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Determining the Integrity of the Flexible Bladder under Marine Underwater Conditions

OCEAN GRAZER

BSc Industrial Engineering & Management

Bachelor Integration Project

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1 Abstract

A marine underwater energy storage system is exposed to biofouling which causes biodeterioration of the material. One of the components is made of Ethylene Propylene Diene Monomer (EPDM) on which the impacts of biodeterioration regarding surface deterioration and mechanical property decrease are investigated. In this study, the extent of both impacts is investigated using experiments with a 3D Optical Profilometer and an Universal Testing Machine (UTM). The former was chosen as weighting material excludes the impact of the particles' dissolution and degradation. It is found that no corrosion occurs on EPDM and also no direct deterioration by macro-organisms is found. Mussels caused an increase in pit depth and quantity after 3 months by a maximum of 0.016 millimetre and factor 4, respectively. Calcium extraction by the mussels is deemed the most likely reason. Since an element is extracted from the compound, it is labeled as biodegradation. Surface roughness alternations of 2 to 4 micrometre were found, which could be due to ocean currents, macrofouler attachment and biotic degradation. Biotic degradation was not found in this study, but is expected to have an impact in the long term. It is suspected that biodeterioration due to biodegradability of EPDMs molecules and its additives determine EPDM's service life. The decrease in mechanical properties could not be determined due to a lack of information about he initial material values.

Key words: Biofouling, Biodeterioration, EPDM, 3D Optical Profilometer, UTM, Biodegradability

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Acronyms

ASTM D412 American Society for Testing Material D412

CMME Computational Modelling and Materials Engineering

EPDM Ethylene Propylene Diene Monomer

EPS extracellular polymeric substance

ESEM Environmental Scanning Electron Microscopy

FTIR Fourier Transform Infrared Spectroscopy

HDPE High-Density Polyethylene

MIC Microbiologically-induced corrosion

MRE Marine Renewable Energy

NNS Non-Native Species

OBD Ocean Battery Design

OG Ocean Grazer B.V.

OWF Offshore Wind Farms

SEM Scanning Electron Microscopy

SRB Sulphate-Reducing Bacteria

SRB Sulphate-Reducing Bacteria

UG University Groningen

UTM Universal Testing Machine

WEC Wave Energy Converters

2 Introduction

Biofouling is the accumulation of sea organisms ranging from micro organisms to small animals where it is not wanted on underwater strutures. The process of biofouling starts minutes after submersion, as minerals including proteins and polysaccharides, naturally dissolved in the seawater adhere submerged structures (Vinagre et al., 2020). Micro-organisms including bacteria follow, and colonise the object's surface within minutes to hours. Macro-organisms settle days later and colonise the submerged structure, creating habitats for additional micro-organism settlements. After a month, larvae of macrofoulers are spawned, and the community reaches maturity in a few years with an increasing variety of species ranging from sessile, benthic and epibenthic organisms (Vinagre et al., 2020).

There are 400 biofouling species worldwide which can be categorised into two classes: microfoulers and macrofoulers (Kyei et al., 2020). Microfoulers include bacteria and diatoms. Macrofouling is divided into hard fouling and soft fouling. Hardfoulers are calcareous animals including Barnacles, Bryozoans, Mollusks and Polychaetes, and softfoulers are non-calcareous organisms including Seaweeds, Hydroids, Sponges, Ascidians and Anemones. In figures 2.1 and 2.2, the most important hard- and softfoulers to the Marine Renewable Energy (MRE) sector are depicted:

[1]

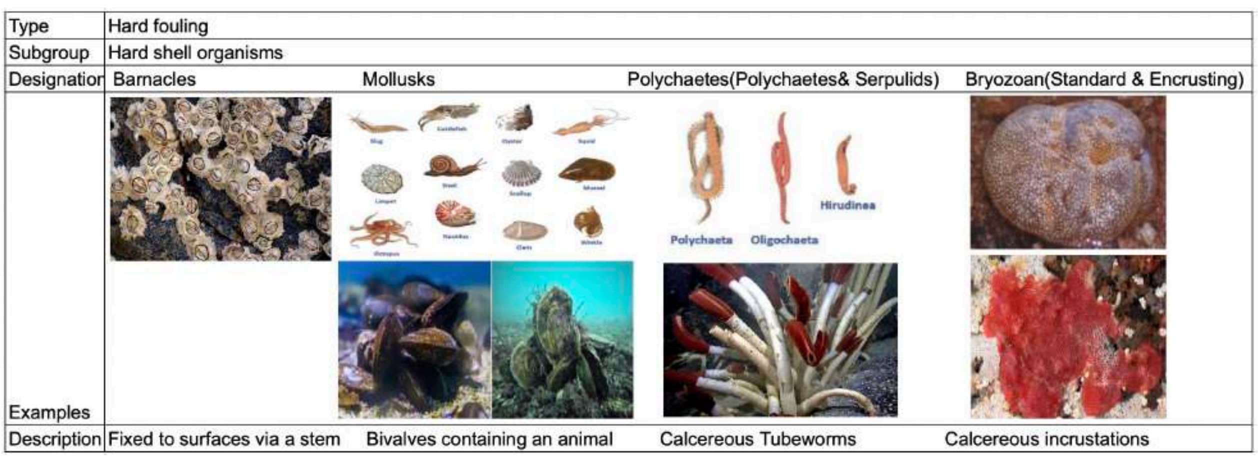


Figure 2.1: Most important Hard Foulers to the MRE Sector (Wikipedia, 2022a) (Khan et al., 2019) (MarineHealthFoods, 2022) (TheWeek, 2022) (Thornton et al., 2014) (AmericanSportFish, 2022) (Lindholdt et al., 2015)

[1]The sources of figure 2.1 and figure 2.2 are in some cases from non-academic sources. Photos of biofouling organisms in academic articles were unclear, so for this reason these alternative sources were used. It was double-checked that the animals displayed in the photos of these sources were correct.

Type	Soft fouling				
Subgroup	Bush type	Spineless organisms			Plant
Designation	Hydroid	Sponges	Ascidians (Sea Squirt & Tunicates)	Anemones	Algae(Green, Brown & Red)
Examples					
Description	Underwater bushes	Pump seawater and filter particles	Spineless bag with two openings	(Poisonous) Cnidarians	Algae, Plants

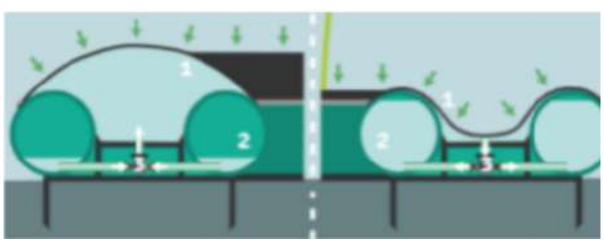
Figure 2.2: Most important Soft Foulers to the MRE Sector (OregonStateUniversity, 2022) (IUCN, 2022) (RaphsWall, 2022) (Wikipedia, 2022f) (EurpoeanCommision, 2022) (Wikipedia, 2022d)

Marine biofouling has been studied throughout history, from wooden ships back in the day to modern marine installations now. The resultant growth of organisms on surfaces is a major industrial problem causing both corrosion and deterioration of offshore structures. A company in the marine sector, the Ocean Grazer B.V. (OG), develops hybrid solutions for the offshore renewable energy sector. Their innovations focus on integrating multiple renewable energy sources with on-site storage technology (OceanGrazer, 2021). This project is related to the on-site energy storage system and the biofouling challenge it faces. This thesis aims to understand what impacts biofouling has on underwater structures and what the extent of these impacts are.

First, the energy storage system of the OG is described, and OG's management question is elaborated on. The literature review explores the phenomena of biofouling and its eventual impacts on the energy storage system. Biodeterioration is one of them and chosen to investigate in this project. Later on, the methodology for experiments to best quantify biodeterioration is explained. Specifically, surface deterioration and mechanical properties decrease due to biodeterioration are investigated. It generates useful information for the energy storage system endurance in marine environments. Small-scale experiments are conducted to generate initial results. Moreover, follow-up directions are set out to define the extent of biodeterioration further.

2.1 Ocean Battery Design

The design(s) of the on-site energy storage system, called the Ocean Battery Design (OBD), is depicted in figure 2.3. The design consists of three main parts: a so-called flexible bladder denoted as 1, a rigid reservoir denoted as 2 and a hydro technology system denoted as 3, as can be seen in 2.3a. The flexible bladder can get inflated and deflated with a liquid as the OBD is charged or discharged and could be compared to inflating a balloon underwater. The OBD uses residual energy from nearby Offshore Wind Farms (OWF) or integrated Wave Energy Converters (WEC) to pump a liquid out of the rigid reservoir into the flexible bladder. Due to a pressure difference between the rigid reservoirs and the pressure of the ocean, the liquid could be routed back from the flexible bladder into the rigid reservoirs with a certain speed. Energy is generated as the liquid passed through a hydro technology system along its way. Momentarily, OG has two designs, as depicted below. In the left figure the deep-sea design(>40m) is depicted and the right figure shows the buried design applicable in shallow waters(<30m). For the deep-sea design, all three components are in a box embedded on the seabed. For the buried design, the rigid reservoir and hydro technology system are in the sea ground. In this way, extra hydrostatic pressure is created due to the extra pressure deeper down and higher buoyancy pressure at greater depths. The flexible bladders will be exposed to biofouling and corrosion for both designs. The impacts of biofouling and corrosion are elaborated on in the literature study section.



(a) Deep-Sea Design

(b) Buried Design

Figure 2.3: Deep-sea Design(a) and Buried Design(b) (OceanGrazer, 2021)

2.2 Management Question

The research group Computational Modelling and Materials Engineering (CMME) of the University Groningen (UG), scientific advisors of the OG, want to know the impacts of biofouling and corrosion on the integrity of the flexible bladder. Both biofouling and corrosion are seen as important challenges for the design of the flexible bladder. An analysis is required that can foresee the impacts of biofouling and corrosion. Consecutively, these outcomes could be used to assist them in constructing effective countermeasures.

A material under selection for the flexible bladder is EPDM, which is a polymeric material, specifically an elastomer already used in the marine sector by large companies(Van Rooij,2021). OG has used EPDM as the material for the flexible bladder for their prototype they are experimenting with in the harbour of Groningen. Also, in June 2021, they have brought a piece of EPDM to water, intending to analyse it later when the piece is exposed to biofouling and corrosion for a certain amount of time. The figures below show EPDM before it was submerged in the harbour, and the same material after some months of exposure to biofouling. This project deals with analysing this piece of EPDM to determine the extent of biofouling and corrosion impacts.

(a) The Piece of EPDM Before Submersion

(b) The Piece of EPDM after Months of Exposure

Figure 2.4: EPDM before(a) and after(b) exposure to biofouling (Van Rooij,2021)

3 Literature Study

In this chapter, biofouling and corrosion their eventual impacts on the flexible bladder are explored. It is retrieved that biofouling and corrosion have eventual technical impacts including additional hydrodynamic loading, material deterioration and material mechanical property decrease. The latter two fall under the phenomena of biodeterioration. The external factors influencing the extent of biodeterioration are described. Furthermore, material knowledge about EPDM is retrieved to get familiar with its material characteristics. Moreover, already known empirical data concerning EPDMs biodeterioration and corrosion resistance was searched for and will be elaborated on. In addition, information regarding biodeterioration of similar materials is described. In the next chapter, an overview of the literature study is provided to summarize the chapter.

3.1 Biofouling & External Factors

There are three stages of biofouling, as is depicted in figure 3.1. The growth of the biofilm, and thus the time in which the stages develop, is dependent on some external factors including:seawater temperature, depth and light availability, currents and distance to shore, topography and wettability of the substrata, material of substrata and colour of substrata (Vinagre et al., 2020). Moreover, Kyei et al. state that salinity, conductivity, pH, and dissolved oxygen content of seawater are other external factors influencing biofouling, as well as organisms already on the substrata and the adhesion strength of organisms. These external factors are elaborated on in this section:

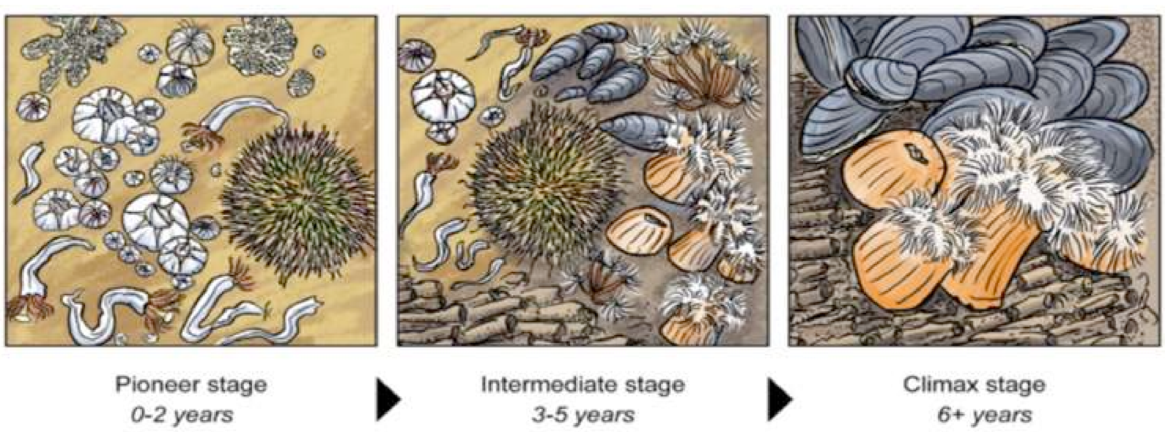


Figure 3.1: Stages Of The Biofouling Community (Canning, 2020)

3.1.1 Depth & Distance to Shore

Biofouling shows a zonation pattern, which can be seen in 3.2. There are four zones: the splash zone, the intertidal zone, the shallow subtidal zone and the deep subtidal zone. Each zone has its dominant species, but this does not mean that a dominant species of one zone is not present at another (Degraer et al., 2020). Observations at Teesside Wind Farm(UK) concluded that soft foulers including plumose anemones, starfish and sea urchin dominate the zone just above the seabed (Canning, 2020) relevant to ocean grazer design. Figure 3.3 shows the correlation between water depth and the dry weight of the biofilm. The dry weight deeper down is smaller , as soft foulers weight is significantly lower compared to hard foulers (Canning, 2020). Moreover, at smaller depths there is a high light-availability, favourable for organisms, resulting in thicker biofilms.

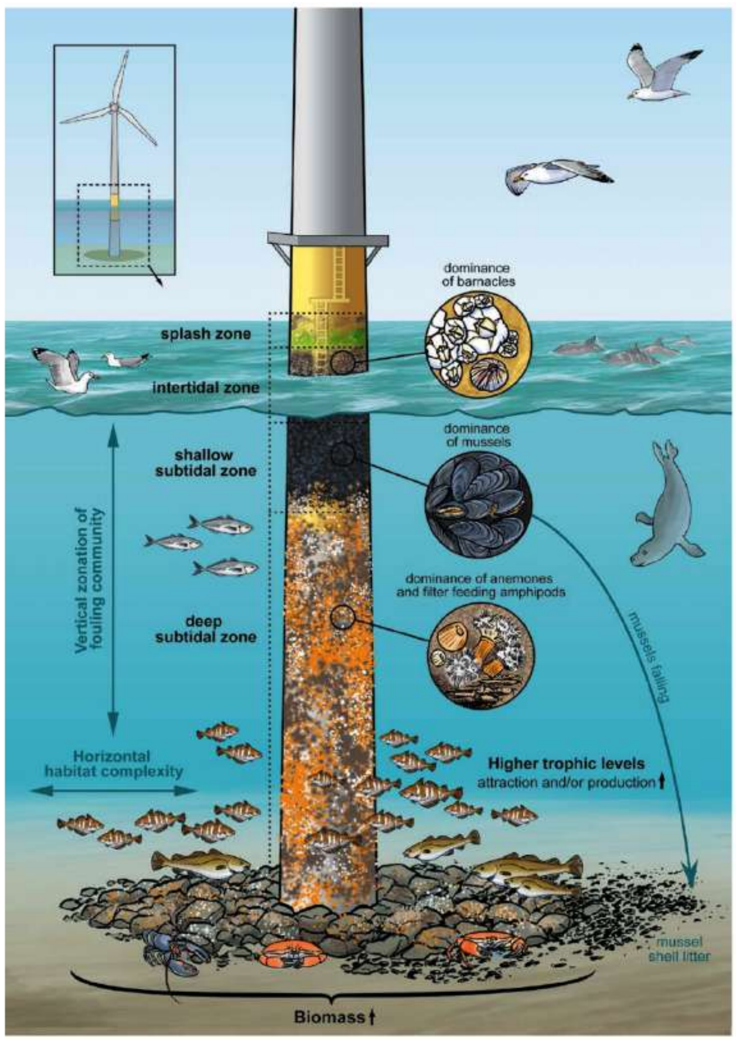


Figure 3.2: Biofouling zonation pattern throuhgout the levels of the sea (Degraer et al., 2020)

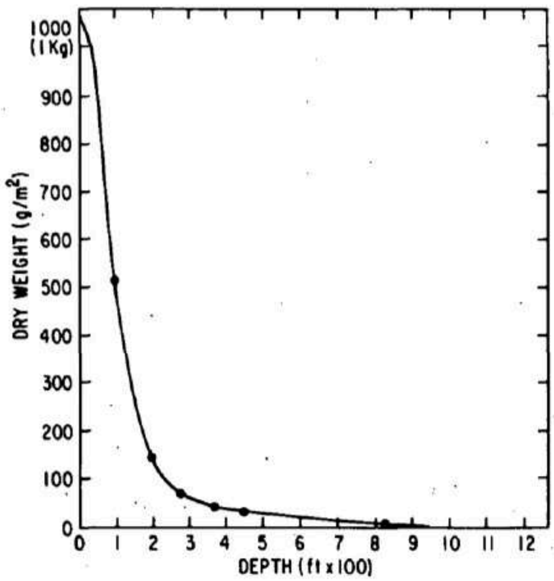


Figure 3.3: Correlation between water depth and dry weight of the biofilm (Mitchell and Benson, 1980)

Table 3.1 enumerates some fouling species and their habitat considering their depth and distance to shore. The macrofouling rate further from the shore decreases drastically. However, once macrofouler larvae have colonised the surface, the impacts are similar to the impacts closer to the shore (Mitchell and Benson, 1980).

Table 3.1: Fouling organisms' habitat concerning depth and distance to shore (Mitchell and Benson, 1980)

TABLE 3. Habitats of Fouling Organisms[a]

Organism	Depth (ft)	Range of Ocean
Hydroids	Surface to bottom	All over
Gooseneck barnicles	Surface to 500 ft	Open ocean only
Mussels	Surface to 100 ft	Shore to 30 miles
Starfish	Surface to 8,000	All over
Snails	Surface to 10,000	Especially in Pacific
Bivalves	Surface to 14,500	Especially in Pacific
Tubeworms	Surface to 16,500	Coastal waters
Sea urchin	Surface to 16,000	All over
Sponges	Surface to 600	Coastal waters
Bryozoans	Surface to 900	All over (coastal waters)
Tunicates	Surface to 500	All over
Borers	Surface to bottom	All over
Jellyfish	Surface to bottom	All over
Fungi	Surface to 600	All over
Acorn barnacle	Surface to 500	Coastal waters (all over)

3.1.2 Flexibility of Structure

Biofilm extent is also influenced by the motion of the submerged object. Free moving objects such as tidal turbines and fixed submerged objects such as foundations show different biofilm extent (Vinagre et al., 2020).

3.2 Biodeterioration

The effect of biofouling on material is called biodeterioration. In this section, the various effects that fall under biodeterioration are elaborated on. First, three impacts of micro organisms- microdeterioration- are elaborated on. Afterwards, three impacts induced by macro organisms - macrodeterioration- are elaborated on.

3.2.1 Microdeterioration (1): Microbiologically-induced corrosion (MIC)

The layer of biofouling is called the biofilm. Under that biofilm, oxygen-depleted zones are created where corrosion processes thrive (Canning, 2020). A figure of such a corrosion process can be seen in 3.4. Bacteria stand at the basis of such corrosion processes, which is called MIC. Various forms of corrosion can be seen in 3.5. It must be noted that these impacts are known to impact steel.

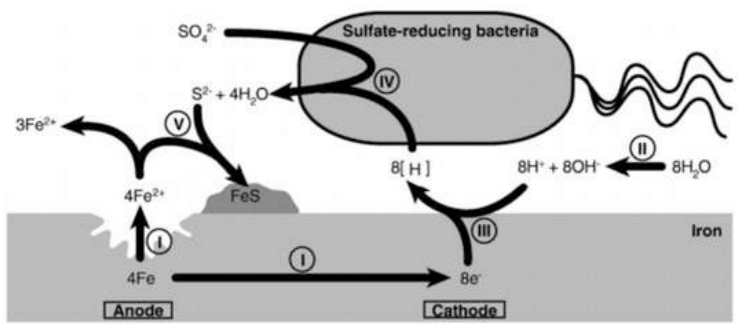


Figure 3.4: Sulphate-Reducing-Bacteria (SRB) - Corrosion Process (Canning, 2020)

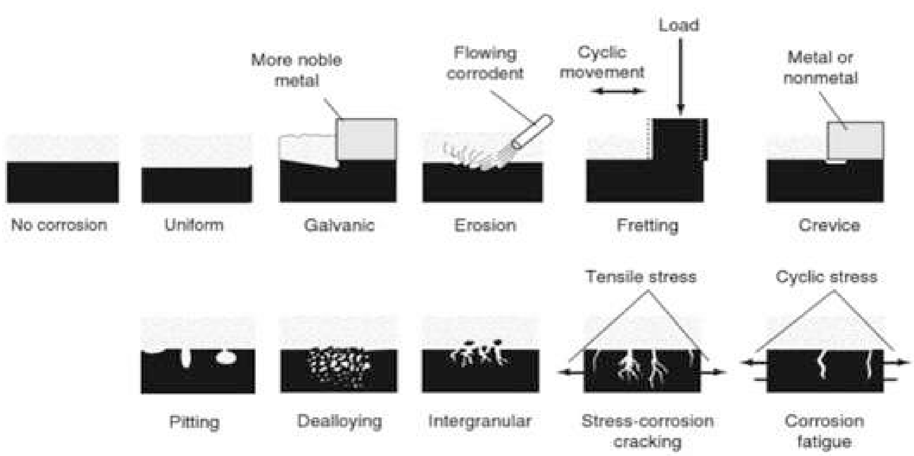


Figure 3.5: Types of Corrosion (Canning, 2020)

Micro-organisms adhere to one another and to rigid substrata with an adhesive called the extracellular polymeric substance (EPS) (Bixler and Bhushan, 2012). Once the EPS is secreted, the attachment of micro-organisms is irreversible (Bixler and Bhushan, 2012). The growth of the biofilm and its corrosion impacts are shown in figure 3.6.

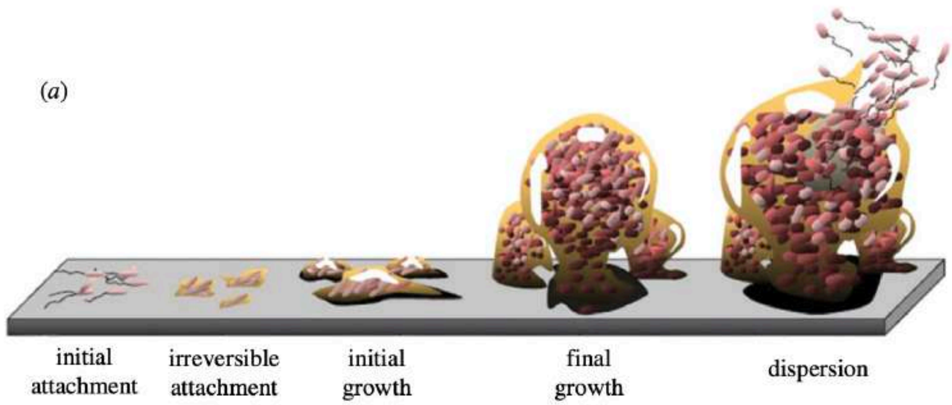


Figure 3.6: Biofilm growth and corrosion (Bixler and Bhushan, 2012)

3.2.2 Microdeterioration (2): Biotic-and Abiotic Degradation

Biotic-and abiotic is the process by which a chemical substance is broken down to smaller molecules by biotic or abiotic means (ChemPro, 2022). Biotic degradation occurs due to the action of enzymes secreted by bacteria and fungi (Sudhakar et al., 2007). Biotic degradation proceeds via surface attack by bacteria present in the biofilm. (Gu, 2005). For instance, polymers are susceptible to biodeterioration by fungi (Gu, 2005). Examples of abiotic degradation are oxidation and hydrolysis.

With Fourier Transform Infrared Spectroscopy (FTIR), a difference in carbonyl and vinyl index was identified for polymers and designated to biotic-and abiotic degradation. Norrish type 1 and 2 degradation and abiotic ester formation were thought to be responsible.

3.2.3 Microdeterioration (3)

Damage to the polymer chains inside the material may be caused due to swelling and bursting of growing cells of the micro-organisms inside the material (Rutkowska et al., 2002).

3.2.4 Macrodeterioration (1): Abrasion & Increased MIC

The forces of waves and currents on macro-organisms adhered to submerged structures cause abrasion due to the macro-organisms adhesion strength in combination with their weight and volume (Vinagre et al., 2020). Furthermore, macrofouling increases corrosion as it induces oxygen-depleted zones (Kyei et al., 2020).

3.2.5 Macrodeterioration (2): Direct Deterioration

The macro-organisms that settle on the object can be destructive as they deteriorate the material by making holes and pits. This impact is labelled as direct deterioration throughout this report. The paragraphs below contain information about the different macro-organisms species which possibly inflict direct deterioration.

Barnacles

Barnacles take advantage of coating imperfections by settling in these pits and inducing pressure, resulting in delamination of the coating layers and even the substrata, which can cause up to 5 millimetres of corrosion in two years (Vance et al., 2014). This data was observed for steel material. Barnacles adhere to objects by extracting an insoluble cement that hardens quickly (Vinagre et al., 2020). They are attached to surfaces via a stem (Kyei et al., 2020). After attachment, barnacle larvae grow into adults. As they grow, their stem increases, similar to what can be observed in trees (Vinagre et al., 2020). The delamination mechanism might be initiated after barnacles larvae settle into small surface pits after which they expand and grown and thus damage the surface (Canning, 2020).

Oysters

Oysters are known to cause extensive localised corrosion, penetrating 2 millimetres deep into stainless steel within 12 months with a maximum corrosion depth of several centimetres (Blackwood et al., 2017). Their form of corrosion is described as "crevice tunnelling".

Pholad and Teredine Boring

Some bivalve Molluscs in the family of Pholads have shells with sharply serrated edges and use these in combination with chemical mechanisms to bore into sea rocks. One pholad, the Martesia, is known to perforate into lead, PVC, nylon and High-Density Polyethylene (HDPE) (Mitchell and Benson, 1980). Other molluscs in the family of Teredines, with species Bankia, Lyrodis and Teredo, are known to attack plastics, where polyvinyl chloride was damaged most severely. Figures of these macrofoulers can be seen in appendix C.

Furthermore, three crustaceans- species related to shrimp and lobsters; limnoriids, Sphacromatids and Chelurids, are known to deteriorate wood. Pholad and Teredine borers are found at all depths attached to all sorts of material. When larvae are born they get completely covered with bacteria over time, allowing them to settle at all materials (Vinagre et al., 2020). These marks in figure 3.7 are from pholad boring on the east coast of North-America.

Figure 3.7: Pholad Boring (Sutton, 2022)

Sponges and Molluscs

Moreover, species such as sponges and molluscs are directly boring into the substrata (Canning, 2020), causing a direct physical attack on the material. Two molluscs species are prevalent on the EPDM piece; Oysters and Mussels.

Direct Deterioration Species

In the table below, these animal foulers' habitat are displaced concerning distance from shore, depth and location in the North Sea.

Table 3.2: Macro-organisms that induce direct deterioration their habitat and deterioration information

	Depth(m)	**Dis.to shore(km)**	**Location**	**Deterioration (mm/year)**	**Material**
Sponges	20-50	<50	West Scotland	-	-
Oysters	1-8	<50	Holland, Denmark	2	Steel
Mussels	<30	<50	all over	-	-
Martesia	all	all	no	see figure 3.7	PVC, HDPE
Teredines	all	all	-	-	Plastics
Barnacles	all	all	yes	2.5	Steel

Degraer et al. describes the spread of Non-Native Species (NNS) over the world due to the ever-increasing international connectivity. Species attach to ships which sail worldwide, ensuring the infiltration of species in new ecosystems (Degraer et al., 2020). Therefore, when a species is not present in a particular ecosystem today, it cannot be excluded that it will not be there in the future.

Several biodeterioration mechanisms are described in table 3.2: physical or mechanical attack by delaminating or boring or perforation, abrasion, bursting or swelling of bacteria from inside the material. Chemical attack, as a structural component is used as a food source by organisms, or organisms excrete waste products that impact the material. The latter is also called biotic degradation, and is explained in section 3.3.3.

Between the time that larvae are born and attach to substrata, they are completely covered with bacteria, allowing them to settle at all materials (Kyei et al., 2020). So when a organisms is known to directly deteriorate a specific material, it could possibly directly deteriorate a wide variety of materials, as it is able to attach to many surfaces.

Table 3.3: Biodeterioration Mechanisms

Microdeterioration	**Examples**
Microbiologically-Induced Corrosion(MIC)	Variety of bacteria extracting molecules out of metals e.g. Sulphate-Reducing Bacteria
Biotic Degradation	Fungi and Bacteria break down chemical substances of polymers into smaller molecules
Swelling and bursting	Micro organisms grow after infiltration into the material
Macrodeterioration	**Examples**
Increases MIC	Macro organisms induce oxygen-depleted zones in which MIC processes thrive
Abrasion	Due to ocean currents pulling on macro organisms
Direct Deterioration	Several macro organisms eventually directly bore, perforate or delaminate material

3.3 Ethylene Propylene Diene Monomer(EPDM) & Empirical Data

3.3.1 EPDM

EPDM is a synthetic rubber. They are polymers, specifically elastomers, synthesised from petroleum byproducts. In figure 3.8, the molecular formula for EPDM can be found. It is shown that EPDM primarily consists of ethylene and propylene. Specifically, the bulk of EPDM is made up of propylene and ethylene ranging from twenty to 80 wt% each. Two to twelve per cent is made up of the diene monomer (GmbH, 2022).

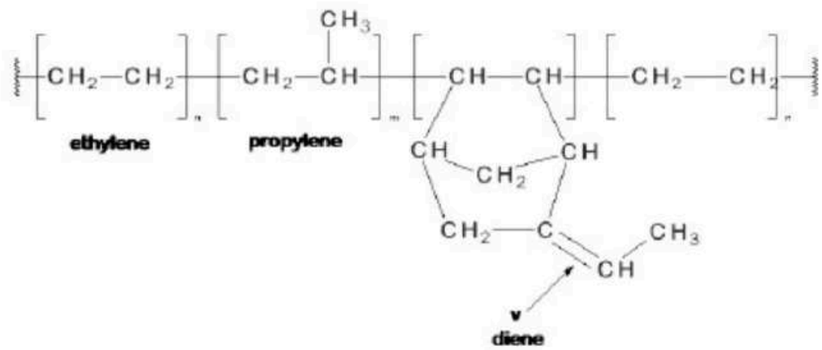


Figure 3.8: Molecular Formula of EPDM (PolymerPropertiesDatabase, 2021)

As will be explained later on, ductility and strength are mechanical properties that are investigated in this thesis. Moreover, corrosion resistance is investigated, as corrosion is one of the causes of biodeterioration. Below a table is shown where these mechanical properties of EPDM are outlined. It must be noted that the abiotic corrosion resistance is displayed here, where zero millimetre per year means that no corrosion has happened. Moreover, strength and ductility differ for different EPDM types. EPDM's composition of ethylene, propylene and diene monomer can differ as well as its fillers and additives, which will be elaborated on below.

Table 3.4: Corrosion resistance[mm/year], ductility, ε,[%] and tensile strength, σ ,[MPa] of EPDM (Wikipedia, 2021), (DesignerData, 2021), (RubberMagazijn, 2021) and (Wang et al., 2020)

	Corrosion Resistance (mm/year)	Ductility (% Elongation)	Tensile Strength (MPa)
EPDM	0	375	6

EPDM is always compounded (Wikipedia, 2021), because the mechanical properties of unfilled EPDM are poor and fillers give strength to the material (Chandrasekaran, 2017). Fillers and additives are added, and the mixed material is vulcanised to obtain an EPDM composite; an example is shown in table 3.5. To define the percentage of chemicals inherent in the compound formulation one can divide a chemical its amount by the total amount of all chemicals.

Table 3.5: Molecular Compound Formulation of a EPDM (Wang et al., 2020)

Chemical ingredient	Amount (phr)
3092M	100
N550	70
Light calcium carbonate	20
300# Paraffin oil	60
Zinc oxide	5
Stearic acid	1
Calcium oxide	10
Sulfur	1

3.3.2 EPDM's Biodeterioration & Corrosion Resistance

Earlier studies have stated that EPDM's tensile strength and elongation at break decreased with sixteen percent within 60 days in artificial seawater (Wang et al., 2020). Elongation at break declined most severe. Its service life was estimated to be 23.5 years at 15 degrees Celcius. However, no surface deterioration was observed through Scanning Electron Microscopy (SEM). By looking at the cross-sectional area, a significant number of micro voids were formed (Wang et al., 2020). This is suspected to be due to the solid particles inherent in the compound formulation of EPDM migrating outwards resulting in the emergence of numerous tiny voids in the samples. This is appointed as a cause for the decrease of EPDM's mechanical properties and potential weight loss (Wang et al., 2020). The degradation or rupture of the polymer main chain, called chain scission, was predicted to be the other cause for mechanical property decrease (Wang et al., 2020) (Rojas Rodríguez et al., 2021). Chain scission happens due to biotic-and abiotic degradation resulting in degradation and rupture the molecular chain.

This paragraph outlines EPDM's degradation in other conditions than seawater conditions. For seal rings used in drinking water supply systems, after three years, EPDM underwent chain scission (Rojas Rodríguez et al., 2021). For power system networks, EPDM insulators were experimentally tested in an environmental chamber by exposing the samples to acidic cold fog with a pH of 3,6. The samples showed several dents and cracks seen on a magnification range of 50 m (Hussain et al., 2017). Furthermore, in amine treating plants, EPDM corrosion was observed under scanning electron microscopy(SEM) for degradation, and no signs of deterioration were observed (Hjelmaas et al., 2017). The most relevant study of the ones stated above can be the EPDM in the sewing system, as this is closest to the seawater conditions of the three. Similarly to what has been found in the paragraph above for seawater conditions, EPDM molecular chain degradates.

3.3.3 Biodeterioration on Polymers

Polyethylene biodegradated three percent in twelve months in the Baltic sea (Rutkowska et al., 2002). Another study found a weight loss of two percent for polyethylene in twelve months (Artham et al., 2009). It was recorded that the tensile strength decreased with a significant amount of thirty percent in one year (Rutkowska et al., 2002). Twelve percent tensile strength decrease was recorded by Artham et al. for polyethylene. Polypropylene and polyethylene showed a weight loss of a half percent and one-and-a-half percent, respectively, in one year (Sudhakar et al., 2007).Several particular bacteria are known to degrade polyethylene (Sudhakar et al., 2007).

3.4 Biofouling Extent and Mechanical Design Impacts

Vinagre et al. elaborate on the Oceanic Project which aim is to observe the extent of biofouling on underwater structures throughout Europe. It provides a database with quantitative and qualitative information about marine biofouling in European seas. A wide range of underwater structures is analysed at different depths, temperatures, wave speeds and ecoregions, as these variables affect the extent and impact of biofouling (Vinagre et al., 2020).

More data concerning marine growth and its extent were gathered by another research studying two WEC systems. A biofilm of 26 millimetre was perceived after ten years (Yang et al., 2017). In warm seas, substrates fully covered with hard shell organisms can weight seventeen kg/m^2 (Mitchell and Benson, 1980). Observations at Teesside Wind Farm(UK) concluded that plumose anemones, starfish and sea urchin dominated the zone just above the seabed, relevant to ocean grazer design (Canning, 2020). The key macro-organisms considering added load and thickness are: Kelp, Barnacles, mussels, Bryozoans and Calcareous Tubeworms (Vinagre et al., 2020). Soft fouling, which mostly happens just above the seabed, its added weight is negligible (Canning, 2020).

Biofouling could influence the dynamic behaviour of the foundations of underwater structures due to the additional weight, and the hydrodynamic loading due to thickness and surface roughness changes (Canning, 2020). The reduction of the material thickness due to external corrosion also increases the hydrodynamic load. Oxygen-depleted zones caused by the macro organisms induce external corrosion.A 15 mm biofilm thickness increases the hydrodynamic loading by 42.5% and fatigue damage by 62.3%, but this is dependent on biofilm morphology (Canning, 2020). Operational lifespan dropped by 54%. Moreover, the fatigue life of the power cables and mooring lines was reduced by 20%, compared to non-biofouling cases (Yang et al., 2017). Also, the WEC absorbed 10% less power from wave energy (Yang et al., 2017).

3.5 Biofouling's Impact on the Ecosystem

Biofouling communities on artificial structures create artificial reefs that affect ecosystem structure and functioning. The concentrations of marine organisms on artificial structures affect ecosystem functioning on a local scale. Artificial reefs create a warmer and more acidic marine environment, changing community dynamics and altering interactions between predators and prey. Suspension feeders enrich local organic matter and affect pelagic and benthic nutrient cycles. However, qualitative data of this effect for almost all dominant fouling species is missing. Availability of such data could yield an estimation of the biogeochemical footprint of underwater structures at the local scale. Integration of this data in oceanographic models could predict the effect of underwater objects on a broader geographical scale. Understanding the mechanisms behind the impact is needed in order to develop effective nature-inclusive designs (Degraer et al., 2020).

4 Problem Analysis

In this chapter the problem context will be summarized. Afterwards, the stakeholder analysis is elaborated on. At last, the problem is stated.

4.1 Literature Study Overview

Trough the literature study, information is gained about eventual design challenges for the flexible bladder regarding biofouling. The phenomena of biofouling spawns a thick biofilm, including numerous micro-and macro organisms. External factors due to ambient marine conditions influence the extent of biofouling including seawater temperature, depth, distance to shore, light availability and seawater pH, among others. Throughout the sea depth, biofouling shows a zonation pattern where the deep subtidal zone is relevant for the OBD on the seabed. Soft fouling primarily happens in this zone, which weight is possibly negligible. Technical biofouling aspects are eventual additional hydrodynamic loading, increased fatigue damage, decreased power absorption for WECs, surface deterioration and decreased mechanical properties. A social aspect is that artificial structures spawn thick biofilms, increasing the number of certain species in an ecosystem affecting its balance.

Eventual surface deterioration and mechanical property decrease fall under the phenomena biodeterioration, which has the following causes. Micro organisms could have impacts such as: swelling and bursting from inside the material, micro-biologically induced corrosion, and biotic-and abiotic degradation. Larger macro organisms might abrade material in the face of heavy currents and could directly physically or chemically attack surfaces. These impacts of biodeterioration could lead to surface deterioration and mechanical property decrease of EPDM. A conceptual model has been set up to overview the system of biodeterioration, as depicted in figure 4.1. From left to right, the influences on the extent of biodeterioration and the possible impacts of biodeterioration on the flexible bladder are displayed. Moreover, the hydrodynamic loading, fatigue damage and ecosystem functioning design challenges are incorporated about which it becomes clear in section 4.3 that they are excluded from this study.

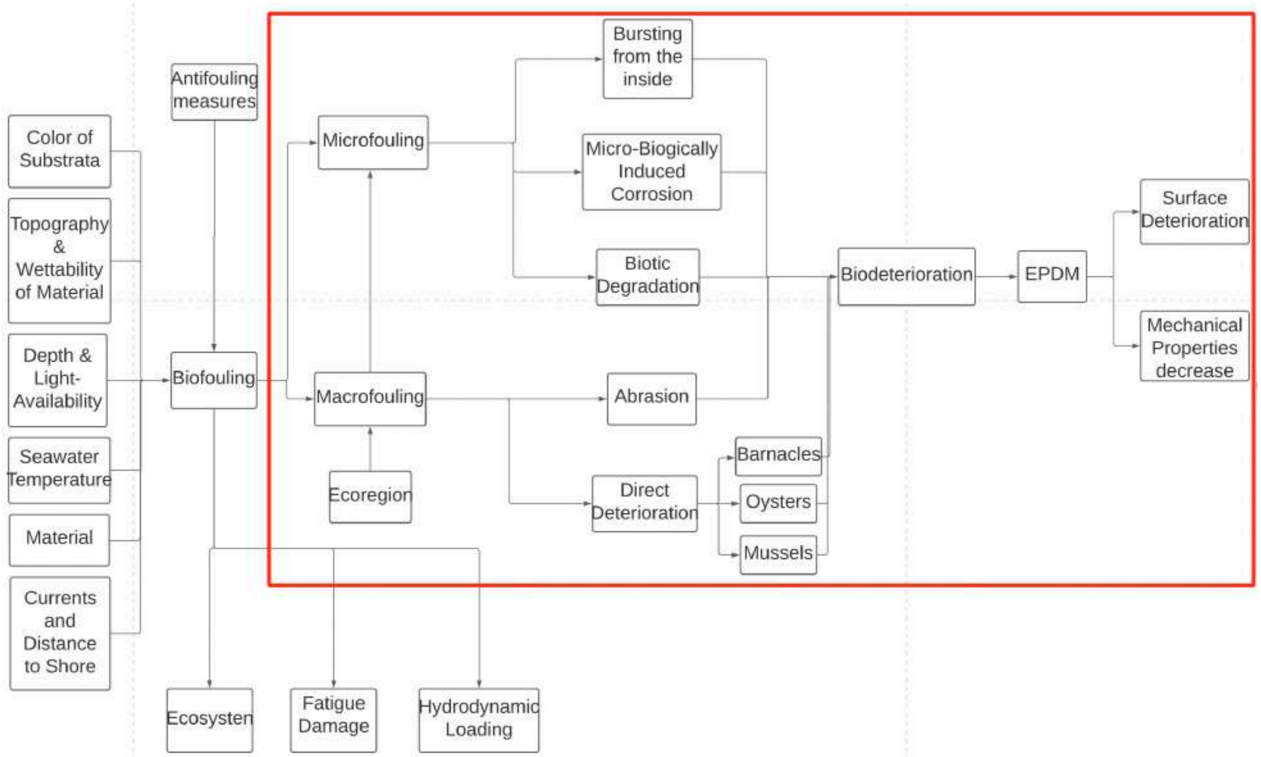


Figure 4.1: Conceptual model: an overview of the influences on and impacts of biodeterioration.

4.2 Stakeholder Analysis

A stakeholder analysis identifies the persons, companies or groups that have a stake in this project.

CTO of the Ocean Grazer B.V.

The CTO of the Ocean Grazer Company might be interested in any useful information about the deterioration of EPDM to incorporate into the material design of the flexible bladder. A requirement was that EPDM specimens in a test setup since another student's master project would be included in the mechanical properties experiments. By doing so, he would obtain information on the decrease of strength and ductility after EPDM is exposed to artificial seawater and cyclic- and tensile stress. However, this could not be incorporated into this project due to time constraints.

Ocean Grazer Research Group

The Ocean Grazer Research Group is a stakeholder as the research group might initiate eventual follow-up studies. Requirements of theirs were that a material analysis is performed on the EPDM to identify eventual micro cracks of the surface of EPDM. In addition, they would like to see a description of a test setup that could be made in the future. With this information, they would be one step closer to accurately investigating the lifespan of EPDM in underwater marine conditions for the OBD they are researching.

4.3 Problem Statement

There is a lack of empirical data about the extent of biodeterioration on EPDM. Until now, empirical data about the endurance of EPDM in marine underwater conditions is solely known for abiotic corrosion/degradation. There is a lack of information concerning EPDMs endurance in marine underwater conditions concerning biodeterioration impacts including direct deterioration, MIC, biotic degradation, abrasion and bursting of micro organisms on EPDM. The eventual surface deterioration and mechanical properties decrease due to this biodeterioration are chosen to examine in this project. It is identified that biodeterioration could lead to operational integrity failure of the flexible bladder in two ways. Surface deterioration could lead to eventual cracks, and mechanical property decrease could lead to eventual failure of the operating constraints regarding ductility and strength. Therefore the problem statement of this project is as follows:

The Ocean Grazer company is lacking information on the effects of biodeterioration on the material EPDM. The lack of information creates uncertainty about the extent of surface deterioration and strength and ductility decrease over time in the deep-subtidal zone and how these impacts affect their flexible bladder operational integrity.

5 Research Design

5.1 Design Objective

The research objective is to investigate the impacts of biodeterioration on EPDM by analysing EPDM samples that have been exposed to biofouling for six months. The sample is going to be examined on surface deterioration and strength and ductility decrease and compared to non-biofouled samples in two months.

5.2 Main Research Question

What is the extent of effects of biodeterioration on surface deterioration and strength and ductility decrease of EPDM after six months?

1.1 What is the extent of surface deterioration on the EPDM piece exposed to biofouling for six months?

-What is the pit depth, Rv_i [μm]?
-What is the number of pits?
-What is the pit width, Rh_i [μm]?
-What is the surface roughness, Ra [μm]?

*Rh_i *is a self-given symbol to the pit width*

1.2 What are the strength and ductility of EPDM after six months of exposure to biofouling?

-What is the ultimate tensile strength, σ [MPA]?
-What is the elongation at break, ε [%]?

1.3 What is the extent of surface deterioration and strength and ductility decrease when comparing the results from the biofouled-samples to the results from non-biofouled samples?

5.3 Design Cycle

As the design objective is to analyse EPDM samples exposed to biofouling for six months, the design of this research is structured according to the experimental cycle. The cycle is depicted in figure 5.1 and presents the following design steps:

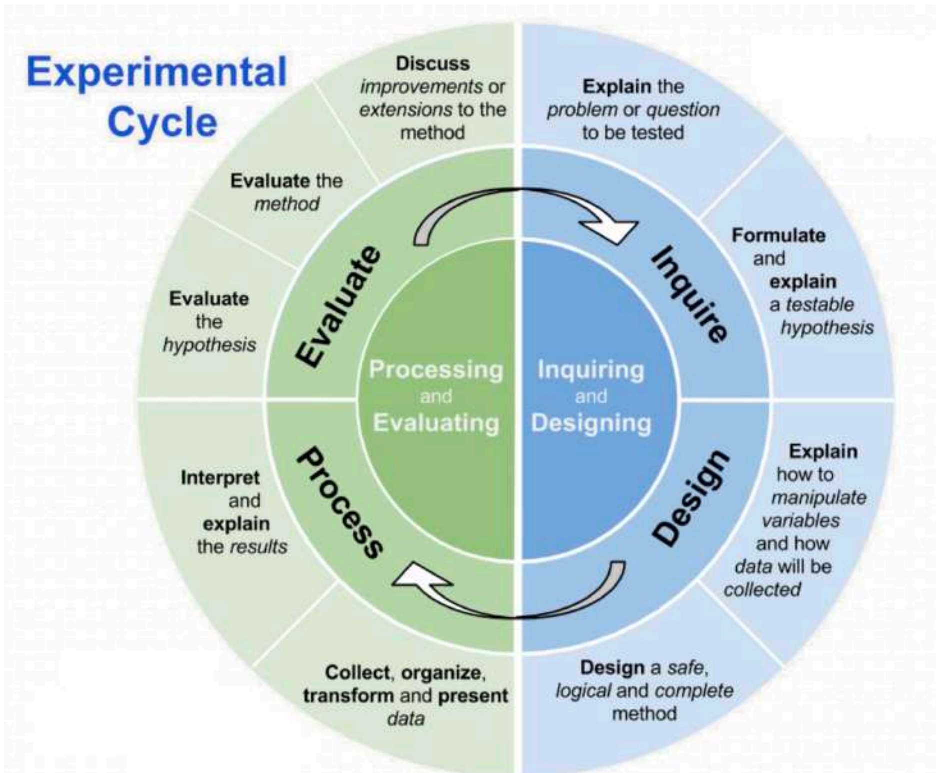


Figure 5.1: Experimental Cycle (I-Biology, 2022)

6 Hypothesis and Measurement

This chapter elaborates on the assumption that the biodeterioration in the harbour test set-up is of a worse-case scenario compared to the shallowest deployment location of the OBD. Thus, the results obtained from experiments on the harbour test set-up are assumed to indicate the maximum amount of biodeterioration found on the OBD and the results from this study are relevant for the OBD. In addition, this chapter contains a hypothesis about the extent of biodeterioration for the test set-up.

6.1 Worse-case Scenario

As described in section 3.1, external factors influence the growth of the biofilm, which influences the extent of biodeterioration. This section elaborates on the external factors of the harbour compared to the external factors of the shallowest deployment location of the OBD. This section elaborates on the assumption that the conditions in the harbour test set-up are of a worse-case scenario. he exact deployment location of the test set-up is in the Eemshaven of Groningen. The assumed deployment location for the OBD is thirty metres down and fifty kilometres offshore.

6.1.1 Temperature

The seawater temperature in the Eemshaven is approximately 11 degrees Celsius (Rijkswaterstaat, 2022). The higher the seawater temperature, the faster the biofilm grows, and the more effects of biodeterioration one will see (Vinagre et al., 2020). Seawater temperature is colder deeper down and further from the shore (KNMI, 2011). Moreover, the rate of eventual chemical deterioration concerning biotic- and abiotic degradation and corrosion, is higher at elevated temperatures (Wang et al., 2020). Therefore, the biofilm is expected to grow slower for the OBD, meaning that the effects of macro- and microdeterioration will be less in time. Moreover, the eventual rate of MIC and biotic- and abiotic degradation is expected to be lower.

6.1.2 Salinity

Seawater salinity is five percent lower at the coast than further offshore (Slijkerman et al., 2017). Low salinity reduces biofouling (de Castro et al., 2018). However, the salinity recorded in the Harbour is of such level that macrofoulers including oysters thrive in such conditions (Blackwood et al., 2017). It is not possible to say with certainty whether salinity will increase or decrease the amount of biofouling in the harbor test set-up compared to the OBD.

6.1.3 pH

The pH at the harbour is higher than further offshore due to rivers flowing into the sea, which reduces biofouling (Peck et al., 2015). Due to the increasing sourness of the oceans, it could be that this effect is nullified, as the pH conditions in the harbour might be what macrofoulers are used to. Again, it is not possible to say with certainty whether pH will increase or decrease the amount of biofouling in the harbour test set-up compared to the OBD. Table 6.1 shows the variables mentioned above, and location variables such as depth and distance to shore for the Eemshaven and the OBD.

Table 6.1: Seawater temperature, T [°C] and Salinity[ppt] and depth[m] and distance to shore[km] that influence the extent of biofouling for the Eemshaven and the Ocean Battery Design

	Seawater Temperature	Salinity	Depth	Distance to shore
Harbour test set-up	11 °C	28 ppt	3.5 m	<0.01 km
OBD	5°C	29.4 ppt	30 m	50 km

6.1.4 Depth

A relatively highly important external factor influencing biofouling is depth. The depth at which the EPDM is submerged influences the extent of biofouling (Degraer et al., 2020). The EPDM piece is submerged at four meter depth, resulting in high light-availability. Macrofoulers are more prevalent at smaller depths due to high light-availability and because they are hunted by crustaceans at greater depths (Vinagre et al., 2020).The thickness of the biofilm is expected to be greater for the harbour scenario as a result. Consequently, the thicker biofilm increases the extent of microdeterioration: MIC, biotic degradation, and macrodeterioration: direct deterioration. From figure 3.3 it can be retrieved that the dry weight of the biofilm in twice as small at thirty metres down compared to at four metres down.

6.1.5 Distance to Shore

Moreover, distance to shore affects the extent of biofouling. Numerous direct deteriorating species predominantly live within 50 kilometres from the shore, see table 3.2. Oysters are more abundant closer to the shore, as they thrive in brackish waters (Blackwood et al., 2017). Therefore it is expected that the extent of impacts of species such as oysters and mussels will be higher for the harbour scenario compared to the OBD. Moreover, MIC and biotic degradation are reduced as a result of less macrofouler presence.

6.1.6 Colonisation Success

The colonisation success of marcofouler's larvae might be higher in the harbour, as the larvae are transported to the shore through the waves (Vinagre et al., 2020). However, more currents further from the shore leads to more nutrients and particles passing by that macrofoulers feed on as they are suspension feeders (Vinagre et al., 2020). There are tides in the harbour and thus currents, but as the test set-up is deployed behind objects, it might be that these are less than in the open sea. It cannot be specifically defined whether this factor increases or decrease the extent of biofouling in the harbour.

6.1.7 Assumption Worse-Case Scenario

For the test set-up, the growth rate and thickness of the biofilm is expected to be higher. Moreover, the presence of direct deteriorating species is higher closer to the shore. Both the greater biofilm and higher presence of direct deteriorating organisms increases eventual MIC and biotic degradation too. Seawater salinity, pH and colonisation success of larvae's effect on the biofouling extent cannot be readily deemed as biofouling increasers or decreasers. All in all, it is expected that the biodeterioration in the harbour is greater than for the OBD. It is assumed that the results from the harbour test set-up are from a worse-case scenario.

6.2 Hypothesis

The hypothesis to be tested in this project is elaborated on in the remainder of this section.

6.2.1 MIC & Micro organisms' Bursting

EPDM is an elastomer, and elastomers are either fully-corrosion proof or deteriorate quickly (Corrosionpedia, 2022). As other companies widely use EPDM in the marine sector, it is deemed implausible that EPDM corrodes quickly and it is expected to be fully corrosion-proof. MIC is expected to be specific for metals and irrelevant for polymers where biotic degradation is microdeterioration relevant for polymers. The difference is that MIC processes involve certain bacteria that deteriorate metals and biotic degradation involves certain bacteria and fungi that deteriorate polymers. Its similarity is that both phenomena are induced by bacteria which extract one element out of material. In turn, no corrosion affects the amount of biodeterioration of barnacles, as barnacles settle in corrosion pits and induce pressure which causes delamination of material. If there are no pits caused by corrosion, the delamination effects of barnacles are lower or non-existent. Furthermore, if there is no corrosion, micro-organisms can not infiltrate the material and swell and burst from the inside. Therefore two of the three eventual biodeterioration causes are already not expected, as well as one of the two eventual direct deterioration mechanisms of barnacles.

6.2.2 Direct Deterioration

Before giving an expectation of the direct deterioration caused by the other macro organisms, it is explained how long these organisms were attached to the material. Photo-monitoring of the sample shows that oysters have been attached for at least twenty days. It takes at least two months for oysters to grow out of their larval phase after being attached in the spring, so it is assumed that the oysters have been attached for at least two months (Hatchery, 2022). The attachment duration of the mussels can be based on their life cycle too, as larvae spawn from spring to late summer and can stay alive for six weeks afterwards (Vinagre et al., 2020). Therefore, it is expected that mussels, similar to the oysters, have been attached for at least two months too. It is estimated Barnacles have been attached for at least three months by looking at the pictures taken over the last six months.

Barnacles are known to directly deteriorate material and cause up to five millimetre of deterioration in steel within two years. These macrofoulers are expected to have directly deteriorated the EPDM by half a millimeter or more. EPDM is not expected to corrode, unlike steel, making the anticipated deterioration lower for EPDM. Polymers are known to be used as anti-fouling material (Maan et al., 2020), which is another reason why the expected amount of deterioration should be lowered in comparison to steel. Barnacles are known to inflict shallow crevice corrosion of materials; see figure 3.5, (Blackwood et al., 2017). Mussels are known to perforate submerged substrata (Vinagre et al., 2020). Their deterioration rate is unknown, so half a millimetre is anticipated. Oysters are known to directly deteriorate steel at a rate of two millimetre per year. It is expected that oysters have an impact on EPDM too. Based on photo-monitoring, no Sponges and Pholads are prevalent, as expected by table 3.2, as thus their direct deterioration will be non-existent. All in all, it is expected that Barnacles, Oysters and Mussels have directly deteriorated EPDM with an estimated amount of half a millimeter.

6.2.3 Biotic Degradation

Figure 6.1 depicts how the EPDM in the harbour test set-up looks like after five months of deployment. The biofilm has grown according to what has been explained in section 3.1. The thick biofilm increases biotic degradation due to a higher presence of bacteria and fungi in the biofilm. Biotic degradation was stated to cause the amount of material deterioration on similar polymers together with abiotic. A weight loss of several percentages was recorded, and it is expected that for the EPDM piece in the harbour test set-up, this results in surface deterioration too. The tensile strength of polymers and rubbers are known to decrease after the materials were exposed to biodeterioration (Muthukumar et al., 2011). The tensile strength of an similar elastomer, silicone rubber, decreased by 13% after one year. Furthermore, section 3.3.3 state several additional relevant mechanical property decrease after polymers were exposed to biodeterioration.

(a) Front view EPDM piece

(b) Back view EPDM piece

Figure 6.1: EPDM piece in the harbour test set-up after five months of deployment. *Enlargements can be found in appendix I*

6.2.4 Abrasion

Abrasion is expected to be prevalent to a lesser extent in the harbour test set-up due to no expected heavy currents.

6.2.5 Hypothesis Statement

Of the five impacts that fall under biodeterioration, two are expected: biotic degradation and direct deterioration. Another non-biotic deterioration aspect is expected to be relevant in marine underwater conditions, namely abiotic degradation. Wang et al. found that EPDM's surface under artificial seawater conditions did not deteriorate, but its mechanical properties did decrease due to abiotic degradation. Which is in contrast to the above mentioned expected weight loss of polymers due to abiotic degradation by Sudhakar et al.. Therefore (Sudhakar et al., 2007) expectation is suspected to be false.

The hypothesis for this experiment is:

Hypothesis: The material sample does not show any sign of corrosion. However, the material samples will show signs of direct deterioration of macrofoulers and deterioration caused by biotic degradation. Moreover, mechanical properties decrease as a result of these impacts and due to abiotic degradation.

6.3 Hypothesis Assessment

6.3.1 Measured Variables

This project aims to measure the degree of surface deterioration and mechanical property decrease of EPDM after exposure to biofouling. The measured variables to quantify the amount of surface deterioration are: number of pits, pit depth, pit width and surface roughness. Impacts on the mechanical properties are determined by measuring: tensile strength and elongation at break, where elongation says something about the ductility of the material, and tensile strength says something about the strength of the material. These variables provide strong indications of the mechanical properties and surface deterioration of EPDM after exposure to biofouling.

Table 6.2: Measured Variables for Surface Deterioration (a) and Mechanical Properties(b)

(a)

Variables	Symbol, SI Unit
Pit Depth	$\mathrm{Rv_i}$, μm
Pit Width	$\mathrm{Rh_i}$, μm
Number of Pits	-
Surface Roughness	Ra, μm

(b)

Variables	Symbol, SI Unit
Tensile Strength	σ, MPA
Elongation at break	ε, %

6.3.2 Acceptance or Rejection Level

For the surface analysis, we zoom down to the micrometer level because of the 2- mm-thick flexible bladder. Any change is reported if the mean of the harbour EPDM differs from the standard deviation of normal EPDM. A difference, within the 3 to 6 months adhesion of different organisms/exposure to biofouling, on the surface, is expected to increase positively exponentially over time, due to biofilm growth over time. In addition, possible side effects may occur. A difference below 5% is discounted to the number of repetitions or uncertainty of the initial values. Any difference above 5% is reported as a sign of biodeterioration. It should be noted that the number of replicates in this study is small.

7 Methods and Materials

In this section, the instruments, tools and materials used are discussed. First, two instruments used in this project are elaborated on. Instruments that can be relevant for biodeterioration testing, but which are not opted for are discussed in appendix F.

7.1 Instruments and Tools

7.1.1 3D Optical Profilometry

To find the extent of surface deterioration a 3D Optical Profilometer is opted. A 3D Optical Profilometer scans a sample using light direction techniques or via a stylus physically moving over the sample. A monitor is connected and displays a 3D model of the sample; an example of such a 3D model is shown in figure 7.1. This technique can quantify surface roughness, feature height, void percentage and defect density, among others (NanoScience, 2021). Deterioration analysis using 3D Optical Profilometry quantifies surface roughness, volume loss, pit distribution, pit depth and pit volume, enabling insights into the size of deterioration (Li et al., 2015). Expected outputs of the 3D Optical Profilometer are displayed in appendix A. Contacting the surface is often an advantage in dirty environments where non-contact methods can end up measuring surface contaminants instead of the surface itself (Ingole et al., 2013). However, light direction techniques might be better, as the stylus can damage the EPDM piece when moving over the material (NanoScience, 2021). Therefore, a light direction technique is opted for in combination with a technqiue for the removal of surface contaminants. The instrument used for this experiment is the Proscan 2000.

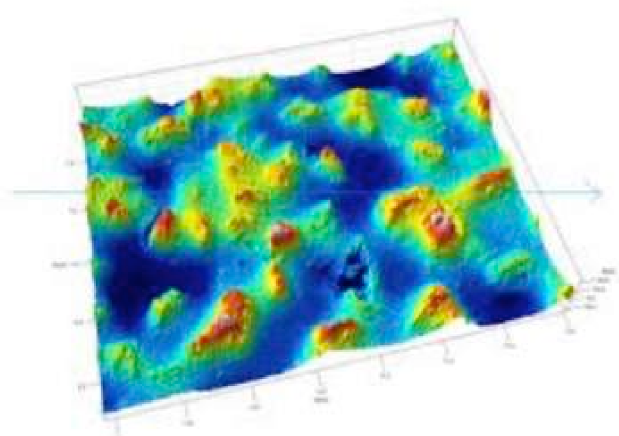


Figure 7.1: 3D Model Made By 3D Optical Profilometry.
Adapted from (RtecInstruments, 2021).

7.1.2 Universal Testing Machine

An UTM, see figure 7.2, is used to test the tensile strength and percentage of elongation of EPDM. An Universal Testing Machine is appropriate to obtain reliable mechanical properties for polymers (Huerta et al., 2010). The machine used for this project is model H25KT from the brand Tinius-Olsen.

Specimen size and machine settings influence the outcome of a Universal Tensile Test (Huerta et al., 2010). American Society for Testing Material D412 (ASTM D412) is the standard tensile testing procedure for elastomers (Polyhedronlaboratiesinc, 2021). An introductory guide is available online; see appendix B. The machine used is set in ASTM D412 modus. The only thing that varies from ASTM D412 method is the specimen size due to no availability of the ASTMD412 dogbone specimen size for the die press cutting punch press at the UG. The specimen size has a gauge length of 2 centimetres and a width of 0.4 centimetres. The speed was set at 50 mm/min. The load cell chosen had a maximum range of 1000 N.

Figure 7.2: Universal Testing Machine (Instron, 2021)

Tools used are:

- An Electronic Caliper to measure specimen thickness
- A Die Cut Punch Press to create dogbone specimens

7.2 Methods of Data Analysis

Before analysis, the gathered quantitative data was prepared, which is explained in this section. The 3D model output by the Proscan2000 is checked for missing data and outliers. Missing data were replaced by the average of other data. For this, the tool "Function xy" was used. The "Auto-level" function was used to remove eventual waviness of the sample. Disturbations from the surroundings of the Proscan were automatically removed by the software itself by deleting all the wavelengths lower than the set step size of 0.01 micrometre. For each sample, the three deepest and widest pits were noted, which could be read from the x-y plots output by the Proscan software. One-quarter of the sample was taken by using the tool "Load area". In this area, the number of pits was manually counted. Pits close to the deepest pits were considered, which could be identified as they showed another colour than their surroundings. Surface roughness was output by the Proscan2000 under "Analysis". The mean and standard deviation are calculated for all variables. All samples were scanned 3 to 4 times for the profilometer tests. Each scan had a target area of 6 by 6 mm, and after 3 or 4 scans, the entire area where oysters or mussels were attached was scanned. A boxplot was made of the variables using Excel 2016. Afterwards, a causal analysis was performed. A step-by-step plan of how the profilometer was used is shown below:

Step 1: Input 6 by 6 millimetre into the proscan2000 as the scanned target area

Step 2: Adjust the height until the proscan shows a green light to indicate a proper distance between the beam and the sample

Step 3: Replace missing data with the average using the tool "Function xy"

Step 4: Remove waviness with the "Auto-Level" Tool

Step 5: Retrieve the three deepest and widest pits from the output x-y plots

Step 6: Use the "Load Area" tool to load one quarter of the target area and manually count the number of pits

Step 7: Retrieve the surface roughness using the "Analysis" tool

The Horizon Software coupled to the H25KT provided stress-strain graphs of the samples. For each sample, the maximum tensile strength and elongation at break were noted. Seven dogbone specimens were used for tensile testing, of which the highest and lowest values were excluded to remove outliers. For the remaining five samples, the mean and standard deviation was calculated. Afterwards, a causal analysis was performed.

7.3 Material

A Stanley knife was used to cut samples. The sample was put in autoclaved (120 °C for 15 min) seawater in a sealed bag. Seawater filtering with an autoclave prevents any accelerated corrosion in the sealed bag. Seawater is used to keep the biofilm alive so that eventual impacts of dead animals are excluded. The number of animals are manually counted. The sample retrieved contained all macrofoulers stated in literature to directly deteriorate material. The samples retrieved include the maximum macrofouler attachment and size to observe the worst-case scenario. The sample retrieved can be seen in figure 7.3.

(a) Front-view Sample

(b) Back-view Sample

Figure 7.3: Front- and back view of the sample after six months of exposure to biofouling

Oyster and Mussel colonies were present, consisting of 5 and 7 species respectively. Numerous Barnacles were attached, thus the most significant accumulations have been chosen - a 10-Barnacles stack at maximum. Three targets areas were identified ,which exclusively consisted of Oysters, Mussels or Barnacles. Additionally, one Bryozoan spot was selected, a hard macrofouler that does not directly deteriorate material and is selected to analyse possible accelerated corrosion on EPDM. A spot with no macrofoulers attachment was also chosen for corrosion analysis. Making a total of five interest groups scanned with the 3D Optical Profilometer. It must be noted that barnacles are also prevalent under the mussels, oysters and bryozoan, as barnacles were the primary colonisers, as can be seen in figure 2.4, after which the Mussels, Oysters and Bryozoan colonised the surface as secondary colonizers. Sample monitoring by photos reveals the attachment duration of the Barnacles, Oysters and Mussels, as discussed in section 6.2. Additionally, it could be derived that the Bryozoan was attached for a month at least.

Macrofoulers were removed using a 10% hydrochloric acid solution, which initiated the chemical reaction formulated below. This ensured that the calcareous matter, of which the macrofoulers primarily consists of, was dissolved.

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$$

EPDM is highly resistant to 10% hydrochloric acid (Guide, 2021). The samples were immersed in the hydrochloric acid solution for 4 hours. The mussels were attached via byssal threads, see figure .4, which were cut and washed off with water and soft hand-scrubbing. The hydrochloric acid was washed off from the sample with plain water. A pH test was performed to check that all hydrochloric acid was removed. Once the pH was 7, the washing was deemed successful. As depicted in figure 7.4, the sample was removed from all biofouling and deemed ready for analysis.

Figure 7.4: Cleaned Biofouled Sample

Before putting the samples under the 3D Optical Profilometer, they were cleaned with water and an air blower to remove possible contaminants (Kohli and Mittal, 2019).

For the Universal Testing Machine experiments, the UG had two dogbone specimen sizes to Die Press. One sized 3 by 1 centimetre was chosen to ensure that enough repetitions could be done. In figure 7.5, the dogbone specimens can be seen. The other size is 15 by 3 centimetres, which does not allow for many repetitions, and would have been a waste of valuable harbour material which can be used over time to study the effects of biodeterioration.

Figure 7.5: Dogbone Specimens for UTM

Tools used are:

- A Stanley Knife
- Hydrochloric Acid and Water to make a 10% Hydrochloric acid solution
- Measuring Cups
- A Tray
- Sealed Bags
- An Autoclave
- Seawater
- Gloves

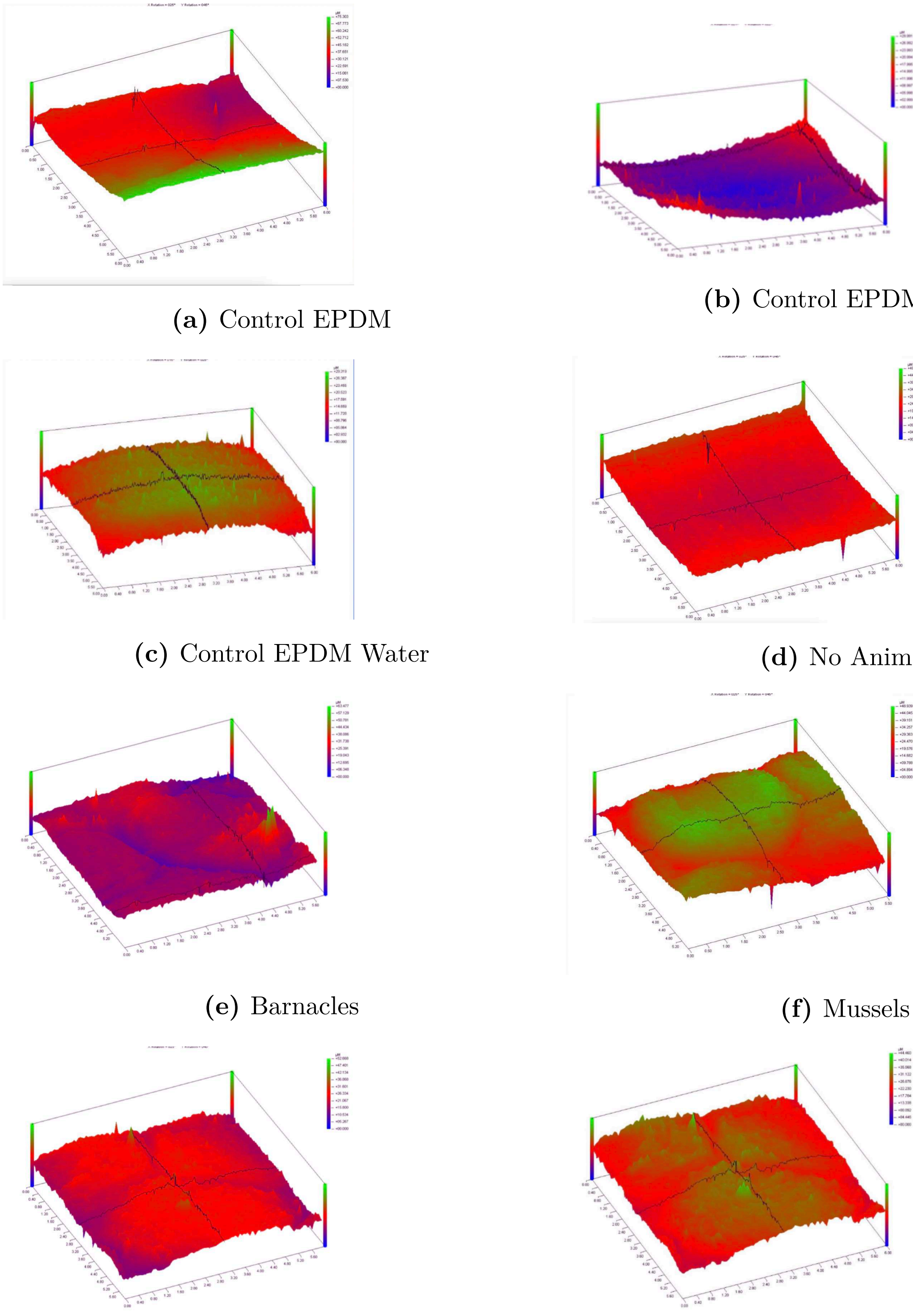
Cleaning techniques and techniques to remove surface contaminants not chosen can be found in appendix G.

7.4 Control Material

Three samples are made as control samples. A piece of EPDM that has not been exposed to biofouling, and a piece of EPDM that has not been exposed to biofouling and has undergone the cleaning technique. In this way, surface deterioration and mechanical properties can be compared to biofouled samples, and possible impacts of the cleaning technique can be identified. Moreover, standard EPDM is immersed in water for the same duration as the sample in hydrochloric acid and is taken as a control material to account for possible impacts of immersion in a liquid.

A critical note is that the control EPDM material for the 3D Optical Profilometer tests was an already used piece of EPDM for unknown tests, as this was the only available piece. Although it does serve as an approximate reference, it is not a perfect one. The experiments performed on the material could have caused alternations on the surface. This is expected not to be the case because no signs of fracture can be seen. However, many surface contaminants have accumulated on the surface. Variables such as pit depth, pit width and surface roughness were based on this material instead of on the initial values for the variables of the EPDM in the test set-up in the harbour before immersion.

8 Results Surface Analysis



(a) Control EPDM

(b) Control EPDM HCL

(c) Control EPDM Water

(d) No Animals

(e) Barnacles

(f) Mussels

(g) Oysters

(h) Bryozoan

Figure 8.1: 3D Optical Profilometer Scans. *Scans showing waviness are shot before the "auto-level" function was used. *Enlargements can be found in appendix H*

8.1 Results

The variables explained in section 7.2 were retrieved and are displayed in table 8.1. In addition, box plots have been created for all variables and can be found throughout the section. It should be noted that two pieces of control EPDM were analysed, designated as control EPDM 1 and control EPDM 2.

Table 8.1: Number of pits and pit width, $Rh_i[\mu m]$ and pit depth, $Rv_i[\mu m]$ and surface roughness, $Ra[\mu m]$ for the control- and biofouled samples

Type	Number of Pits	Pit Width (μm)	Pit Depth (μm)	Surface Roughness (μm)
Control EPDM 1	36.00 ±17.28	63.00 ±1.90	16.55±2.79	3.73±2.02
Control EPDM 2	22.67 ±3.77	46.00 ±4.80	3.88±0.74	2.40±0.33
Cleaned Control EPDM	26.67 ±9.42	65.00 ±16.00	4.22±1.13	1.18±0.11
Control EPDM Water	38.67 ±4.98	58.00 ±12.00	16.55±2.91	1.03±0.06
Biofouled EPDM No Animals	56.00 ±17.28	58.00 ±13.00	19.11±2.18	2.25±0.19
Biofouled EPDM Barnacles	41.33 ±4.98	51.00 ±10.00	19.67±2.39	2.36±0.025
Biofouled EPDM Bryozoan	20.00 ±6.53	47.00 ±8.01	14.55±3.83	3.93±0.086
Biofouled EPDM Oyster	26.67 ±9.42	44.00 ±18.00	15.77±6.82	2.50±0.086
Biofouled EPDM Mussels	100.00 ±47.95	48.00 ±8.90	26.33±6.71	2.56±1.00

8.2 Pit Width

A box plot for the pit width is shown in figure 8.2. The pit width of all biofouled samples did not increase compared to the control samples. This indicates that no biodeterioration has taken place on all biofouled samples.

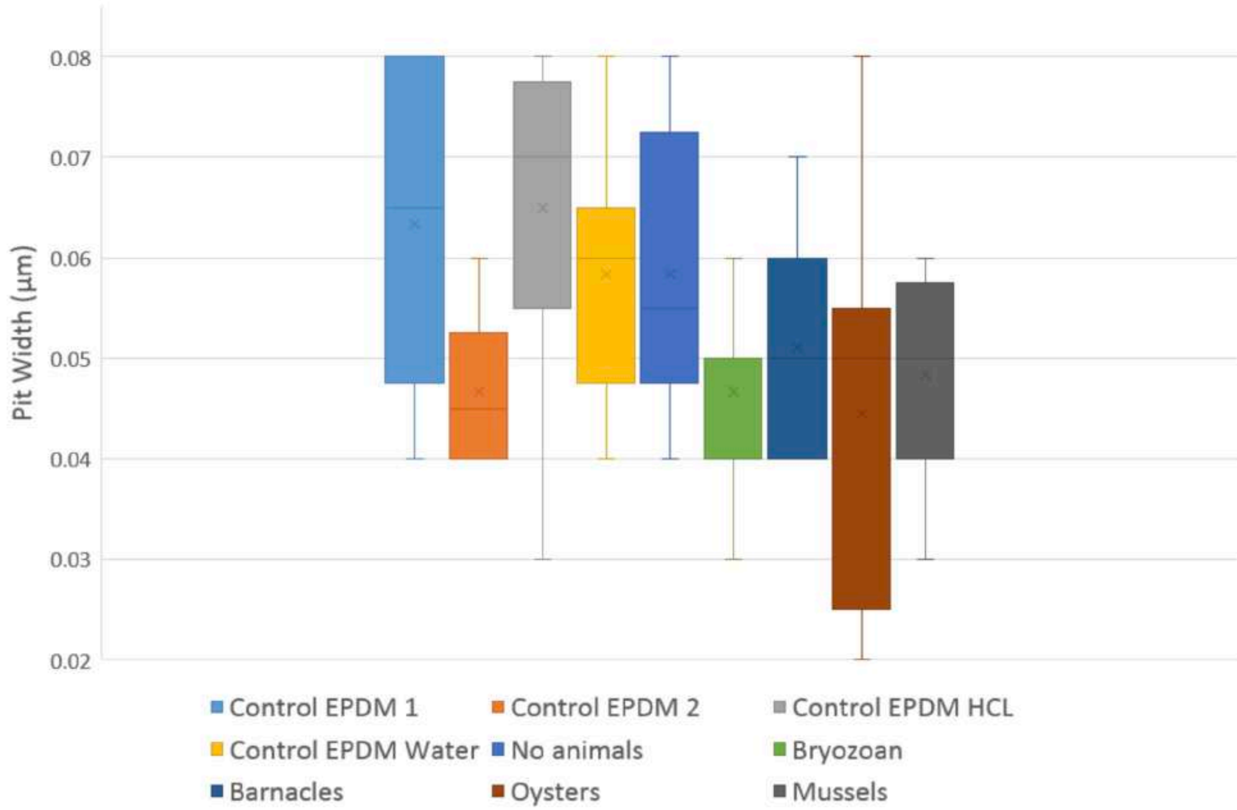


Figure 8.2: Pit width, $Rh_i[\mu m]$ for the control- and biofouled samples

8.3 Surface Roughness

The surface roughness of Control EPDM 1 & 2 were unexpectedly high. Possibly due to contamination, as the control sample had been laying around the workplace and was used for earlier experiments. Profilometers working via light direction techniques could end up measuring these surface contaminants (Ingole et al., 2013). The in-water immersed control sample showed a significant decrease in surface roughness after 4 hours of immersion. It is expected that the surface roughness further decreases more after more prolonged immersion. Moreover, this suspicion is partly based on the observation that a white substance gave the Control EPDM a white tint, which reduced significantly after immersion. Another reason could be that the "auto-level" function tool of the Proscan 2000 was forgotten be applied before retrieving the surface roughness. One target area namely showed a significant different value of 6.5 micrometres compared to the average of 3 micrometres for the other target areas. Therefore, the surface roughness reference is deemed unreliable. Instead, as a reference for the initial surface roughness value, 0.25 micrometres is taken (Adam et al., 2019). The surface roughness increased on average by two micrometres for no animals, barnacles, oysters and mussels, and by up to four micrometers for bryozoans. This result indicates biodeterioration and is discussed in section 9.

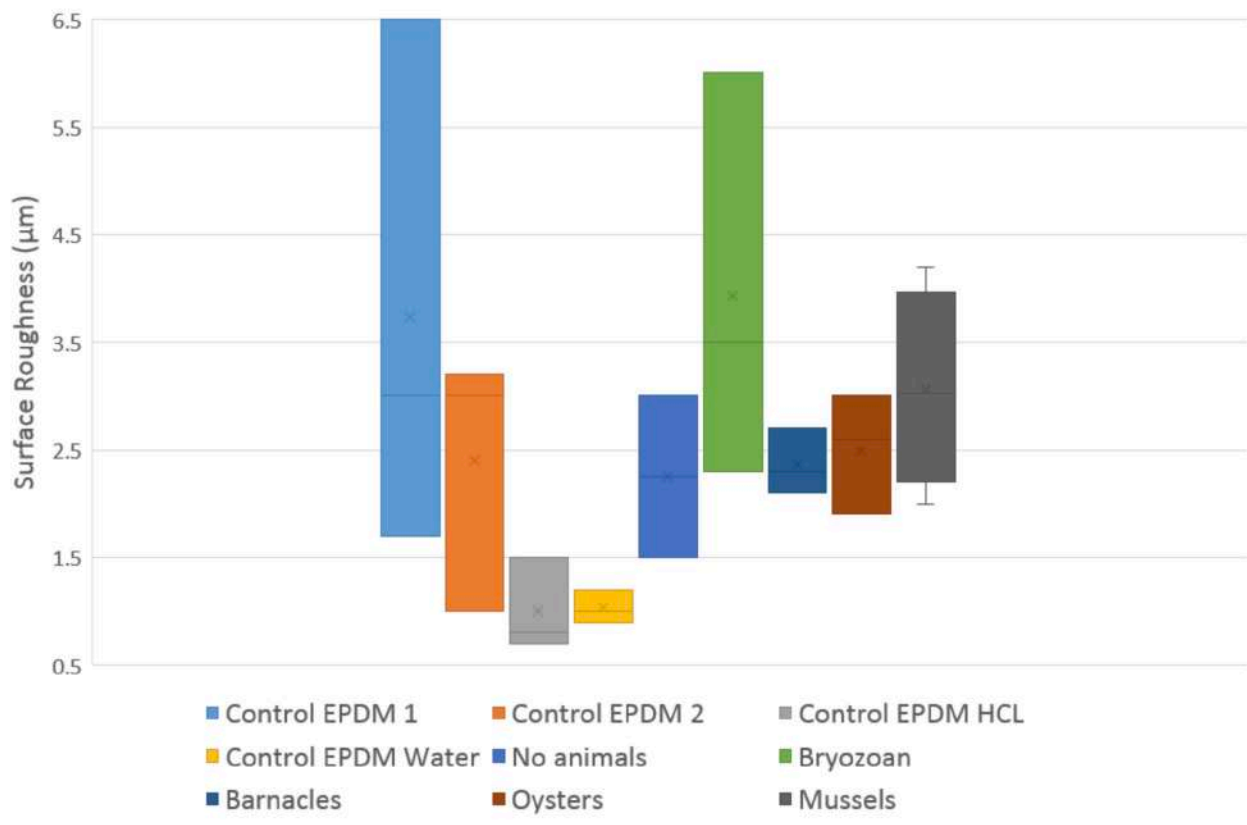


Figure 8.3: Surface roughness, Ra[μm] for the control- and biofouled samples

8.4 Pit depth & Number of Pits

The mean pit depth and number of pits for Barnacles, Bryozoan, Oysters and "no animals" does not deviate from the standard deviation of the control samples. This indicates that no biodeterioration has happened. For two targets areas taken for corrosion - under a relatively thick biofilm due to a Bryozoan, and a spot without macrofouler attachment - the same applies.

For the mussel colony the pit depth has increased with 59% on average and 71% maximum. The number of pits for the mussel colony has increased with 177% on average with a maximum of 180%. This does indicate biodeterioration. 0.016 millimeter increase in pit depth was found within 3 months of mussel attachment. Concerning the 2-mm flexible bladder thickness of the OBD, it has perforated 0.8% vertically into the material. Through literature the validity of these results was looked out for, which is discussed in chapter 9.

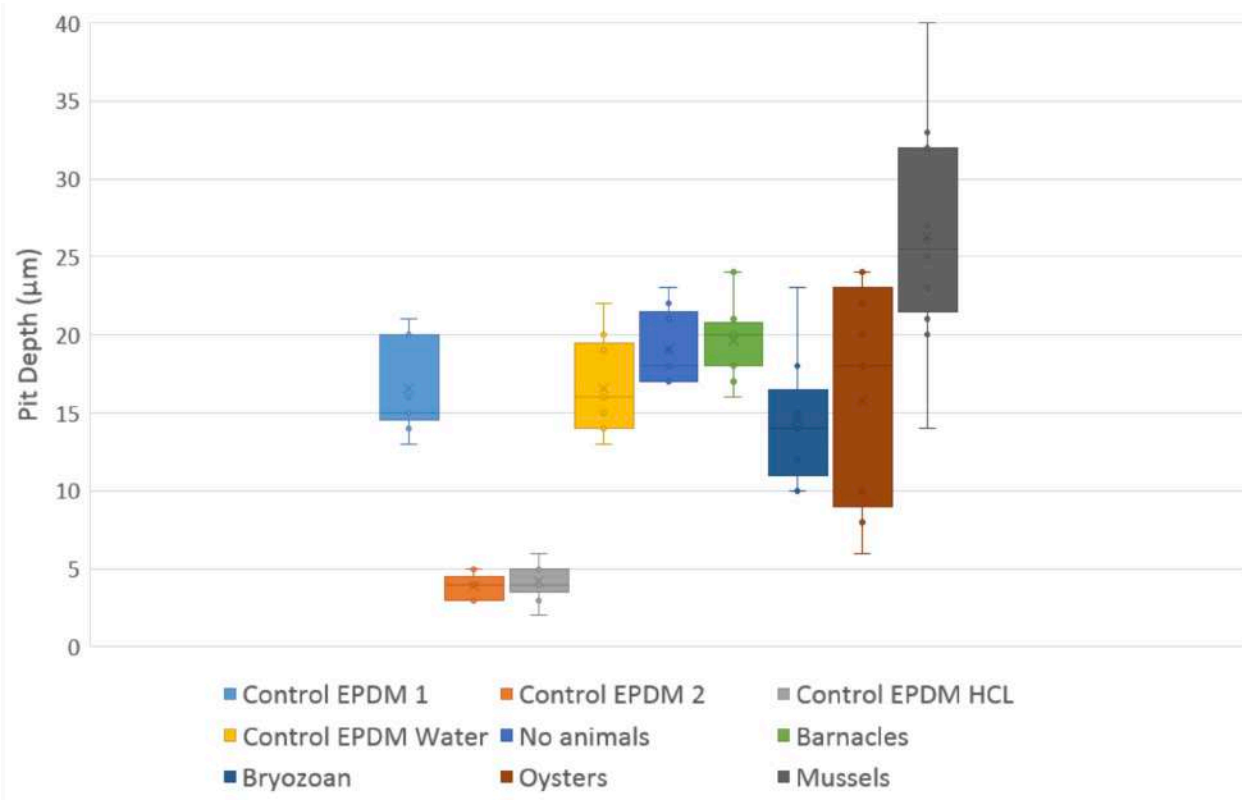


Figure 8.4: Pit depth, $Rv_i[\mu m]$ for the control- and biofouled samples

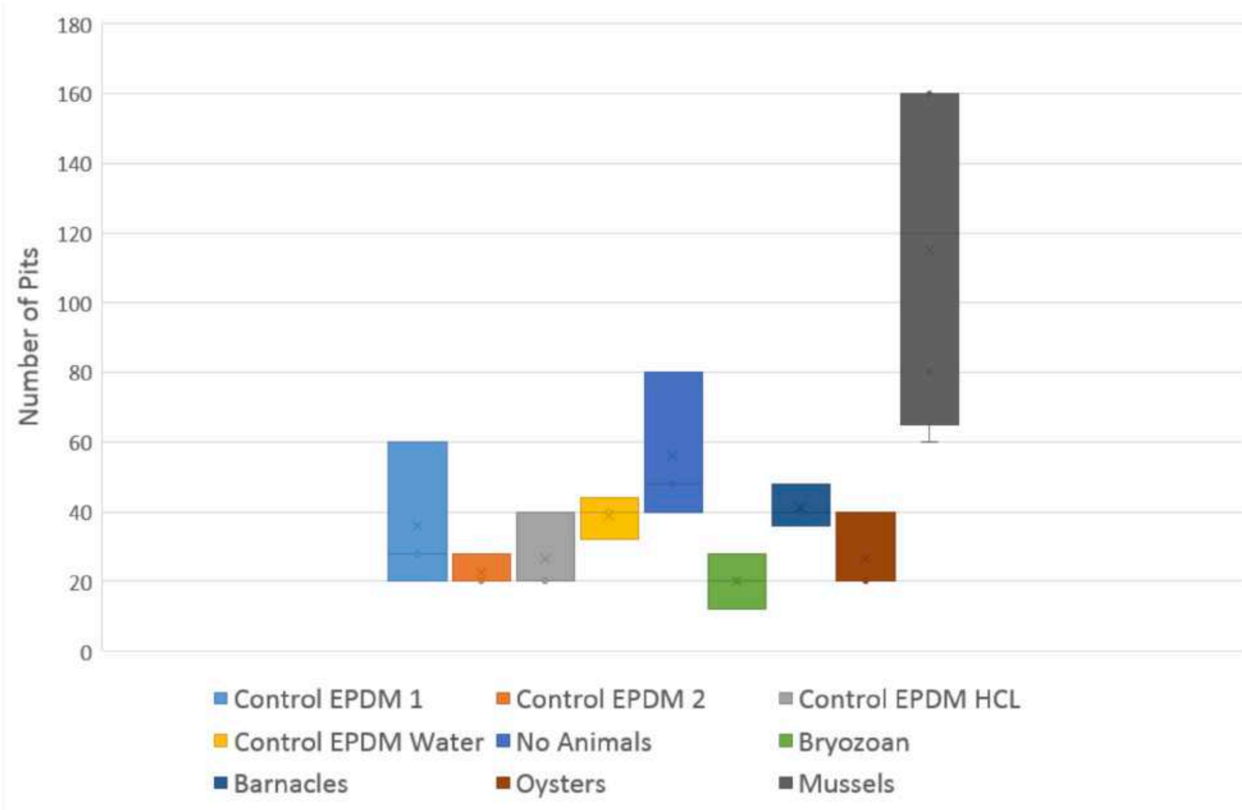


Figure 8.5: Number of pits for the control- and biofouled samples

9 Discussion Surface Analysis

A surface analysis is conducted to find the extent of surface deterioration on EPDM after exposure to biofouling. A 3D Optical Profilometer was used to retrieve pit dimensions and surface profile roughness. In this chapter, a discussion of the results is given concerning the increase in surface roughness, increase in pit depth and quantity under the mussel colony and the indifference between the biofouled samples and non-biofouled samples for the remaining results. The results are compared to previous studies, and new studies are found to acquire information about outstanding results. Alternative explanations for the findings are discovered, and the most likely one is reasoned out. Experiments to validate the reasoning are described. A new frame on how to approach the research is given, and experiments are suggested that could be included in further research.

9.1 Biotic Degradation

For the biofouled samples, a slight increase in surface roughness is found. A small change in surface roughness could be attributed to cementeous products of organisms still present on the surface and to ocean currents that alter surface characteristics (Muthukumar et al., 2011). For example, barnacles attach via cementeous layers, which were not removed after cleaning. In figures 8.1e,8.1f, 8.1g and 8.1h, the circular cementeous stems of barnacles can be seen. Moreover, Sudhakar et al. & Gu state that macrofoulers alter surface characteristics of material upon attachment. Besides the macrofouler attachment and oceanic currents altering surface characteristics, biotic degradation could have occurred and is possibly co-responsible for the found difference in surface roughness. EPDM and its additives are predominantly organic compounds resulting in a certain rate of biodegradability. In literature section 3.3.3, the bacteria and fungi responsible for eventual biotic degradation are explained, as well as the its deterioration mechanisms. Biotic degradation might have occurred during the six months of deployment in the harbour too. Biotic degradation is not visible in the variables for pit size and quantity thus its extent can not be specified if it was happening. Due to the assumed initial values, a possible biotic degradation could not be reflected in these variables. Now that more proper initial values have been set, further experiments could identify the extent of eventual biotic degradation. Concerning the results of this experiment, biotic degradation could possibly be retrieved by looking at the degree of change in surface roughness. A change in surface roughness of 13 to 250 micrometres in one year was reported for polymers in a previous study (Muthukumar et al., 2011). This experiment found a surface roughness change of 2 to 4 micrometres in half a year. Results cannot be extrapolated over the whole year as the biofouling extent differs throughout the year. Moreover, the test set-up of Muthukumar et al. varies from the test set-up studied in this project. Therefore, these considerations need to be included to say anything about the relative durability of EPDM in marine environments concerning the surface roughness. To account for the ambient conditions difference for the test set-ups, eventual experiments for the harbour test set-up could be initiated to define the amount of dry weight of the biofilm and compare it to Muthukumar et al. perceived dry weight. However, this would exclude that the variety of micro- and macro organisms differ. Therefore, follow-up studies are possibly the most accurate way of defining the extent of eventual biotic degradation best. Looking at eventual changes in pit size and quantity is most straightforward, as by looking at the surface roughness, ocean currents and macrofouler attachment need to be considered.

9.2 MIC and Direct Deterioration

MIC could be another cause of the above discussed difference in surface roughness. An increase in pit size and quantity for the two MIC target areas is not found in this experiment. Similar to biotic degradation, its eventual extent could not be reflected in the results due to the assumed initial values. An artificial seawater experiment performed by Wang et al. was conducted to test whether EPDM corrodes abiotically, and its surface showed no sign of dents in an SEM observation after the test, but only its chemical bonds inside the material, and thus its mechanical properties altered. However, it did not include MIC, such as Sulphate-Reducing-Bacteria (SRB) inducing biotic corrosion. Still, it is expected that EPDM does not corrode, as MIC processes are specific for metals. Additive supplemented to EPDM are expected to possibly corrode. For example, if sulphate is added, it can be expected that SRB extract sulphate out of the EPDM compound. It is recommended to determine the variety of MIC processes, stated by Canning, such as the SRB process. An Environmental Scanning Electron Microscopy (ESEM) analysis could be conducted to find eventual depletion of certain elements in the compound formulation of EPDM due to these MIC processes. Additives prone to MIC could be selected afterwards or preventively.

This experiment has not found direct deterioration mechanisms of two of the three native North-sea species, Barnacles and Oysters, expected to cause direction deterioration. Again, due to assumed initial values, eventual impacts could not be reflected in the results. Canning suggested that entrapment of water under barnacles facilitates accelerated corrosion compared to its surroundings, which was expected to be the reason for its direct deterioration on steel. Likewise, the reported direct deterioration of Oysters on steel was thought to be based on localized accelerated corrosion (Blackwood et al., 2017). This experiment cannot affirm

these suggestions due to the assumed initial values. However, if one assumes that the initial values are exact, the results of this study would suggest the same as Canning & Blackwood et al.. Barnacles' delamination mechanism was not found either. Barnacles' minimum larvae size is 0.241 millimetres, being greater than the maximum found pit width of EPDM (Yan, 2003). Which might be a reason which prohibited the barnacles from settling into pits and consecutively delaminating the material. Assuming that the initial values are proper, the results indicate that barnacles and oysters do not directly deteriorate EPDM. Moreover, if this is true and its direction deterioration mechanism is based on accelerated localized corrosion, it might be an indication that EPDM does not corrode too.
Due to the growth

9.3 Mussel biodeterioration

An increase in pit depth and quantity was found under the mussel colony. The byssal threads - strong silky fibers that the mussel uses to anchor to surfaces- is known to invade concrete material, which was observed via SEM experiments (Pérez, 2003) (Yao et al., 2017). Specifically, the byssal threads caused fissures -long and narrow cracking- which is similar to what has been found in this study. It must be noted that the information from Pérez is based on an abstract, and Yao et al. use the surface instead of the cross-section as evidence for the physical invasion of the byssal threads. Meaning that the physical deterioration might not be justified well. Pictures to clarify what the byssal threads are, can be found in appendix D. Moreover, byssal threads' diameter is 0.07 to 0.3 mm, meaning that physical deterioration should also be visible in the pit width (Qureshi et al., 2021) & (Aldred et al., 2007). Furthermore, in the bulk of literature, the byssal threads are stated to solely function as an adhesion mechanism on material, and rather use proteins that contain high concentrations of L-3,4-dihydroxyphenylalanine molecules functioning as an adhesion glue, inspiring engineers looking for synthetic underwater glues (Harrington et al., 2018). Without substantial justification of physical deterioration found elsewhere, it is suspected that the byssal threads do not penetrate into the material. For confirmation, SEM photos can be shot of the cross-section of samples with previously attached mussel colonies.

Mussels have been found to chemically attack concrete, as they extract calcium inside the material to build their shell plates (Yao et al., 2017). This could be equally true for EPDM, as calcium is used as an additive in the compound formulation of EPDM to increase its mechanical properties, see figure 3.5. The chemical deterioration results in fissures and increases the number of pores. To be precise, 7.5 % of EPDM is made up of calcium for the compound formulation referenced above. However, this might not be representative for all EPDM material as the type of additives and their amount varies for various EPDM types. Information about the initial compound formulation of the type of EPDM studied at hand is unknown. What is known about the calcium absorption mechanism is that it works via the soft animal inside the shells, which extracts ions diluted in the seawater and via food uptake (Machado and Lopes-Lima, 2011). Nowhere is stated that the byssal threads function as calcium absorbers, and the exact way in which the mussels extract the calcium from material is not well understood (Yao et al., 2017). Yao et al. reported a calcium reduction of 40% in one year and 80% in twenty years. Therefore, the chemical deterioration might increase negatively exponentially over time during the colonization period. It is unknown whether the mussels absorb calcium until a certain vertical point in the material. The calcium extraction of the mussels could be a reason for the found mussel biodeterioration. Rather labelling it as biodegradation as one element inherent in the material is removed out of the compound. Dealloying fits the biodegradation best, as one element is removed throughout all layers of the material. Except without the normal accumulation of the element on the surface, but in the mussels shells. Eventually resulting in slight pitting corrosion on the surface of the material too. Momentarily, there are no expected side effects, as the other expected impact, biotic degradation, is not expected to increase due to an equally exposed surface area, and as EPDM is homogeneous. A reason for the indifference in pit width might be that the grain size of the calcium is lower than the initial pit width dimensions. To test this interpretation of calcium depletion, ESEM analysis can be performed, with which the chemical composition of material can be analysed. A sample with a previously attached mussel colony could be compared to samples without mussel colonies to determine this and its extent over time can be determined as such. A literature research to retrieve whether other macro orgainsms similarly extract calcium was not conducted in this project.

9.4 Outlook

If the initial values are proper, the mussel biodeterioration is caused by calcium depletion and biotic degradation happens. The research might shift towards the biodegradability of EPDM. Any biodeterioraton on EPDM might be due to biodegradation on the material compound where the expected type of deterioration is dealloying. EPDM's biodegradability could be tested with accelerated degradation experiments to find its lifespan in underwater conditions. For EPDM's abiotic degradation, Wang et al. performed such an experiment through heightening the temperature in a test chamber and extrapolating the results to the ambient conditions of the marine sector via the Arrhenius equation. Additionally, bacteria and fungi could be added to account for the biotic degradation factor. Meanwhile, additives could be selected that have a good resistivity to biodegradation. Other additives instead of calcium may be selected for EPDM to avoid biodeterioration of mussels. The enhanced strength and ductility that calcium provides is not necessary for the flexible bladder to operate effectively. Moreover, other additives that might replace calcium's strength and ductility can be researched.

Earlier studies did not consider weight loss due to additive dissolution or degradation, described by (Wang et al., 2020). Which might have misled their confirmation of the significant extent of bacteria and fungi biotic degradation, which might be lower in reality. As a material, they use sheets on a regular internet site, and not sheets with specifically selected additives for the marine sector. It is useful to determine whether the weight loss is due to the additives or to the material itself. One would have to set up a control experiment to see what effect water absorption has on the transport of the additives out of the material. If possible buy a sheet without additives or buy material designed for marine use. Then one could map out how fast the biodegradation on EPDM is and make a positive exponential prediction as it is predicted that the bacteria and fungi increase as the biofilm grows. Therefore, the weight loss of earlier studies might be a false indication of actual biotic degradation, questioning whether biotic degradation leads to surface deterioration at all or solely to decreased mechanical properties as for abiotic degradation.

10 Limitations Surface Analysis

The results discussed above are subject to limitations that limit the significance of the experiment, which are discussed in this section.

10.1 Non-Native Species

NNS their impacts could not be sampled, but their impacts may be prevalent when they are introduced to the North Sea Ecoregion. Sponges solely live in the ecoregion west of Scottland and not in the North Sea (NatureScot, 2022). They are reported in the literature as to directly deteriorate material (Canning, 2020). Similarly, the bivalve species: Martesia is found on the east coast of North America, where it is known to bore into polymers in the same way it does on rocks, see figure 3.7. Again, this species might be introduced as an NNS. Moreover, not all Molluscs have been investigated. Oysters and mussels were present, but eventual boring impacts of others have not been included in this study.

10.2 Byssal Threads' Abrasion

The byssal threads were cut with a small scissor and removed by light hand-scrubbing with water. This could have abraded a tiny chunk of material during removal. Moreover, considering that the mussels attach with a very strong glue. However, that should then be visible in the pit width, as the byssal threads have a diameter of 0.07 to 0.3 millimeter, and the plaques have a diameter three to five times as large (Qureshi et al., 2021). Which was not the case, as the pit width was 0.048 millimeter on average, and therefore it is assumed not to have caused damage to the sample.

10.3 Assumed Initial Values

The initial values for the biofouled samples are unknown and based on other material. It could be that the actual initial values for the variables were lower in reality, and thus several impacts of biodeterioration were not reflected in the results. Through literature, the maximum pit depth, Rv_i, for EPDM is sought for but unfound.

10.4 Hydrochloric acid solution Impacts

The cleaning technique is assumed to have no impact on the results. No variables differed from either Control EPDM 1, Control EPDM 2 or Control EPDM Water. It is found that the surface roughness of the cleaned Control EPDM is significantly lower than that of Control

EPDM but not distinct from Control EPDM that has been submerged in water for the same amount of time. Thus, this may be due to submersion in a liquid rather than due to the hydrochloric acid solution. It is assumed that the control EPDM was heavily contaminated as it was lying around in the workplace. Therefore the surface roughness of EPDM found in literature is taken as a reference for the surface roughness compared to the the biofouled samples. This results in an increase rather than a decrease in the surface roughness, which was expected, which might add to the reliability of the assumption.

10.5 Seasonality Changes

The material has been exposed to potential biofouling from July to December. Results from December to July should be reported to comprehend for seasonality changes of macrofouler attachment. Therefore, the extent of biodeterioration cannot be drawn linearly over the whole year and data throughout the year is needed. 2 months of winter, the entire spring season, and a month of summer have not been incorporated in the results. Which might caused the results to be higher or lower than in reality.

10.6 Side Effects

Side effects after mussel deterioration are not expected. Multiple pits that collide due to the number of pits increasing, subsequently facilitating barnacle larvae settlement and thus delamination, is assumed not to happen. The pit percentage of the mussel within their area of attachment is approximately 1.4%, which can increase on maximum to the calcium percentage inherent in the compound formulation. An eight percent calcium compound formulation has a tensile strength and elongation at break of eighteen megapascal and 650 percent. The mechanical properties for the Habour EPDM are far lower. As calcium increase the mechanical properties, a lower calcium percentage is assumed. Assume that the harbour EPDM has five percent of calcium. Which is assumed to be too low to cause any collision. Moreover, larvae might not be able to reach the surface once a biofilm has attached to the surface.

10.7 Statistical Significance

Statistical significance is weak. For this experiment, only a part of the EPDM piece was analysed to preserve material for further experiments. To consider the impact of biodeterioration, data over several years is needed due to biofilm growth. The experiment needs to be repeated at least 3 or 4 times to draw reliable conclusions.

10.8 Total Material Loss Matlab

This study might not have addressed the total material loss of the surface. Only the variations in the larger pits are looked at, thus neglecting the increase of pit sizes for the smaller pits. Matlab was aimed to be used to calculate the area under the mean line. However, Matlab files for the profile scans were only partly exported, as the timeframe was deemed too short. It is recommended to do this in further studies.

An explanation of how to increase reliability about the impacts of the cleaning technique, increase statistical significance and establishing initial values as a control in subsequent studies is described in section 14.

11 Results Mechanical Properties

EPDM's strength and ductility are reported on in this section. The tensile strength defines EPDM's strength, and the percentage of elongation at break defines EPDM's ductility. Tensile strength and elongation at break for the control- and biofouled samples can be found in table 11.1.

Table 11.1: Tensile Strength,σ,[MPa] and Eongation at break,ε,[%] for the control-and biofouled samples

Sample	Tensile Strength (MPa)	Elongation (%)
Control EPDM	4.82±0.42	250.52±30.51
Control EPDM HCL	4.82±0.25	246.42±13.12
Control EPDM Water	4.58±0.26	235.06±15.05
Biofouled EPDM	9.69±0.35	338.46±17.03

The tensile strength and elongation at break of the control- and biofouled samples differ significantly from each other. It was expected that the mechanical properties would decrease for the biofouled samples compared to the control samples. The odd increase for the biofouled samples indicates that the two pieces of material are of a different type of EPDM due to alternations in compound formulations. Initial values for the EPDM in the harbour test set-up were unknown. Thus, unfortunately, the control EPDM does not serve as a reference and no eventual decline, and its extent can be defined.

12 Discussion Mechanical Properties

It was aimed to look at mechanical property decrease due to biotic degradation of bacteria and fungi, abiotic degradation of seawater and direction deterioration of macrofoulers. The two former would result in rupture or degradation of EPDM's molecular bonds, which give the material its strength and ductility (PolymerPropertiesDatabase, 2021). Eventual organisms induced deterioration, including the dealloying of mussels due to calcium extraction, would also decrease mechanical properties as calcium provides increased strength and ductility. However, due to unknown initial values, eventual strength and ductility decrease could not be defined.

Instead, some results from literature are used to explore eventual mechanical property decrease. It must be noted that this analysis is performed roughly due to time constraints. Mechanical property decrease due to abiotic seawater conditions has been readily performed. Wang et al. report that the mechanical properties of EPDM, including its tensile strength and elongation at break, reduce negatively exponential over time in an experiment where EPDM was exposed to artificial seawater. A service life of 23 years was calculated for EPDM at fifteen degrees Celcius, considering that a 50 percent elongation at break would be the end of the service life. By roughly extrapolating this to an assumed five percent elongation at break as the operating conditions for the flexible bladder, the service life is expected to be in the hundreds of years due to a negative exponential decline. The decreased mechanical properties were mainly attributed to additives depletion or degrdation. It must be noted that this study is for a particular compound formulation of EPDM. To make a full expectation for its service life, the biotic factors of biodegradation need to be included. In experiments where samples were submerged in the Indian sea, Sudhakar et al. report a two percent decrease of tensile strength and zero elongation at break decrease for Propylene. Moreover, High-Density Polyethylene (HDPE) showed no tensile strength decrease and a three percent elongation decrease (Sudhakar et al., 2007). These are the bulk of materials EPDM consists of (Wikipedia, 2022b). HDPE is taken as a replacement for ethylene in this consideration. This is the closest information that could be retrieved for saying something about the biotic degradation of EPDM. However, for their study, the material was bought at a construction market without specific additives for the marine sector. Nonetheless, the study does not show a significant increase in degradation compared to the artificial seawater experiment. Making the expected service life still in the hundred of years. Any mechanical property decrease due to calcium extraction of mussels can be mitigated by selecting another additive than calcium. Furthermore, to have durable mechanical properties over time, additives highly resistant to biodegradability could be selected.

13 Conclusion

The objective of this project is to determine the extent of surface deterioration and mechanical property decrease of EPDM after exposure to biofouling. Surface deterioration was investigated to find out the integrity 2-millimetre thick flexible bladder considering eventual surface cracks. In addition, strength- and ductility decrease could indicate the lifetime flexible bladders concerning the mechanical operating conditions. Previous studies have shown that steel corrodes heavily in marine environments due to MIC, and that various organisms were stated to directly bore, perforate and delaminate steel. In addition, several non-native species were stated to bore into different materials, including polymers. Direct deterioration of native species attached for at least two months was also expected to affect the surface of EPDM in the test set-up in the harbour. Direct deterioration was also expected lead to results in a decrease in strength and ductility. Biotic degradation by bacteria and fungi was expected to deteriorate the material, as previous studies had shown that polymers had significantly decreased in weight after one year. Biotic- and abiotic degradation were expected to decrease the mechanical properties of EPDM through rupture and degradation of the polymer molecular chain.

For this project, surface deterioration was tested with 3D Optical Profilometer scans. Previous studies weighed the samples without considering the transferral of additives outwards upon immersion, and the water absorption of EPDM. An effective way to remove the biofilm enabling observation of surface profiles is to use a 10% hydrochloric-acid-solution that dissolves the calcareous organisms. No implications of the hydrochloric acid solution on EPDM's surface were found. Strength and ductility were measured with an Universal Testing Machine, according to the ASTM D412 standard commonly used for polymers.

All native species were sampled and showed no sign of direct surface deterioration. It is suspected that the direct deterioration mechanism of barnacles and oysters is based on local accelerated corrosion which is expected to be in vain on EPDM. Moreover, in the absence of surface defects, barnacles cannot delaminate material. One outstanding result is that mussels appear to have deteriorated the material. This was attributed to either chemical degradation of calcium inherent as an additive in EPDM or physical invasion of mussel's byssal thread. The former was considered most likely because previous studies showing mussel byssal thread invasion were not justified well and the pit widths found for the biofouled samples did not match the width of the byssal threads. As for chemical degradation, mussels are known to extract calcium from concrete, leading to dealloying of the material. Such chemical degradation resembles biotic degradation, since one element of the material is used by the organisms. Since other additives can replace calcium, this is not considered a direct deterioration of EPDM. It must be noted that this is an interpretation of the results, which can be confirmed by ESEM. Physical invasion of the mussesls is considered unlikely but can only be definitively rejected after SEM. Effects of biotic degradation were not definitively found in this study. Nevertheless, it is expected to have an impact in the long term because EPDM contains predominantly organic compounds, and organic compounds have a certain degree of biodegradability. The initial values for strength and ductility were unknown and could not be retrieved, so there is no reference for eventual decrease and its magnitude. The additives inherent in EPDM are supposed to have a major influence on the decrease of mechanical properties, so it is recommneded to select additives that are highly resistant to degradation. One quarter of the hypothesis is rejected because there are no signs of direct deterioration. An alternative hypothesis would still include: surface deterioration due to biotic degradation, strength and ductility decrease due to biotic- and abiotic degradation, and no expected signs of corrosion.

Alternative hypothesis: EPDM does not show any sign of corrosion. Direct deterioration by macro organisms does not occur. The direct deterioration mechanisms of Oysters and Barnacles are based on localized accelerated corrosion. The delamination mechanism of Barnacles occurs only when the pits are larger than about 0.2 millimetre. Biotic degradation leads to biodegradability of EPDM and consecutively to surface deterioration, which is significant only after a great amount of time. Biotic-and abiotic degradation lead to a decrease in strength and ductility, with the failure of operating constraints of the flexible bladder after only hundred of years. Transferral and degradation of additives lead to a decrease in strength and ductility, and dealloying contributing to surface deterioration. If additives with high resistance to biodegradation are selected, surface deterioration and mechanical property decrease can be reduced. It must be noted that stress-corrosion cracking and corrosion fatigue due to tensile stress and cyclic stress have not been considered in this hypothesis, although they are expected are have an impact.

So far, the two millimetre thick flexible does not seem to be threatened by surface cracks or mechanical property loss leading to component failure. The research topic might be shifting towards biodegradability and selecting additives with high resistance to biodegradability. A new way to frame the research problem could be to determine which additives are best endurable in marine environments and test the biotic- and abiotic degradation of EPDM with or without these additives. For example, through mimicking a biofilm, using the data on the number of bacteria and fungi present in one, found by, for example, Sudhakar et al., and by increasing the temperature. In this way the degradation process can be accelerated and information is obtained on biotic degradation's long-term effect.

14 Recommendations

In this study several experimental set-up problems were encountered resulting in less exact outcomes. It mainly concerned the initial values of the material that was analysed. Moreover, experience has been gained from which recommendations can be given to improve further studies.

14.1 General Recommendations

- It became clear that additives play a role in the biodeterioration of EPDM. Therefore, additives that endure well in marine conditions could be found. Information can be found about EPDM compound formulations used in the marine sector. Alternatively, an EPDM compound formulation can be chosen that include additives highly resistant to biodegradability.
- Stress-corrosion cracking and corrosion fatigue due to tensile stress and cyclic stress could be taken into account in further studies. In order to find impacts of these phenomena, the biofouled samples could be exposed to tensile stresses that the flexible bladder are subject to. In this way eventual increased cracking of the pits formed by deterioration might be investigated.

14.2 Test Set-Up

- This study helped produce initial values for the EPDM currently in the test set-up in the harbour. Whenever a new test set-up in made, a surface profile- and mechanical property analysis before immersion is recommended to conduct to serve as a reference.
- The test set-up in the harbour is expected not to be exposed to heavy currents thus not accounting for eventual abrasion. A new location could be selected to account for this effect.
- Eventual increased pollution due to boat traffic in the harbour might influence the extent of biofouling found. Therefore, a location more in the open sea might be better. For instance, 30 kilometre for the shore.
- Muthukumar et al. & Sudhakar et al. elaborate on their used methods for test set-ups which might be considered when looking for alternative ways of deploying the test set-up. In short, they use a raft on which they hang coupons at several dozens of kilometre

from the shore. Find the information in the methods section. Appendix E includes more identical studies.

14.3 Experimental Set-Up & Procedure

- To account for any particles transferral outwards upon immersion, a control experiment in plain water can be set-up. In this way the extent of deterioration is measured more exact and extrapolation of the results is possible. Moreover, this would pave the way for accurate immersion testing, which generates another possibility of measuring total material loss.

- A more advanced 3D Optical Profilometer can be sought which speed can handle larger samples making eventual further studies with higher repetitions more bearable and reduces the time if higher experimental repetitions be performed.

- To provide more accurate results, the area under the mean line of the samples can be calculated via Matlab.

- Some tool that can cut through chalk might come in handy during retrieval of further samples of the current test set-up. The amount of macrofoulers grows, so spots without hard chalk become fewer. Moreover, one might need to cut more than needed which would be a waste.

- It is recommended that every two months, the sample is monitored. So that eventual macro-fouler colonies can be dated.

- With ESEM, the element composition change inside the EPDM can be observed. An ESEM experiment could point to whether element degradation happens after biofouling and consecutively what the extent of is.

- To achieve appropriate statistical significance, more EPDM test set-ups could be deployed to have sufficient material for repetitions. Roughly speaking, target areas of 6 by 6 millimetre were used as one repetitions in this experiment. Three to four repetitions were performed per interest group. To achieve experimental statistical significance, the experiment should be repeated at least three to four times. For one interest group, for example mussels, 10 by 10 centimetre would be needed for one experiment at a given time. Thus, if one were to repeat the experiment periodically for all interest groups, more test set-ups might be useful

- It is recommended to use an alcohol such as 70% Ethanol or Isopropanol to as surface contiminants removal technique before 3D Optical Profilometry experiments. EPDM is highly resistant to both (Guide, 2021).

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Appendices

A Output Examples 3D Optical Profilometer

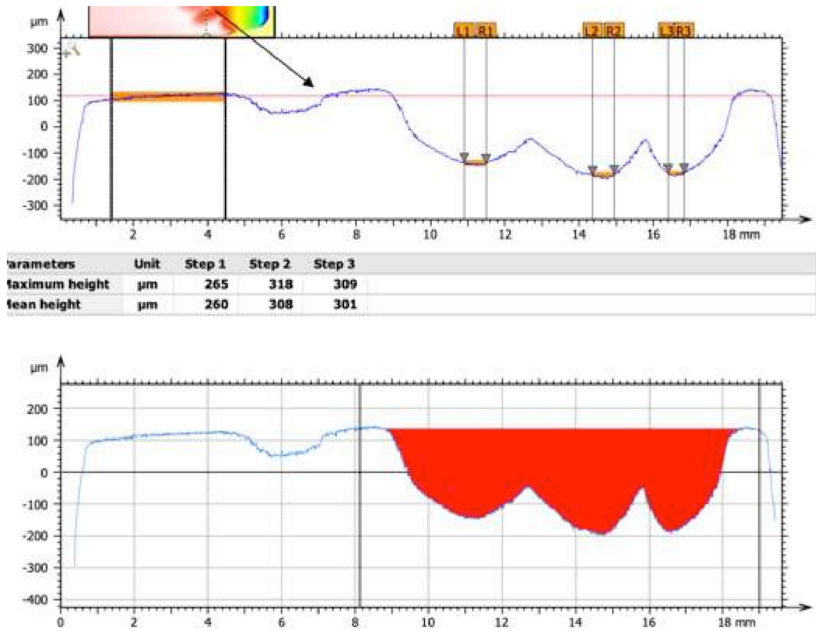


Figure .1: Output Graphs of 3D Optical Profilometry (Li et al., 2015).

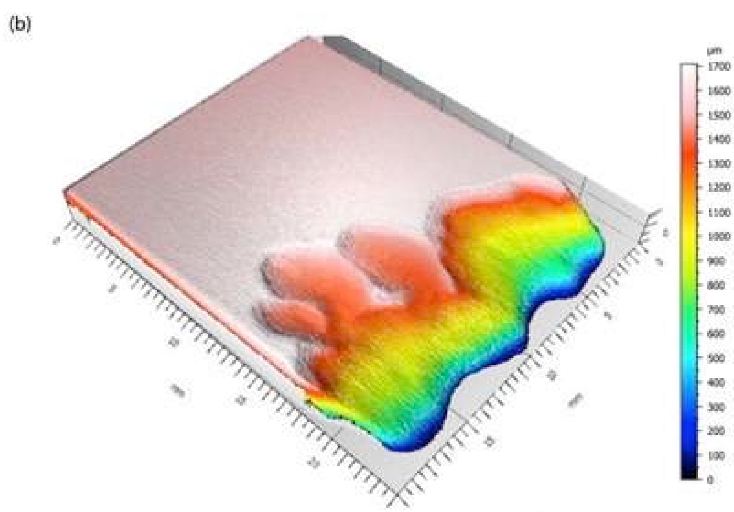
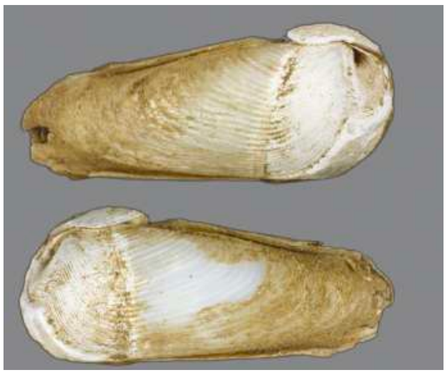


Figure .2: 3D False Color View of a Sample (Li et al., 2015).

B ASTM D412

- https://www.instron.com/en/testing-solutions/by-standard/astm/astm-d412

C Pholad and Teredine Borers



(a) Martesia

(b) Lyrodis

(c) Teredo

Figure .3: Pholad and teredine borers. Martesia(a), Lyrodis(b) and Teredo(c) (Wikipedia, 2022c) (Wikipedia, 2022e)

D Adhesion Mechanism Mussels

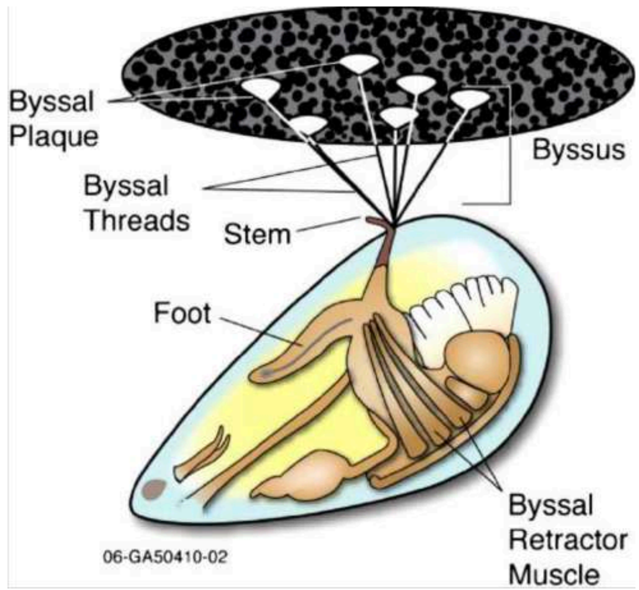


Figure .4: The byssal threads and byssal plaques (Silverman and Roberto, 2007)

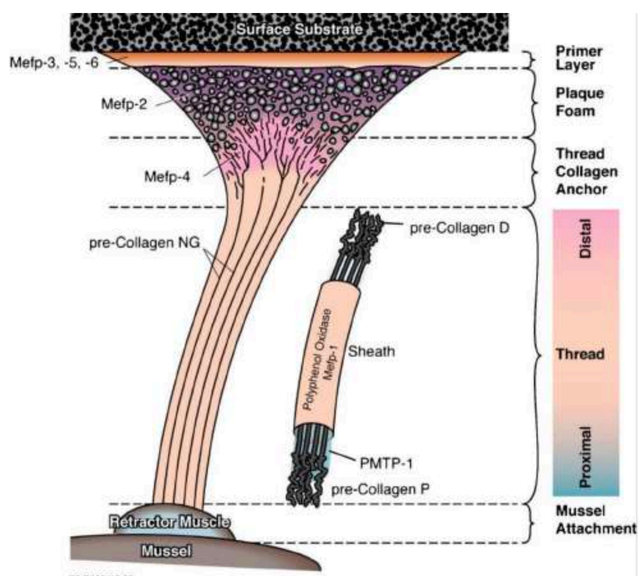


Figure .5: A byssal thread (Silverman and Roberto, 2007)

E Test Library

- https://www.sciencedirect.com/science/article/pii/S0010938X17307837
- https://www.researchgate.net/publication/225103868_Fouling_and_Degradation_of_Polycarbonate_in_Seawater_Field_and_Lab_Studies
- https://www.researchgate.net/publication/225274316_Effect_of_Biofouling_on_Stability_of_Polycarbonate_in_Tropical_Seawater
- https://www.sciencedirect.com/science/article/pii/S0141391007001267
- https://www.sciencedirect.com/science/article/pii/S0141391010003113
- https://www.sciencedirect.com/science/article/pii/S0964830510002052

F Instruments not chosen

Optical Microscopy & Scanning Electron Microscopy

Optical microscopy and Scanning Electron Microscopy (SEM) are two microscopy methods for taking zoomed-in images of samples down to the nanometer. Optical microscopes use visible light and an array of lenses to obtain magnified images of samples. SEM produces images of samples using an electron beam, which interacts with atoms in the sample to generate signals that contain information about the topography of the surface. The output images from these microscopes can be displayed on a computer screen to examine the sample. Both instruments can capture dimensions from nanometers to millimeters. The instruments record a portion of the sample and take images of a target area. To analyze complete samples, multiple images of target areas can be sketched side by side. This method is not chosen because it is less effective for quantifying information about possible pits. However, this method is perfect for determining whether pits are present at all, and is recommended to be used in further experiments.

Energy Dispersive X-ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDS) emits X-rays onto the sample. Signals are returned from the sample that contain energy characteristics. Since each element has a specific energy characteristic, the chemical composition of a sample can be identified. The technique is used to determine the chemical composition of the corrosive layer on top of the sample. However, it is not applicable to determine the degree of deterioration of a sample, and is therefore not chosen in this project.

Immersion Testing

Immersion testing weights a material before and after exposure to corroding environments. The weight loss is recorded, which can be transferred to the amount of corrosion. This is done with the use of the following formula:

$$\frac{KW}{atd} \tag{1}$$

K = a constant with the value $8.76e^4$ (for the units mm/y)

W = weight loss (g)

d = the density of a material (g/cm^3)

a = exposed area of the coupon (cm^2)

t = exposure time (hours)

However, elastomers absorb an amount of the liquids that they come into contact with, particularly organic liquids(Ahmad et al., 2010). This may result in swelling, and it is recommended to not use material that absorb water for immersion testing. Furthermore, immersion testing could lead to fine particles in the compound of the EPDM to move outwards of the material, as reported by (Wang et al., 2020), which decreases the weight of EPDM.

Coupon Testing

For coupon testing, coupons of the material are put in a polyethelyne or glass chamber along with nutrient-enriched seawater. The temperature in such chambers could be altered to see material endurance at different temperatures. The set-up of such an experiment can be seen in figure .6.

The drawback of this method is that it solely looks at the effect of corrosion on a material, as the nutrient-enriched seawater includes micro-organisms but no macro-organisms, and therefore the effect of macrodeterioration is excluded. This method is therefore not be used for this project.

Figure .6: Coupon Testing Set-Up (Canning, 2020)

A study in which such coupon testing has been performed, can be found in section 3.3.2.(Wang et al., 2020)

Spray/Fog Testing

Spray or Fog testing is based on spraying or fogging a 5% NaCl solution on material over time to see whether a material corrodes. The time that samples resist against this environment is the criterion for their durability. Similarly to coupon testing, it excludes the effect of macro fouling. Therefore, this method is not opted for this project.

Visual Examination

The amount of deterioration could be examined visually. The number of pits and their pit depths could be manually counted and measured with gages, respectively. Another option of visual examination would be to use a magnifying glass. However, The dimensions sought for in this project range from millimetres to micrometres. Thus, visual examination is not precise enough.

Optical Coherence Tomography

Optical Coherence Tomography(OCT) can make images through a layer. It provides similar 3D models as 3D Optical Profilometry. The biofouling layer may be a maximum of 2mm thick for the OCT to work. However, OCT is mainly used to make biofilm images and not examine the material under the biofilm.

G Cleaning- and Surface Contamination Removal Techniques not chosen

Cleaning techniques not chosen were the following. Water-jet cleaning :138, 276, 827, 1655 kPa, would possibly destroy material as pits, cracks and crevices could have depleted the material properties of the EPDM to an unknown degree. Therefore it was unsure whether the material could handle these pressures. Furthermore, it could have caused abrasion. Scrubbing with a sponge would have caused abrasion of the material as the macrofoulers are attached strongly via cementeous layers.

Alcohol could be used for further experiments. One chemical was already used, and chemicals in combination could harm the material Guide (2021), which would have needed two more control experiments, which would have taken too much time for this thesis. Contaminants including bacteria could still have been on the sample. It is advised to do this in future experiments, as it effectively removes surface contaminants. 70% Ethanol and Isopropanol and effective alcohols to remove surface contaminants. EPDM is highly resistant to both (Guide, 2021).

H Enlarged 3D Optical Profilometer Scans

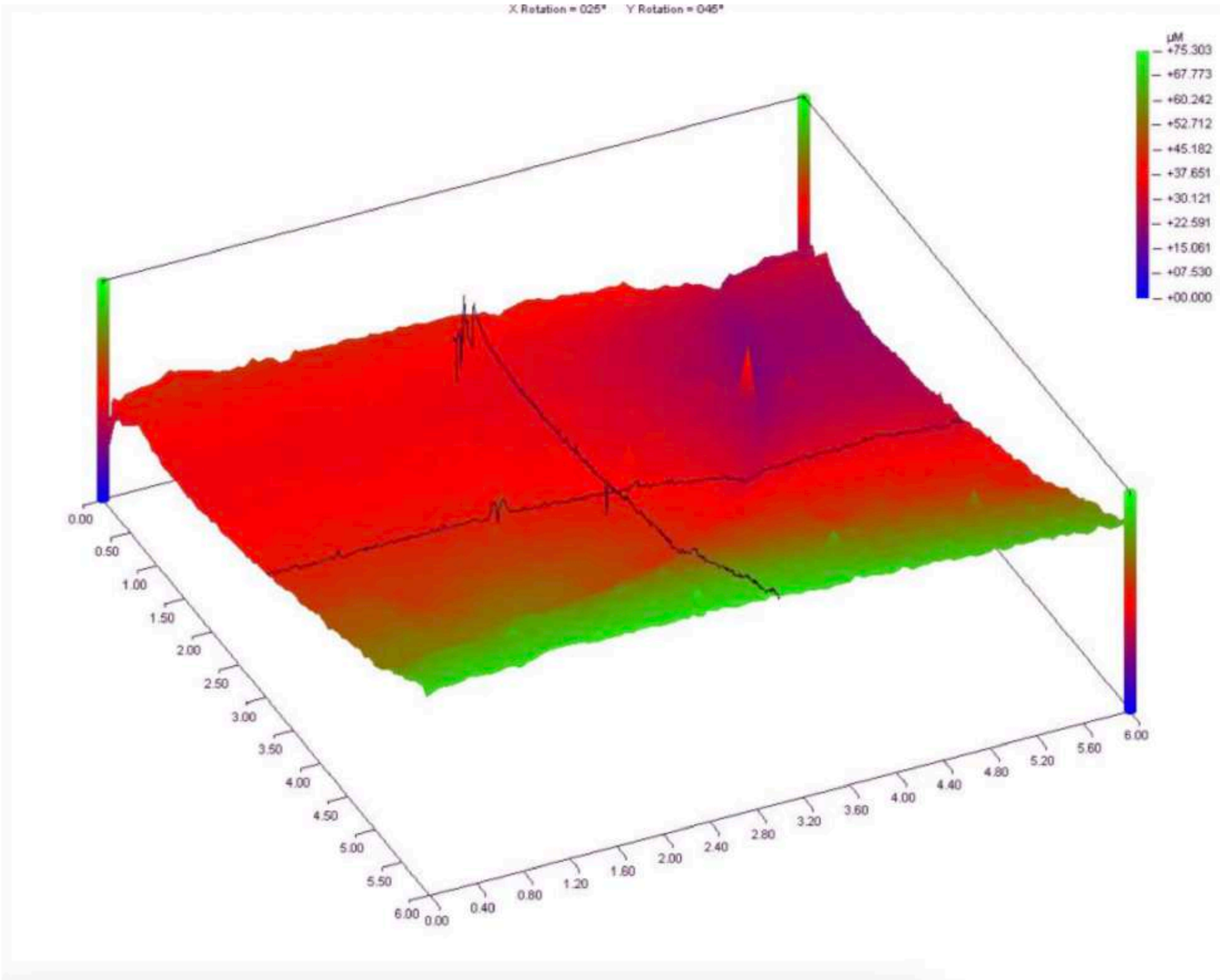


Figure .7: Control EPDM

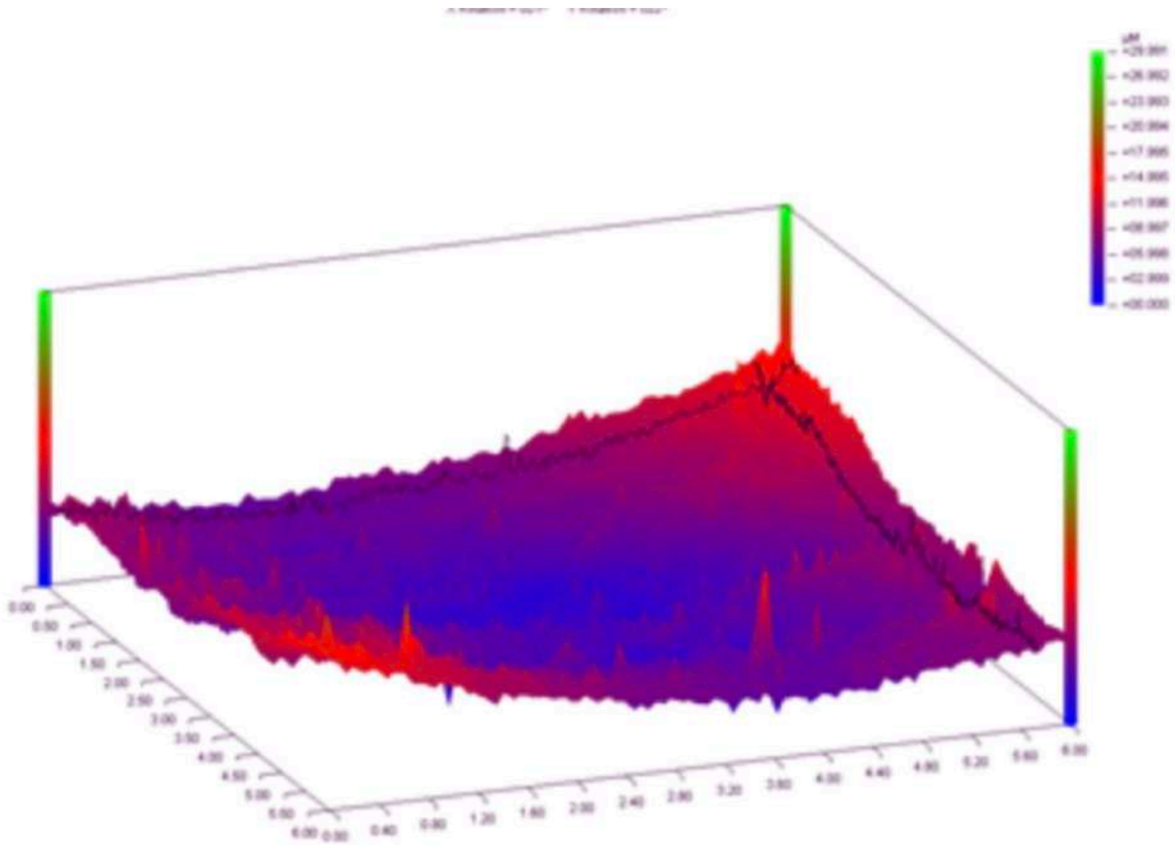


Figure .8: Control EPDM HCL

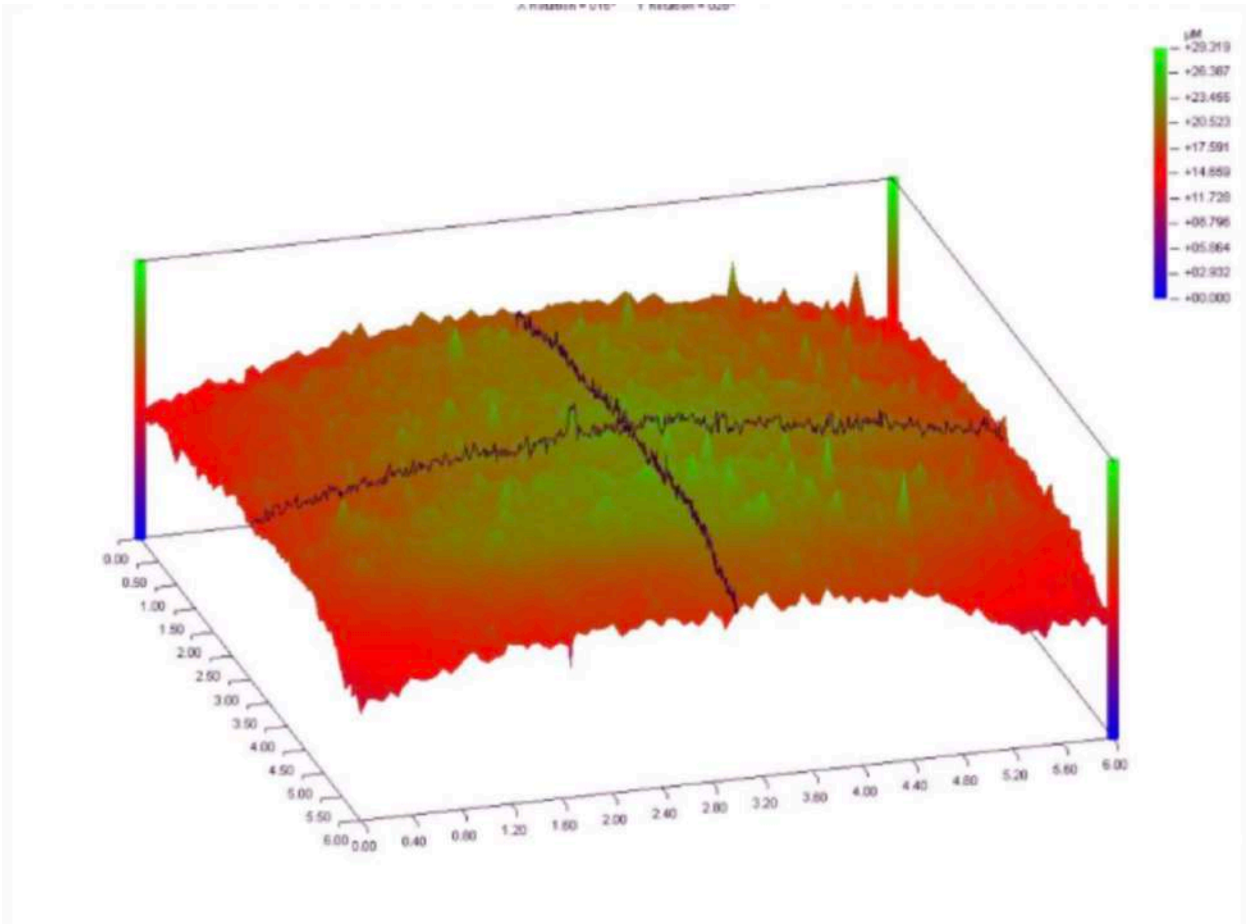


Figure .9: Control EPDM Water

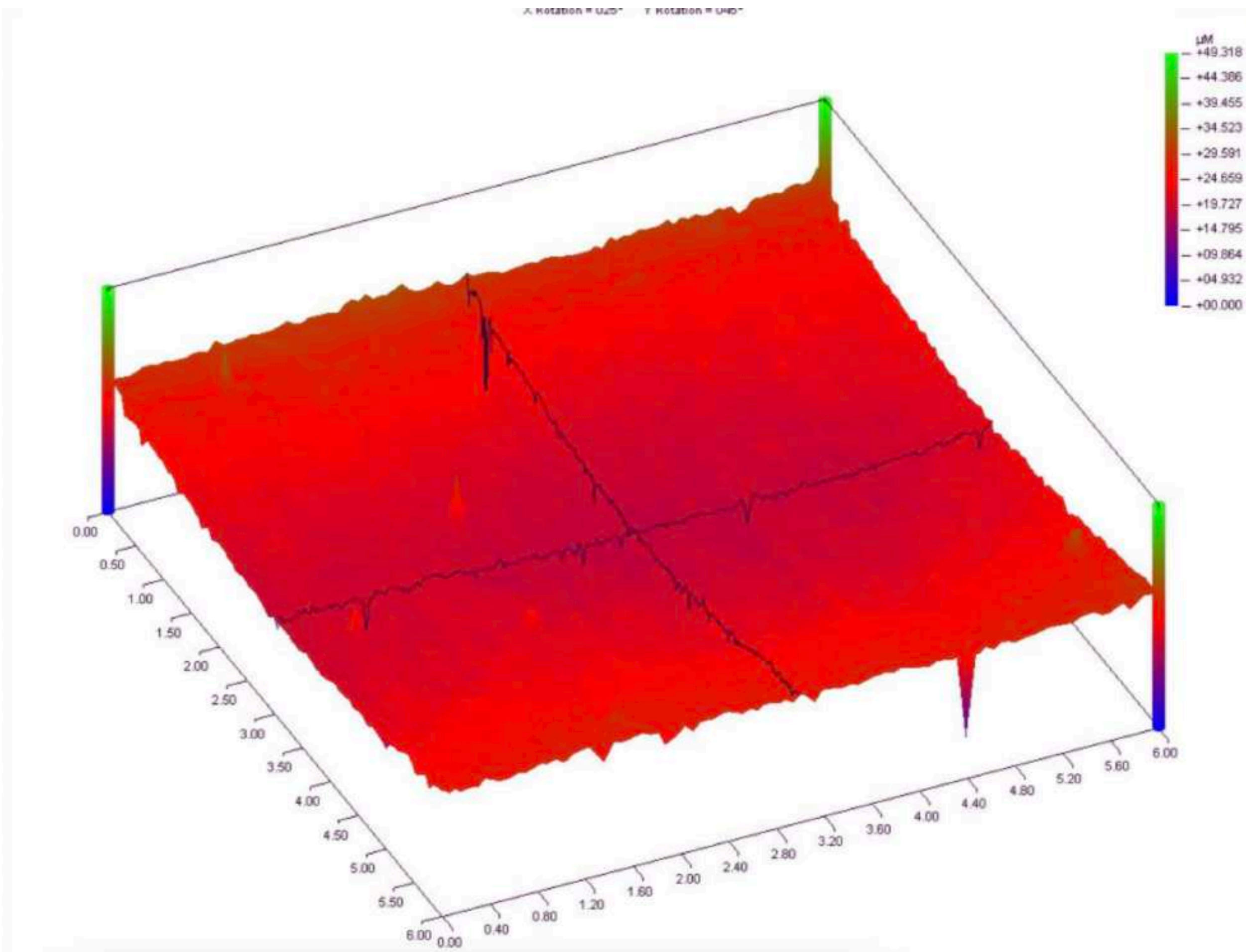


Figure .10: Biofouled sample- No animals

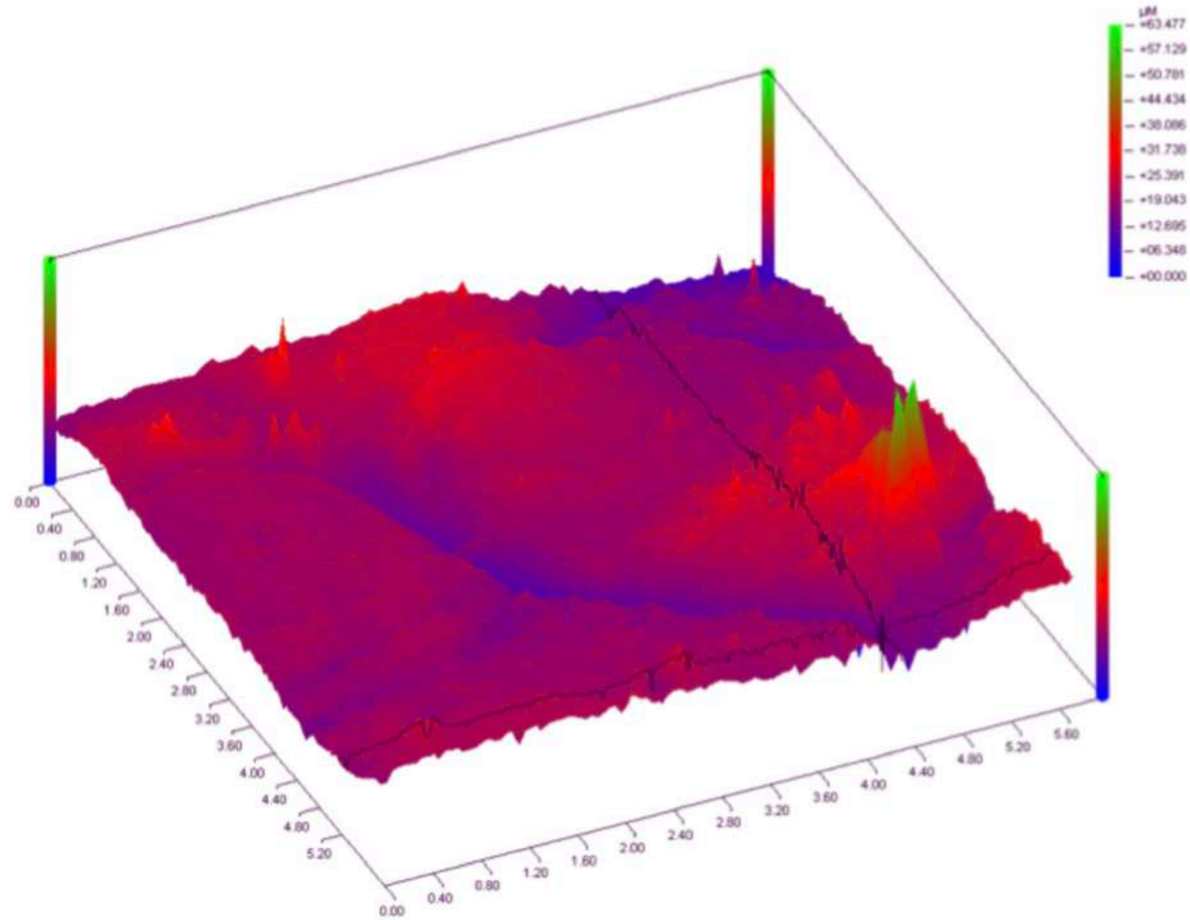


Figure .11: Biofouled sample- Barnacles

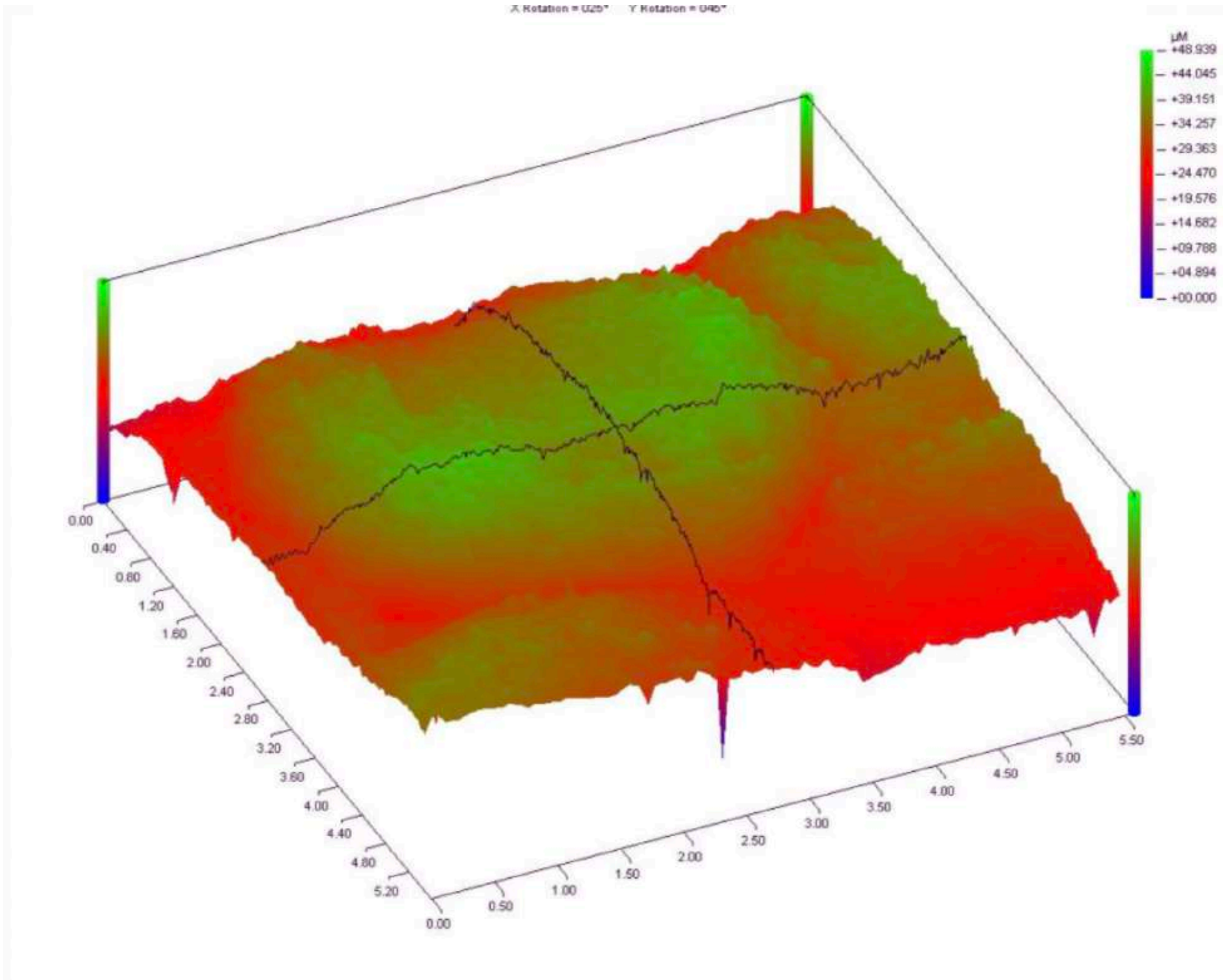


Figure .12: Biofouled sample- Mussels

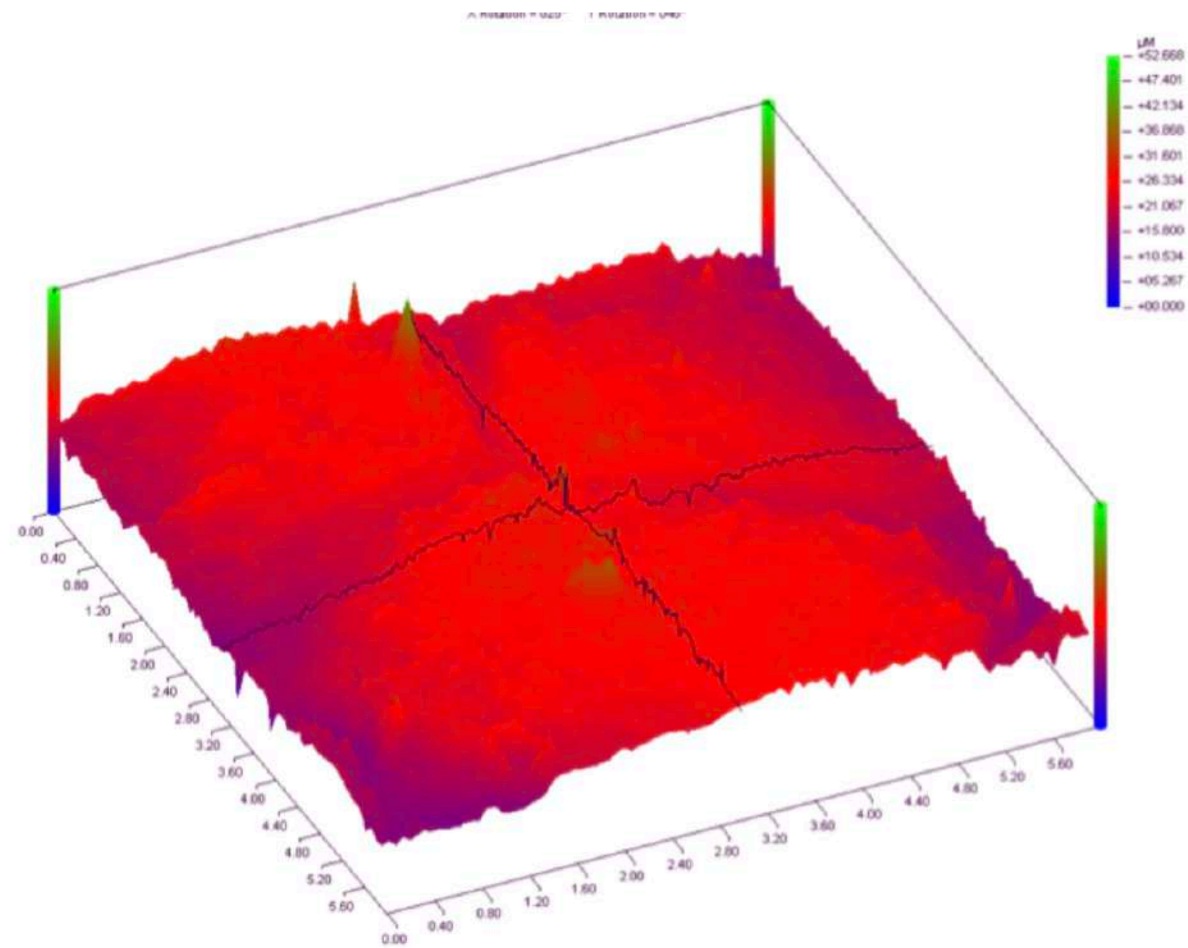


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Figure .13: Biofouled sample- Oysters

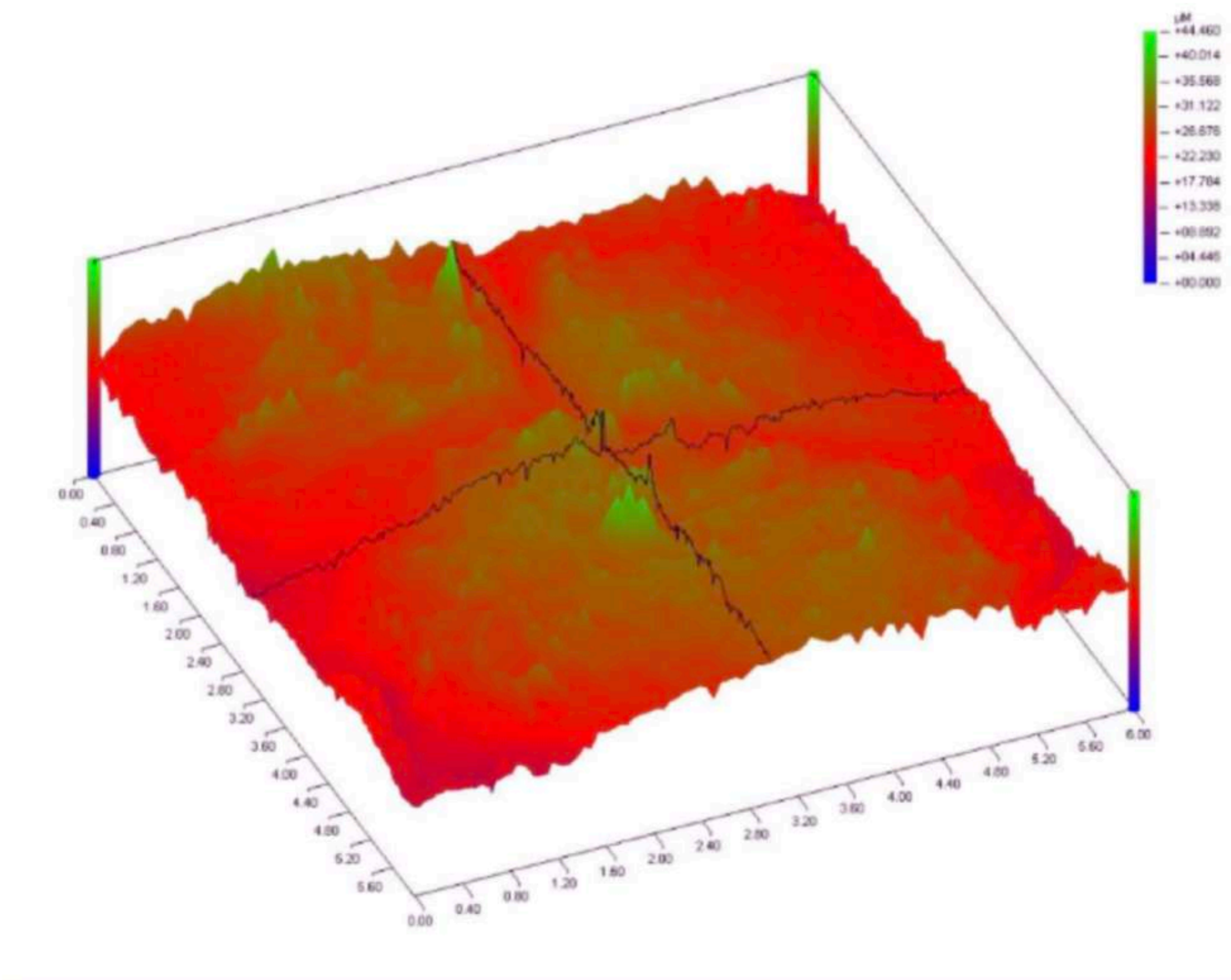

Figure .14: Biofouled sample- Bryozoan

I Enlarged Photo-monitoring

Figure .15: Front-view enlarged

Figure .16: Back-view enlarged