness and strength for the gillnets (Figure 14). It was observed that the knots in the PBSAT nets were not as tight as in the PA nets.

Wetting of new PBSAT gillnets led to an increase in average tensile strength by 42%, while the strength was reduced by 6% for the PA gillnets. After having been immersed in seawater for 25 months, both the PA and PBSAT gillnets exhibited a significant reduction in tensile strength while no noticeable difference in stiffness was found.

A slight increase in stiffness, reduced tensile strength and elongation at break was observed for both PA and PBSAT monofilaments after the field trial, indicating degradation of both polymer materials.

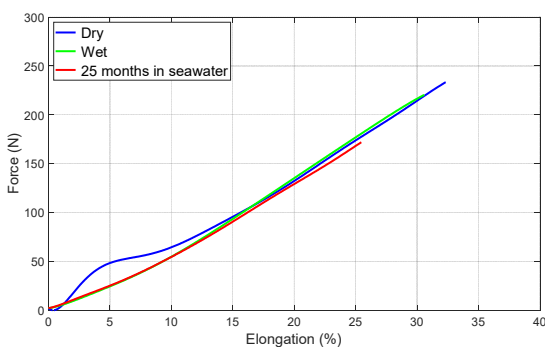


Figure 13. Force-elongation curves of the PA gillnets before (Dry and Wet) and after field trial at Location 1. Elongation is given relative to initial length in percentage.

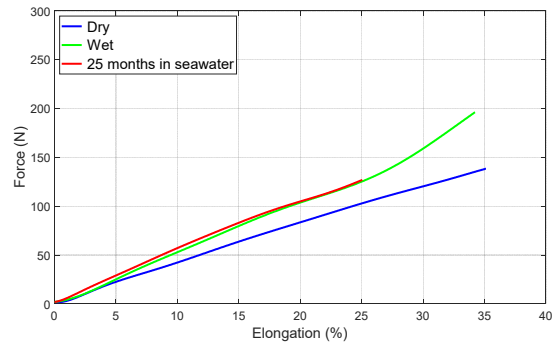


Figure 14. Force-elongation curves of the PBSAT gillnets before (Dry and Wet) and after field trial at Location 1. Elongation is given relative to initial length in percentage.

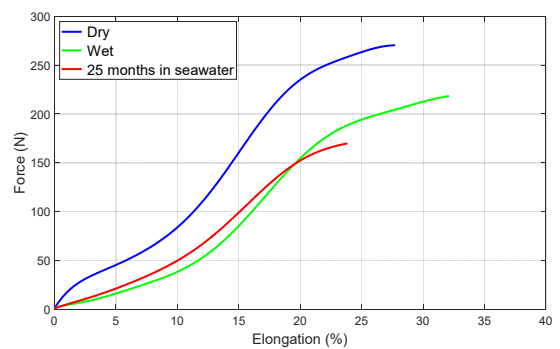


Figure 15. Force-elongation curves of PA monofilaments before (Dry and Wet) and after field trial at Location 1. Elongation is given relative to initial length in percentage.

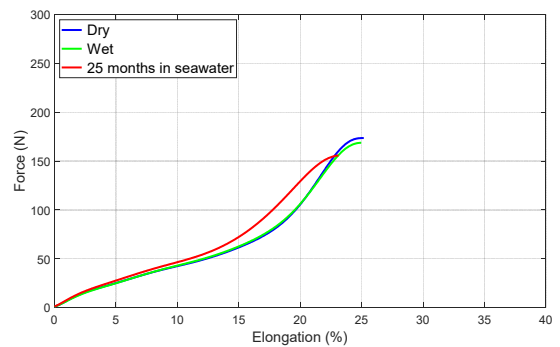


Figure 16. Force-elongation curves of PBSAT monofilaments before (Dry and Wet) and after field trial at Location 1. Elongation is given relative to initial length in percentage.

Influence of water temperature on the degradation process

Figure 17 shows recorded water temperatures at two different locations, where the water temperature at Location 2 was on average 2 to 4 °C higher than at Location 3. Location 1 had similar temperature as Location 2, and Location 4 had similar temperature as Location 3. Temperature varied between 6-15 °C at Location 1 and 3-9 °C at Location 3. Figure 18 and 19 show the change in strength and elongation of PBSAT gillnets at the two locations. During the field trial, the strength of PBSAT gillnets at Location 2 was on average 5% lower than at Location 3 (which showed no significant change in strength of PBSAT gillnets). Gillnets at both locations showed similar reduced elongation at break, increasing in time up to 6 % after 15 months immersion.

It was shown in a previous study [21] that biodegradable gillnets made of a blending of PBS-PBAT resin had a higher degradation rate in higher water temperatures in summer, and slowly degraded in cold seawater (< 5 °C). In our study, we do not see such correlation. However, no degradation of the gillnets was observed at Location 3, while both PA and PBSAT gillnets degraded at Location 1. This imply that degradation of PBSAT may be a temperature dependent process. It is well-known that degradation of polymers will increase with increased temperature.

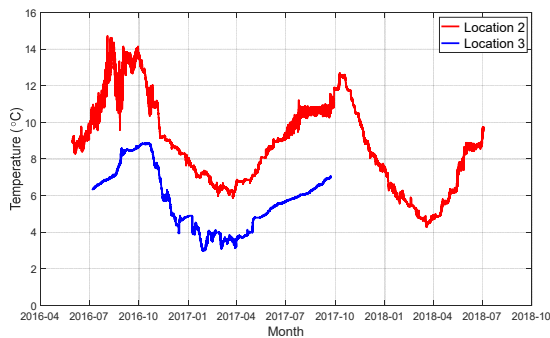


Figure 17. Water temperature during the degradation test at Location 2 (middle Norway) and Location 3 (northern Norway).

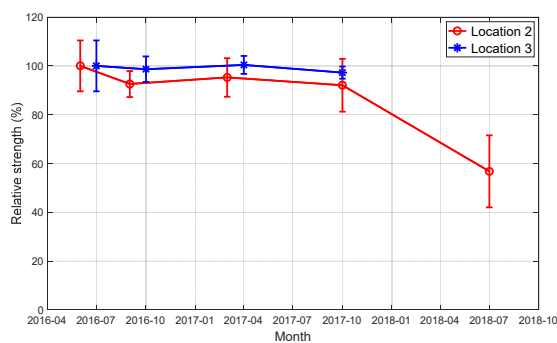


Figure 18. Relative tensile strength of the PBSAT gillnets after the degradation test at Location 2 and Location 3. Given by the average value with standard deviation.

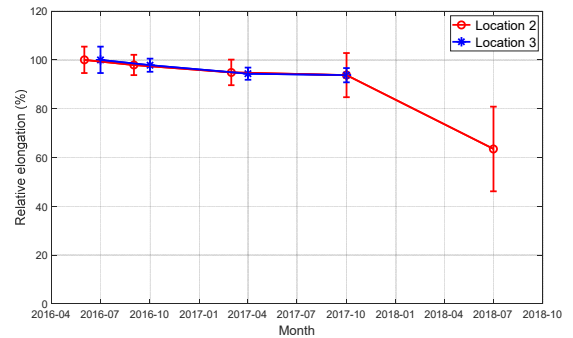


Figure 19. Relative elongation of the PBSAT gillnets after the degradation test at Location 2 and Location 3. Given by the average value with standard deviation.

Possible degradation mechanisms and observations

The degradation of PA and PBSAT fibers used in this experiment was the result of chemical and mechanical changes that occurred during the 25 months' experimental period. The degradation led to loss of strength and elongation, and distortion and discoloration of fibers was observed. Different mechanisms of degradation might have acted simultaneously on the PA and PBSAT fibers, and some of them probably had a stronger effect than others. Although this experiment was unable to identify and quantify the effect of specific mechanisms of degradation of the samples that were studied, possible degradation mechanisms are discussed below.

As shown by the results, both PA and PBSAT gillnets exhibited a reduction in tensile strength and elongation at break after having been immersed in seawater. The PA gillnets exhibited a significant strength reduction in the first 3 months while there was no significant reduction from the 9th to 25th month. The PBSAT gillnets showed a slight strength reduction during the first 16 months, while a large reduction was found after having been immersed in seawater for 25 months. This finding is consistent with a previous study [21], which showed that the biodegradable gillnets (made of a blending of PBS-PBAT resin) began to degrade after about 2 years when immersed in seawater.

Possible degradation mechanisms during the field experiments are microbiological degradation, hydrolysis, oxidation, and mechanical damage from crabs. Polymers are also known to also be vulnerable to UV-exposure, however at more than 25 meters depth we consider the UV-radiation to be negligible. Abandoned, lost, or otherwise discarded fishing gear will in addition experience wear and abrasion damages. The damages will be similar as found in used nets. During fishing trials [23], damages due to use and wear was documented (i.e. abrasion in the hauling machine, friction due to contact with hard surfaces when the gillnets were operated on deck). Figure 20 shows a representative example of the gillnet damages observed with a scanning electron microscope (SEM). It was found that the gillnet damages had contributed to loss of tensile strength.

For microbial degradation to take place, it is crucial that the right types of microbes are present at the location and are established on the samples. The samples from the Locations outside Tromsø did not have any visible bio-fouling or bio-film, opposed to the samples from Hitra that contained visible biologic material. Especially the last samples after 25 months submergence contained significant biofouling, including algae, spirorbis worms (Figure 21) and starfish. Biofouling was also observed inside the knots of the gillnets, which may affect the strength of the knots during mesh strength tests [24].

At Location 2, several crabs were found entangled in the specimens when retrieving samples after 25 months. It was observed that the PBSAT samples were entangled, and the filaments were bent and crushed (Figure 21 and 22). In comparison, the PA filaments seemed undisturbed. This indicates that the degraded PBSAT was vulnerable to mechanical damage due to compressive loads and bending. This was also experienced during mesh strength tests: The size of the grips had to be increased in order to reduce compressive loads on the fibres and fracture in the grips. The fractures after tensile testing were frayed (Figure 23), the degraded PBSAT appears to be fragmented into axial fibers.

During a mesh strength test, gillnets usually break in the knots, where the material is subjected to compressive, bending and shear loading. In the present study, it was found that PBSAT gillnets had a higher reduction in strength and elongation than the monofilaments (Figure 5 and 6), which may be due to compressive loads in the knots during stretching and biofouling particles inside the knots.



Figure 21. Net samples retrieved from Location 2 after 25 months of submergence. PBSAT samples were entangled (left).

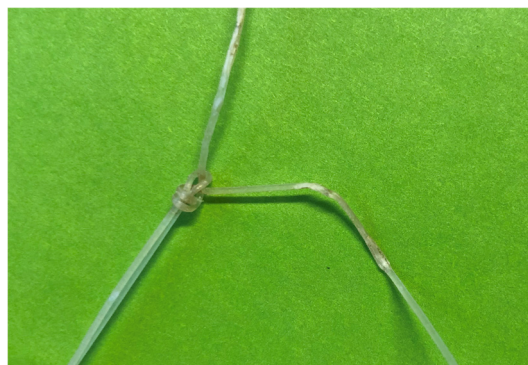


Figure 22. Bent and crushed PBSAT fiber from Location 2 after 25 months of submergence.

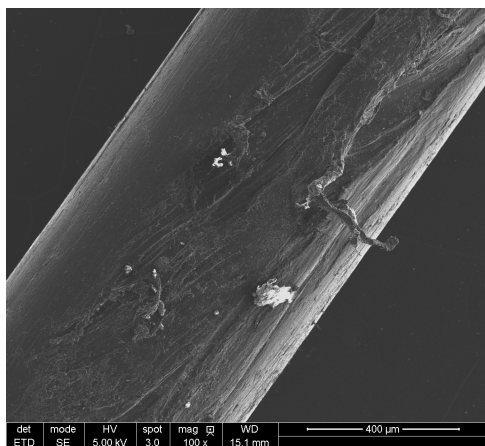


Figure 20. Scanning electron microscope (SEM) image showing a representative example of abrasion damages caused by use and wear throughout fishing trials [23].



Figure 23. Frayed fracture of PBSAT fiber from Location 2 after 25 months of submergence.

CONCLUSION

After the field trial, most samples from Location 1 and 2 showed reduced strength and elongation at break, indicating degradation of the material. The strength loss was up to 43 % for the PBSAT gillnets at location 2. There were no signs of degradation of the samples at Location 3 and 4.

PA nets and monofilaments experience reduced properties after 3 months in sea, after that, no significant changes are found throughout the total test duration of 25 months. The PBSAT gillnets showed a slight strength reduction during the first 16 months, while a large reduction was found after having been immersed in seawater for 25 months. After 25 months immersion in seawater, the PBSAT gillnets exhibited a significant reduction of tensile strength due to seawater exposure (35%), and the tensile strength of PBSAT gillnets was then 26% lower than the average strength of the PA net samples. Reduction in elongation corresponds with reduction in strength. In the present study, a possible correlation between the degradation of PBSAT gillnets and water temperature was not significant.

Reduced tensile strength and elongation at break, and a slight increase in stiffness was observed for both PA and PBSAT monofilaments after the field trial, indicating degradation of both polymer materials. Possible degradation mechanisms during the field experiments are microbiological degradation, hydrolysis, oxidation, and mechanical damage from crabs.

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