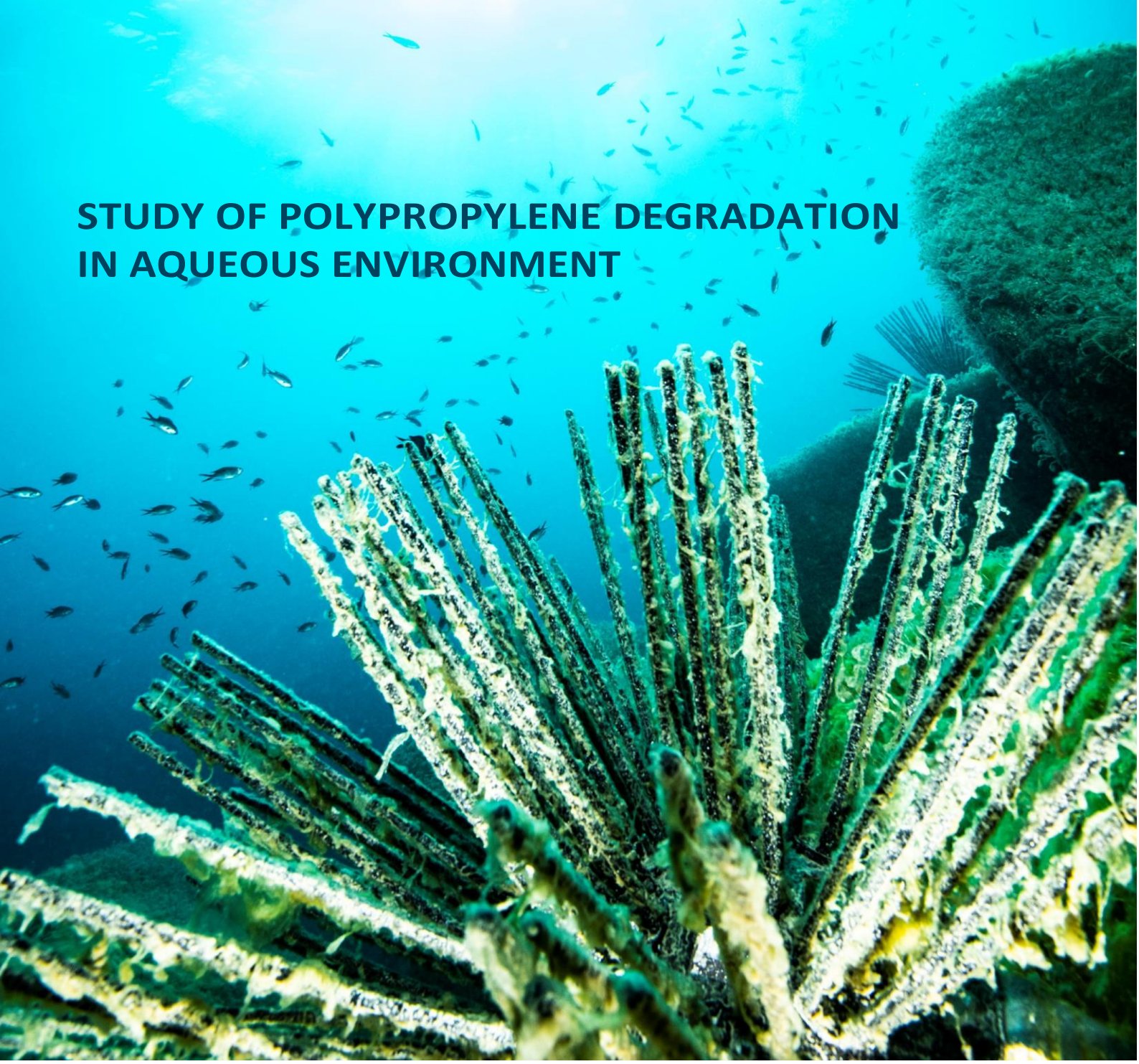# MASTER THESIS

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Arthur Waldmann

SEABOOST

STUDY OF POLYPROPYLENE DEGRADATION IN AQUEOUS ENVIRONMENT

Study of polypropylene degradation in aqueous environment

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Abstract

Plastic waste in sea, originating from common synthetic polymers, is a major contemporary environmental concern. Even though degradation mechanisms of plastics in sea have already been studied and described, there is still more to be discovered about the resilience of many of the widely used polymers. Polyamide (PA), polyethylene (PE), and polypropylene (PP) account for 80.7 % of ocean plastics pollution (1). This document presents an experimental study on the degradation of PP immersed in seawater. Filament shaped samples were aged for a time varying from one to seven years in 3 different locations around the French coast. The samples were subjected to mechanical, morphological, and chemical analysis through traction tests, scanning electron microscopy (SEM) and infrared spectroscopy and compared to a suitable control reference, that is, an unaged PP sample. The study focused on three degradation factors that are hydrolysis, sediment abrasion, and UV alterations. The role that microbial colonization may play in the degradation of the polymer by biofouling is also discussed. Results shows that PP is strongly durable in sea environment. While some surface degradation can be seen by SEM, the mechanical properties were not markedly altered. At times, even a 20% increase in Young's modulus was observed after seven years in immersion. No chemical alterations were observed with IR spectroscopy but a more thorough study with MALDI-TOF analysis was suggested for the future to study degradation more in detail. An experimental protocol was also suggested in order to create a model for an in vitro accelerated ageing of polymers while reproducing a natural degradation environment. In a more applied context that triggered the research in this thesis, the results yielded important knowledge on how man-made plastic systems in sea can withstand natural conditions under prolonged time spans. Such systems include Roselière : PP strands attached to a strap that are introduced to coastal regions to protect native seagrass populations from hydrodynamic fluxes and provide shelter for juvenile fishes.

Keywords   Aqueous, Biodegradation, Degradation factors, Polymers, Polypropylene, Pollution, Protocol, Sea, Water.

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Preface

I want to thank my academic supervisor Dr. Eero Kontturi for its continuous guidance during these six months full of twists and turns.

I also address my gratitude to my advisor Mr. Alexandre Musnier and Seaboost for having me during my internship and transmitting me their passion for the marine biodiversity. I also want to thank the others interns for all the good times we had.

Finally, thank you to all my friends and family for supporting me this whole time.

Montpellier, 26 July 2022
Arthur Waldmann

Symbols and abbreviations

Symbols

E   Young's modulus
ε   Strain to rupture
σ   Stress to rupture

Abbreviations

ASTM	American Society for Testing and Materials
DDT	Dichlorodiphenyltrichloroethane
CH_4	Methane
CO_2	Carbon dioxide
ESS	Ecosystem services
GPA	Gigapascal
HALS	Hindered amine light stabilizers
HDPE	High density polyethylene
H_2O	Water
IR	Infrared light
ISO	International Standard Organization
LDPE	Low density polyethylene
MALDI-TOF	Matrix Assisted Laser Desorption Ionization - Time of Flight
NGOs	Non-governmental organizations
MPa	Megapascal
N_2	Dinitrogen
PA6	Polyamide 6
PA11	Polyamide 11
PBT	Persistent bio-accumulative
PCBs	Polychlorinated byphenyls
PCL	Polycaprolactone
PE	Polyethylene
PET	Polyethylene terephthalate
PHB	Polyhydroxybutyrate
PLA	Polylactide acid
PNMBA	Parc Naturel Marin du Bassin d'Arcachon (Marine Natural Park of the Bay of Arcachon)
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
RESTCOAST	Large scale RESToration of COASTal ecosystems through rivers to sea connectivity
SEM	Scanning electron microscope
T_g	Glass temperature
THC	Thermohaline circulation

UHMWPE	Ultra-high molecular weight polyethylene
UV	Ultraviolet light
-C = O	Carbonyl bond
-CO$_2$	Carboxyl group

I. Introduction

This study takes place within the frame of the research for the European project *RESTCOAST*. This document will explain how the experiments presented here have supported *Seaboost* actions, a French subsidiary company of the EGIS group, one of the actors of the project.

a. Project *RESTCOAST*

Project *RESTCOAST* (Large scale RESToration of COASTal ecosystems through rivers to sea connectivity) is a European project financed by the Green Deal, carried by a consortium uniting 40 actors including universities, laboratories, associations, and companies for the restoration and/or preservation of the European coastal environment. The project representing an investment of 18.5 million €, largely financed by the EU (17.8 M€) started on the 1st of October 2021 for a period of 54 months. The RESTCOAST project aims at evaluating ecosystem services (ESS) of sea grass beds, wetlands, and coastal dunes in order to reduce risks of erosion and flooding while enhancing the biodiversity and the blue carbon (carbon stored in coastal and marine environment). ESS defines any value brought by ecosystems to humans. It can be carbon storage, food supply, coastal protection, natural intrinsic fertilizing…, applied to a specific biome like a mangrove, a forest, or a river. RESTCOAST will develop a river-coast connectivity at large scale and will enlarge habitat spaces in proximity of shores in order to furnish resilient coastal ESS.

RESTCOAST leads nine pilot projects within the main seas of European Union (Baltic Sea, Black Sea, Northern Sea, Atlantic Ocean, and Mediterranean Sea).

Seaboost is in charge of one of these nine pilot projects which is located on the North-East coast of the Atlantic Ocean in the Bay of Arcachon. This pilot project concern Seaboost and the PNMBA (Marine Natural Park of the Bay of Arcachon).

The pilot project is tackling the issue of two sea grass species of the eelgrass family (*Zostera Marina* and *Zostera Noltii*) illustrated on Figure 1, being largely destroyed within the Bay of Arcachon. The continuous degradation of the Eelgrass habitat is in the heart of the problem, cascading into multiple issues such as the acceleration of erosion phenomenon and the
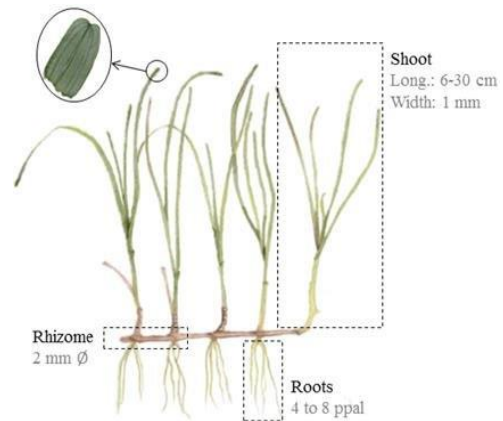

Figure 1 : Zostera illustration

augmentation of turbidity preventing photosynthesis leading to the degradation of the local biodiversity (including the Eelgrass population). Indeed, eelgrass is a natural solution for the attenuation of hydraulic fluids and wildlife habitats. The eelgrass population in the Bay of Arcachon used to be in a stable state with its environment, being an ecosystem engineer and a foundation specie. Many kelp species are foundation species and autogenic ecosystem engineers that create and maintain entire ecosystems (2,3). They structure marine communities by forming dense forests (4), that many species depend on for food and habitat (5) and thereby provide services that are vital for the functioning of the ecosystem (6). Like other seagrass species, it attaches to the soil by roots that are also able to take up nutrients. Too powerful hydraulic fluxes results in an uprooting of the plant.

Eelgrasses used to be settled on the sides of subaquatic channels on the bay of Arcachon as shown on Figure 2. Those marine angiosperms were helping canalizing hydraulic fluxes through the natural channels, highly reducing fluxes on the other parts of the bay, where the sea grass was thriving. Due to contamination (pollution) and heat wave incidents that emphasized contamination effects, the rows of Eelgrass

at the proximity of the channels degraded and disappeared. From that point onward, the fluxes were not efficiently contained in the channels. By snowball effect, the eelgrasses from previously protected areas suffered too strong hydraulic fluxes that uprooted them row by row. Eventually, the habitat of eelgrass drastically reduced as shown on Figure 3.
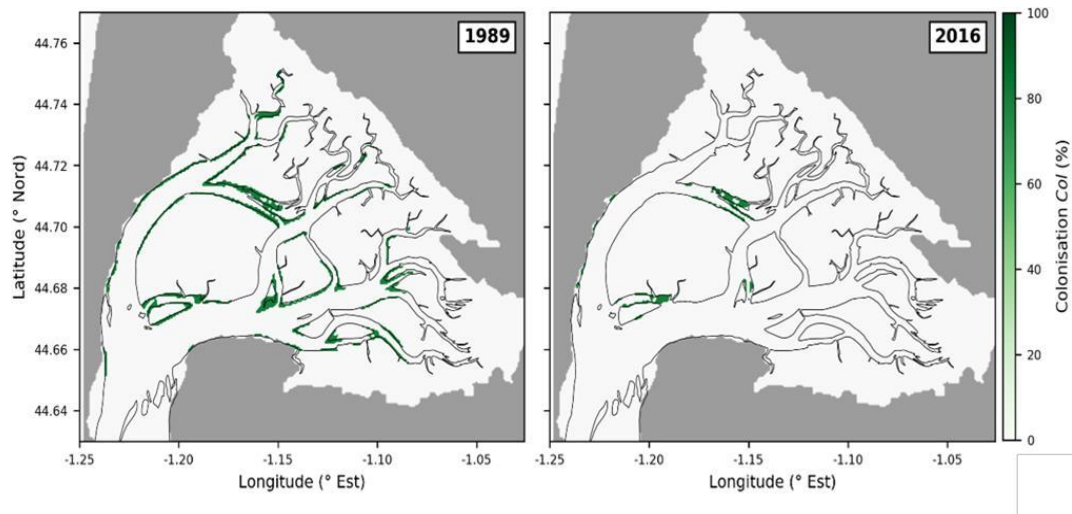

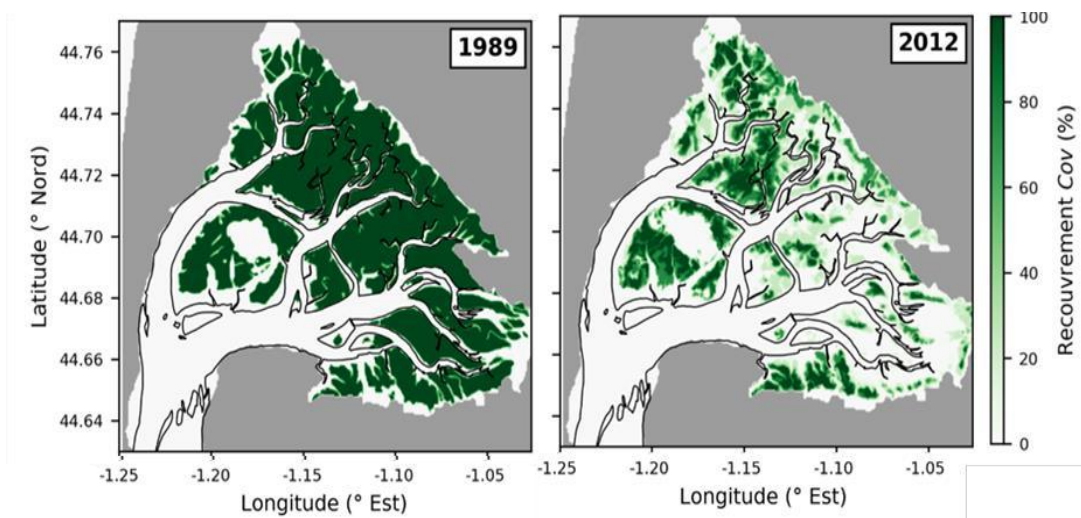*Figure 2 : Comparison of Zostera population in the Arcachon bay along the channels between 1989 and 2016*

Figure 3 : Comparison of the Zostera population in the Arcachon bay between 1989 and 2016

While the overall population of sea grass decreased, fluxes were not slowed anymore which caused large movements of sediments. It created an enhanced turbidity, detrimental for biodiversity and partly damaged the channels. Those channels are essential to boats transiting between the coast and the ocean. Nowadays, they need to regularly be dredged in order to maintain those transport lines for boats. Recreating the eelgrass population to limit the hydraulic fluxes would annihilate all the cascaded issues caused by contamination and heat waves.

Of course, the problem will persist if the contaminant environment remains the same. Fortunately, throughout the years, the bay of Arcachon deployed an important number of measures to control pollution within the bay, diminishing the overall contaminant content. Therefore, it is acceptable to believe that freshly grown Eelgrass will persist and thrive in this restored environment.

b. Seaboost approach, ecological engineering

As an actor of the RESTCOAST project and leader of one of the pilot projects, Seaboost tackles the problematics using ecological engineering.

Ecological engineering is a type of engineering which needs to be completely described in order to fully understand the frame of work of the company, the objectives and the constraints of the Roselière.

Ecological engineering is not only considering ecology within engineering development. It is the development of engineering around the ecological problematics. Because of this definition, ecological engineering embodies a large spectrum of purposes. It can be distinguished by area of application (sea, air, land, mountain, river…), by functionality (habitat, pressure deport, rehabilitation, capping…) or even by the species targeted (juvenile fishes, salmon, wolves, Posidonia, trees…). Figure 4 illustrates this definition.
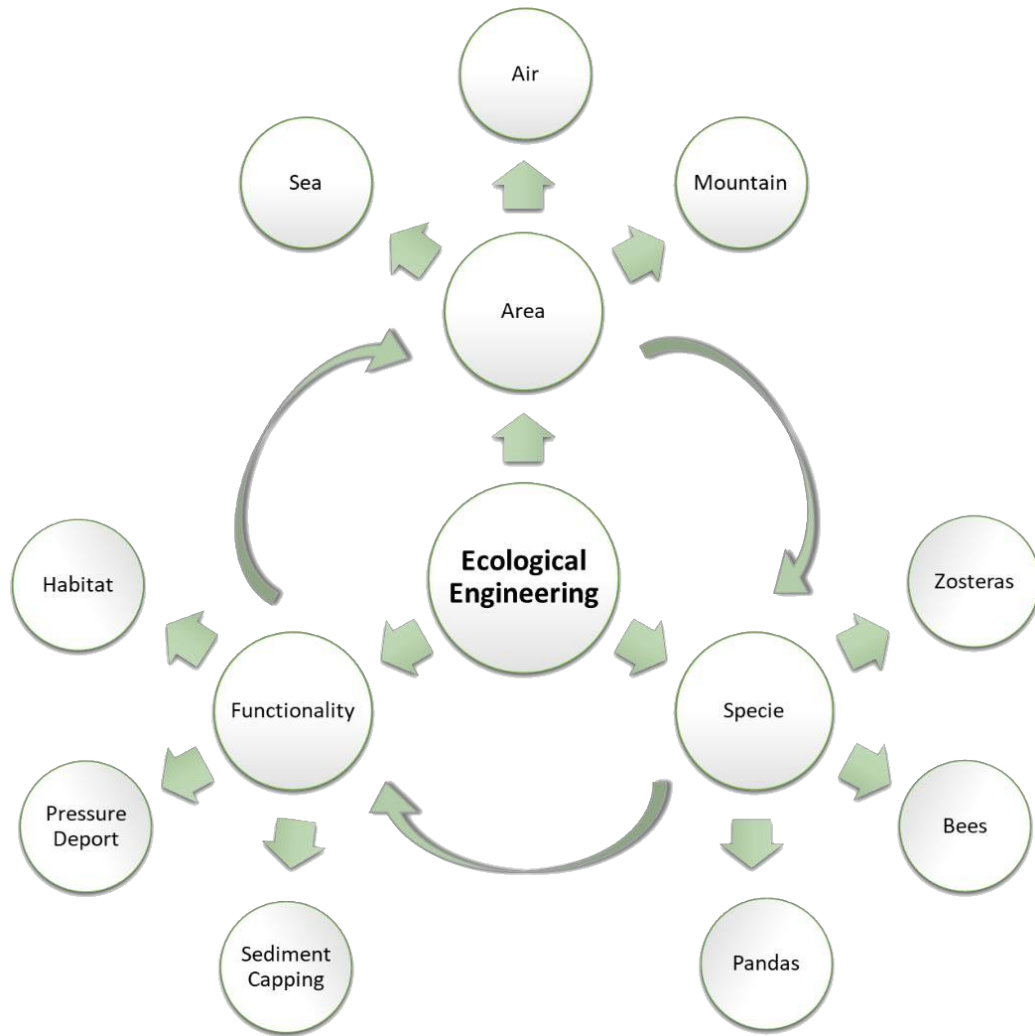
Figure 4 : Ecological engineering aspects

Another critical point about ecological engineering is that any project aiming at restoring a biodiversity, must not only provide resources for the biodiversity to thrive again. It also has to remove the pressures that led to the critical situation, otherwise, the project will eventually fail because the remaining pressures that initially destroyed the local ecosystem will have the same effect on the freshly restored ecosystem.

Seaboost solution, the *Roselière*

As an actor of *RESTCOAST*, *Seaboost* is taking its part by developing an ecological solution to lower the hydrodynamic fluxes in order to protect the eelgrass population and prevent its uprooting. Seaboost is coming up with a bio-mimetic solution consisting in the implementation of artificial seagrass at critical points. Those strategic locations are at the front line of degradation of the eelgrass where water currents are the strongest because no eelgrass population have reduced it and along the natural channels of the bay. The solution is called the *Roselière* illustrated on Figure 5 and is composed of polymer strands attached to a strap. It is a soft solution for the attenuation of swelling phenomenon.
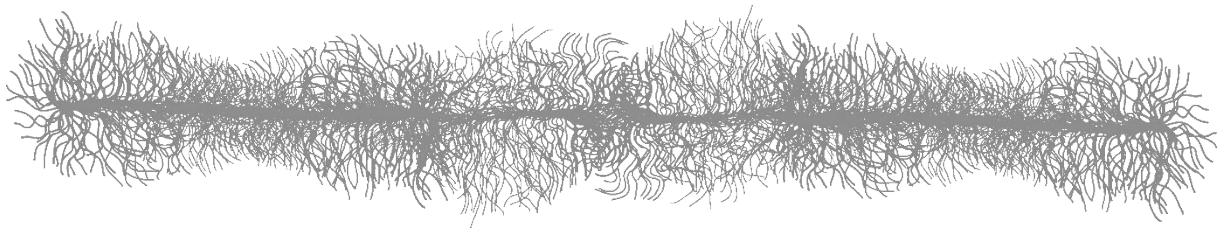
Figure 5 : Roselière illustration

Considering the multiple aspects of ecological engineering, a product like the Roselière can be described in multiple ways : for water environment (area of application), serving for habitat and swell reduction purposes (functionality). The habitat can serve as a nursery for multiple species of juvenile fishes while the swell attenuation can provide a protection against erosion as well as a shield for eelgrass (species targeted). Figure 6 shows the ecological engineering functions of such module.
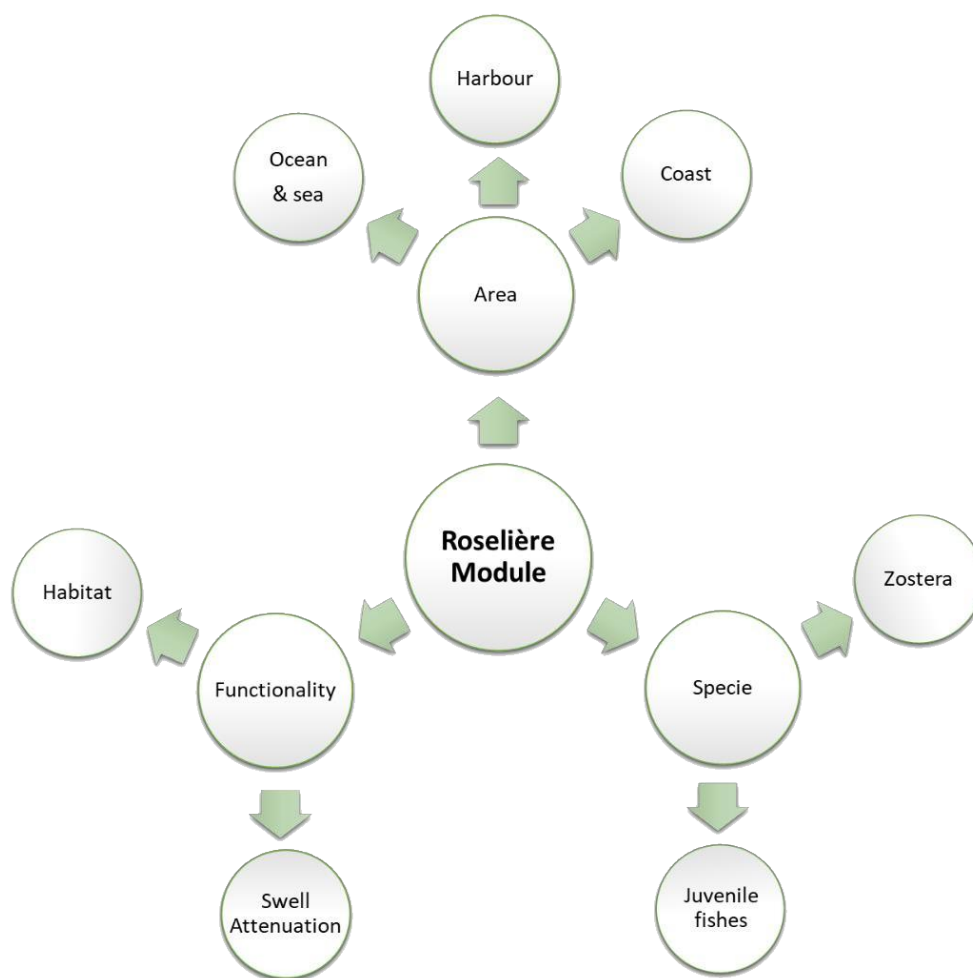
Figure 6 : Roselière engineering purposes

The pilot project aims at protecting eelgrass population of the Bay of Arcachon from the swells, tearing out the roots of the sea grass. Here, the Roselière serves not a habitat purpose but is used to reduce hydraulic fluxes with the specific objective of protecting the sea grass so it can develop and reconquer all the living area they used to thrive in. Here, the mission's objective is the rehabilitation of an ecosystem. A rehabilitation of an ecosystem implies to repair a single ecological function of a biome (opposed to restauration which imply to repair all ecological functions of a biome). In our case, the addressed function is the erosion protection by the eelgrass population.

Seaboost is, through the development of solutions like the Roselière, applying the principles of ecological engineering. The solution answering the problem has been

thought and design around an ecological approach. Therefore, apart from the efficiency of such installation for reducing hydrodynamic fluxes that need to be verified through prototype in-situ testing, *Seaboost* is facing additional constraints proper to maritime ecological engineering that will be described below within the Specification section. Figure 7 illustrates the potential use of Roselières in harbor and coast application.

Figure 7 : Illustration of Roselière module used as harbor covering (left) and pontoon complexification (right)

d. Specifications

The ecological engineering aspect provides 3 criteria defining the backbone of the specifications :

- **Feasibility :**
    - Technical feasibility : Is it manufacturable ? Is it possible to deploy it in the water ?
    - Legal/Administrative feasibility : Artificialization of marine areas is strictly controlled by the French government. Legally, only 1% of the surface of a protected area can be artificialized. Is it possible to obtain

the accreditations at all scales (European, National, Regional, Departmental Communal) for putting artificial product at sea ? Local non-governmental organizations (NGOs) can also be opposed to such a project and put pressure on the administrative side of the project.

- o Economic feasibility : Simple but essential, is it economically viable ?

- o In situ management : If ever your product is placed at sea, is there any maintenance to do ? And if so, is it doable ? How does your product age ? Will it be detrimental for the environment as it degrades ? If necessary, how do you take it out of the water ?

- **Efficiency :**
  - o At short term : How fast the solution is going to impact the environment ?
  - o At long term : It is the most important factor for the efficiency. It answers the question whether or not the solution is going to fulfill its mission. Long term efficiency is also the hard to measure because it usually takes years to observe differences on the biodiversity. Even if the short-term efficiency is high, nothing assures that this efficiency will be maintain through the years so it is always essential to monitor progression on the area where solutions are implemented.

- **Equivalence :** of the restituted ecological functions.
  - o Does the solution provides equivalent ecological functions ?
  - o If the destruction of sediment habitats for fishes are compensated with artificial habitats of different nature like rock our concrete habitats that, will we retrieve the lost population ?
  - o Are we going to help the targeted specie at all or is it going to be colonized by some others ? It is always necessary to proceed to

biological studies before and/or during developing ecological solutions to consider this aspect.

For the *Roselière* to be implemented at a large scale for attenuating swells and other hydrodynamic fluxes, the low environmental footprints of the production and the end of life, as well as the non-toxicity of the solution needs to be proven.

The large-scale deployments of *Roselières* do not only require efficient swell attenuation and environmental considerations. There are also economic, environmental, and industrial constraints that needs to be taken in account during the development process.

e. Study objectives

This study aims at analyzing and characterizing polypropylene Roselières immersed in seawater for various amount of time. It will characterize the evolution (degradation) of the mechanical, structural, and chemical properties of samples collected at three distinct locations on the coasts of France.

Its purpose is to support the development of ecological solutions for the restoration of the marine environment by furnishing a solid empiric basis for the development of the updated version of the *Roselière* of *Seaboost*. This product will have a durable behavior in marine environment and will additionally ensure a non-toxicity for the marine wildlife during its lifetime. Finally, the *Roselière* will have, from cradle to grave, a carbon footprint as low as possible.

II.   Literature review

a.   Plastic at sea

Plastic pollution in seas and oceans has been first noticed in the early 1970s by scientists from the National Academy of Sciences studying plankton. Despite the fact that synthetic plastics had already been invented 100 years ago, its utilization massively increased after World War II and even more after the invention of the first plastic bottle made out of polyvinyl chloride (PVC) in 1963, first commercialized in 1969 in the United States. Soon after, it was discovered that plastic does not disintegrate in oceans but it breaks down to the state of microplastic as it was observed that seabirds were ingesting plastic (7,8). Since then, plastic has completely taken over oceans and seas to the point that plastic waste is retrieved from the most remote and isolated waters across the globe. This is due to the fact that plastic waste drifts away at the discretion of oceanic fluxes and currents. Moreover, because of gyres, plastic pollution naturally tends to regroup in what is called Garbage Patches. Oceanic gyres are large rotating current systems formed by predominant winds and currents. It is created by Earth's rotation forces, more particularly by Coriolis effect. There are 5 major oceanic gyres across the globe. There are a total of 5 major Garbage Patches across the globe : North and South Pacific, North and South Atlantic and Indian Ocean. Their location is displayed on Figure 9. The largest of all is the North Pacific one, commonly called the "Great Pacific Garbage Patch" illustrated by Figure 8. It spreads over 1.6 million km², the equivalent of 4.5 times the German territory (9). Its center, located at equidistance to California and the

Figure 8 : Great Pacific Garbage Patch

archipelago of Hawaii, displays the denser concentration of plastic, reaching more than 100 kg/km². It is estimated that this area contains more than 20k tons of plastics.

When considering the entire North Pacific Garbage Patch, the numbers climb up to 100k tons with a concentration of at least 10 kg/km² (10).
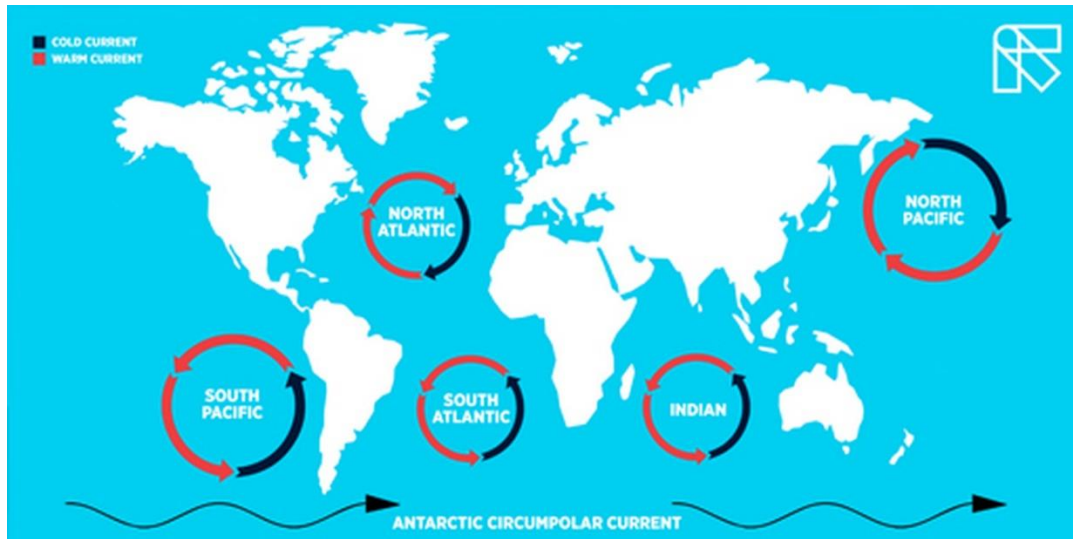

Figure 9 : Location of the 5 major Garbage Patches

The scientific community estimates that each year, around 8 million tons of plastic is rejected to water. According to WWF, in 2019, 600,000 tons of plastics were polluting the Mediterranean Sea. Despite being the greatest economical force of this region, France is struggling to recycle its plastic efficiently as in 2016, 76% of its plastic wastes were incinerated whereas only 22% were recycled. There are still some plastics being released to the environment (80,000 tons) and a non-negligible quantity of it finds itself a new home within the Mediterranean Sea (approximately 10,000 tons). Considering only the plastic released to the Mediterranean Sea, WWF estimates that 79% originates from coastal and land activities, 9% from marine industry and activity such as fishing gears and nets and 12% is rejected by rivers to the sea. In fact, there are two main sources of plastic pollution that are the mismanagement of the plastic waste in coastal environment and rivers that transport waste straight into oceans (11).

Figure 10 is a map retrieved from the WWF displaying the concentration of floating plastic waste in sea in 2017 as well as its origin (11).
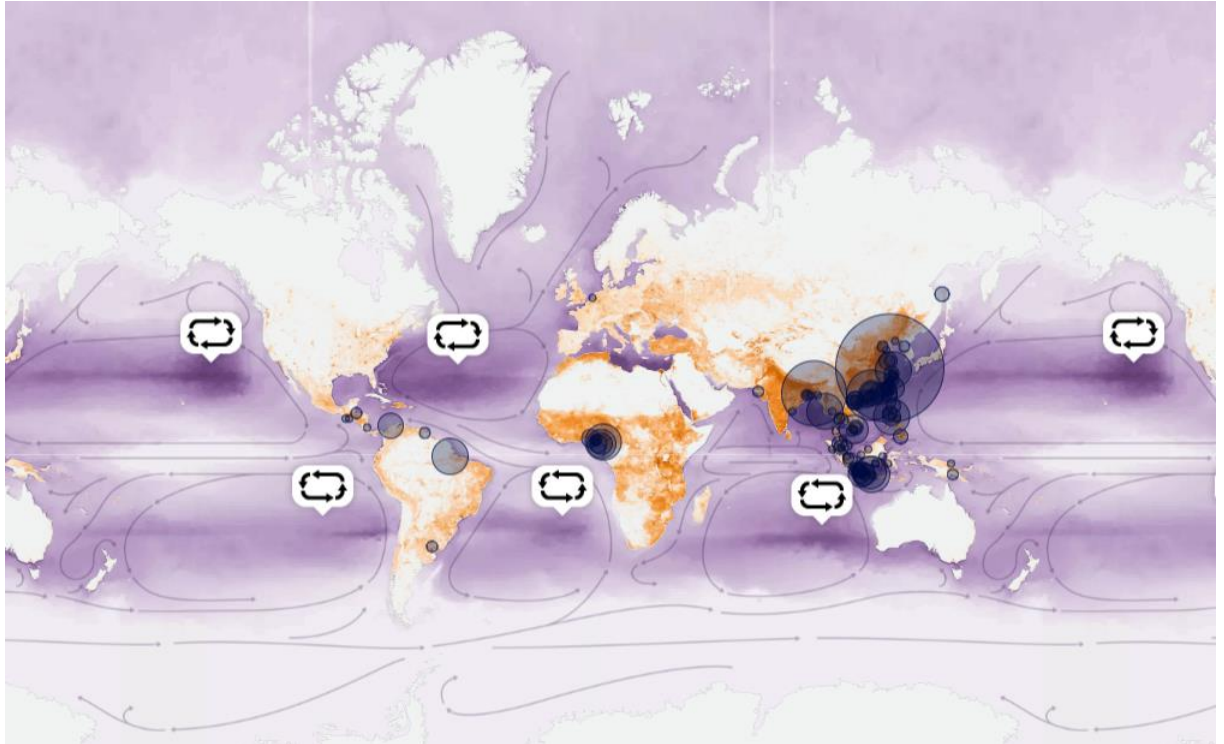
Figure 10 : WWF mapping of plastic waste concentration and its sources

The purple shades increase with the concentration of floating plastic waste varying from less than 1 to more than 100k g/km without even considering plastic parts smaller than 0.33 mm². In total, it is estimated that over 5.25 trillion plastic pieces float across the globe representing a weight of 268k tons (12). It is shown how plastic has settled in all parts of the water surface of the world and how that waste tends to regroup into the Waste Patches described earlier at the center of the gyres displayed by the circling icon. It also indicates the prevailing currents of seas and oceans (arrows) responsible for carrying waste across the globe. The origins of the plastic waste are also presented on the map. The shades of orange on the continents are representative of the mismanaged plastic waste quantities by km² (Varying from 1 to more than 100,000 of kg / km²). In total, it is estimated that a total of 80 million metric

tons are annually not disposed in good conditions, which represent 47% of global annual municipal waste (13). The inputs of the 122 most contributing rivers to oceanic waste are also displayed by the blue circles. Their diameter is proportional to their annual emissions (ranging from 1k and less to 333k tons of plastic per year). In total, the contribution of rivers to oceanic plastic waste varies between 1.2 and 2.4 million tons annually. The 20 most polluting river are accountable for 66% of those quantities (14).

The mismanaged plastic waste numbers include failing waste managing systems, coastal littering as well as illegal dumping to the sea. Therefore, it makes sense that the areas less impacted by this category are either the one where the population density is low or where the waste management systems are efficient. Similarly, the amount of waste discarded by a river is proportional to the population density but also to the level of industrialization and urbanization close to those rivers.

Most of the plastic floats for over a year where they represent a great danger for marine species that eat those plastics unconsciously. Some of them sink to the bottom of the sea where they extremely slowly degrade and pollute, some of them are brought back to shores. A small amount biodegrades, and even smaller quantities are actually bio-assimilated by the biodiversity. The floating plastic is unfortunately often not visible for the humans nor the wildlife. In fact, according to the Tara Ocean Foundation, 93% of polluting plastic at sea is smaller than 5 mm. Under 5 mm, a polluting plastic is defined as a microplastic (15). It is estimated that 5,000 billion microplastics are nowadays found in sea. In the Mediterranean Sea, it has been approximated that the microplastic concentration varies from 1/10 to ½ of the zooplankton concentration. Zooplankton is an animal organism floating in water. It is at the very base of the food chain ad represent an abundant source of nutriments for a wide spectrum of marine wildlife. It means that it is impossible for marine species to not ingurgitate those plastic particles. Eventually, those particles can either kill them by clogging their digestive system or be transmitted through the food chain and impact the health of other species all the way up to the humans (16). Indeed, toxic molecules can bioaccumulate in species, eventually poisoning them. Eventually,

bioaccumulation can cause diseases and eventually results in the death of the specimen. Bioaccumulation is a process of accumulation of molecules or substances in an organism. It occurs when a specie absorbs a particular substance at a higher rate than it eliminates it. The phenomenon is derived in two distinct categories : bioconcentration and bioamplification. Bioconcentration is considered as a direct bioaccumulation. A specie, usually at the lowest trophic levels, is in direct contact with a particular substance and eventually feeds from it. The contaminant then bioaccumulate in the body of the specie. Species from the first or second trophic level (productors and primary predators) like krill and shellfishes can accumulate molecules through bioconcentration. The upper trophic level species (secondary and ternary predators) can indirectly suffer from the pollution by bioamplification while predating on their usual preys already contaminated. Bioamplification is considered as an indirect bioaccumulation. It usually happens to predators that feeds from species that has been contaminated by bioconcentration. The more a specie is situated higher in the food chain, the more molecule of that contaminant is bioaccumulated in its body because of predation and the more toxic risks exists for this specie. In other terms, super predators like humans are the most impacted by the pollution of the environment. In fact, these processes imply that a polluted environment results in the contamination of all trophic levels living in that environment. Figure 11 illustrates the bioaccumulation of contaminants in the food chain.
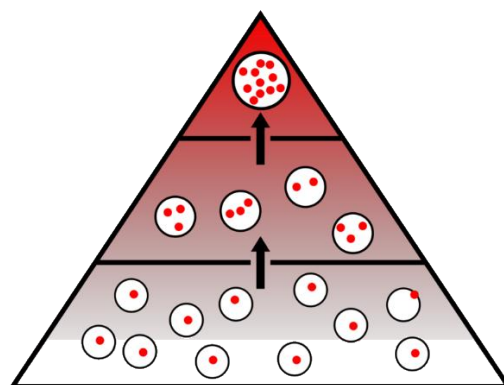

Figure 11 : Illustration of the evolution of bioaccumulation phenomenon climbing up the food chain

Apart from the fact that polymers can be toxic as a whole if ingested, plastics at sea are good dispersion vectors for other molecules and especially for toxic molecules. Those molecules can originate from the plastic composition itself like additives that are so commonly used in the industry to enhance polymer properties (like phthalates and biphenyls), but can also be external molecules and pollutants that are adsorbed to the polymer surface (like hydrocarbons, pesticides, DDT and PCBs) (17). When adsorbed, those molecules become more persistent in the water environment and consequently accumulate in some regions, resulting in catastrophic damages of ecosystems. Those substances commonly qualify as persistent bio-accumulative toxic (PBT). PBTs are a class of compounds that displays a strong resistance to biodegradation, a high mobility within its environment (especially in water) as well as a high toxicity for species. Logically, PBTs have a remarkably high tendency to bioaccumulate in all trophic level of its environment. Those compounds are classified into 3 level of impact, the level one being the most preoccupant. This level one class includes chemicals like Mercury, PCBs (Polychlorinated Byphenyls) and some pesticides like Mirex and Chlordane.

b. Biodegradation process

Many studies have been dedicated to the description of physical, chemical, and biological steps of the decomposition of polymers. The biological degradation is largely caused by microorganisms, essentially bacteria. Those bacteria form the most abundant and diverse organism group found in seas and oceans. They number in over hundreds of millions per liter of sea water with up to 500 different varieties that, therefore, represent nearly as much metabolic capacities. Two of the most important ones are the saprophytes, responsible for half of the mineralization of organic carbon provided by food chain wastes, and the hydrocarbonoclasts, capable of degrading hydrocarbons which compose the majority of synthetic polymers (18). Saprophyte organisms are capable of feeding on decomposing organic wastes and releasing

mineral matter. Hydrocarbons are organic compounds essentially composed of carbon and hydrogen elements and hydrocarbonoclasts are bacteria feeding on those hydrocarbons. The most common ones are *Alcanivorax sp.*, *Cycloclasticus sp.* and *Marinobacter hydrocarbonoclasticus*.

Polymers at sea are firstly submitted to abiotic degradation that are physical (hydraulic fluxes, temperature, ultraviolet light (UV)) or chemical (oxidation and hydrolysis) that will fragilize the polymeric structure and fragment it. It is only afterwards that the biological degradation (biodegradation) takes place (19).

The 4 steps of biodegradation

The biodegradation can be segmented in 4 distinct steps :

The bio-deterioration initiate the biodegradation process. It follows the abiotic degradation. It is the beginning of the interaction between the biome and the material recognizable by the formation of a biofilm on the material surface. This interaction is usually mechanical but can be chemical as well if the biofilm allows it by its composition. Indeed, chemolithotroph and chemoorganotroph bacteria are able to produce acid compounds that may damage the polymer (20). Chemolithotroph are bacteria feeding on chemical bonds of mineral compounds while chemoorganotroph are bacteria feeding on chemical bonds of organic compounds.

1. The biofilm exploits the cracks formed by the abiotic degradation and push the alteration process forward (21).

2. The bio-fragmentation is the second stage of the biodegradation process. Bacterial enzymes, liberated by bacteria are fixed on the damaged surface of the polymer. Following the continuous degradation of cracks during the bio-deterioration, enzymes favor the cleaving (depolymerization) of polymers onto oligomers, dimers, and eventually monomers. The most important

enzymes engaged in the process are the oxygenase, which facilitates bacterial degradation by rendering polymers more hydro soluble, the lipase and the esterase, which specifically target and break carboxyl groups, and the endopeptidase which targets the amine groups (22). Carboxyl groups are molecular group ($-CO_2$) commonly present in organic compounds. This process fragilizes the structure of the material. Eventually, when the damages are too important it is fragmented into microplastics by any efforts applied by its environment (like a wave in our context). For some materials, this step can lasts decades in function of the environment factors. Unfortunately, for many materials, especially the polymers, this step is dependent on environmental factors (humidity, temperature, pH, pressure…) and can be extremely long (up to centuries). It is the case for the most common polymers found in the state of sea wastes (PP, PE, PA6).

3. The bio-assimilation is the third and environmentally most major step of the biodegradation phenomenon that implicate microorganism for the assimilation and final transformation of the matter. The particles reduced at the microscopic scale by the bacterial enzymes are small enough to be completely incorporated into the microorganisms. Those organisms then digest the particles of matter and transform it into biomass and cellular compounds.

4. The mineralization is the final stage of biodegradation that leaves no macro nor microplastics in the environment. The microorganism have assimilated the matter and rejected biomass (23). This process can happen in both aerobic and anaerobic conditions. Most seas, oceans and rivers present aerobic conditions with the oxygen contained in the water. This parameter defines the process of mineralization. Indeed, under such conditions, bacteria use the oxygen elements as electron acceptors that contribute to the formation of tinier organic molecules. Following this, the remaining matter is transformed.

Oxidized molecules including N_2, CO_2, H_2O and other residues are then emitted to the environment (24,25). In anaerobic conditions, oxygen is not available so other components such as sulfates , nitrates, iron, carbon dioxide and manganese can play the role of the electron acceptors. In the end, CH_4 and other metabolic products are emitted in addition to the ones cited in aerobic conditions (24). Figure 12 briefly illustrate the biodegradation process.
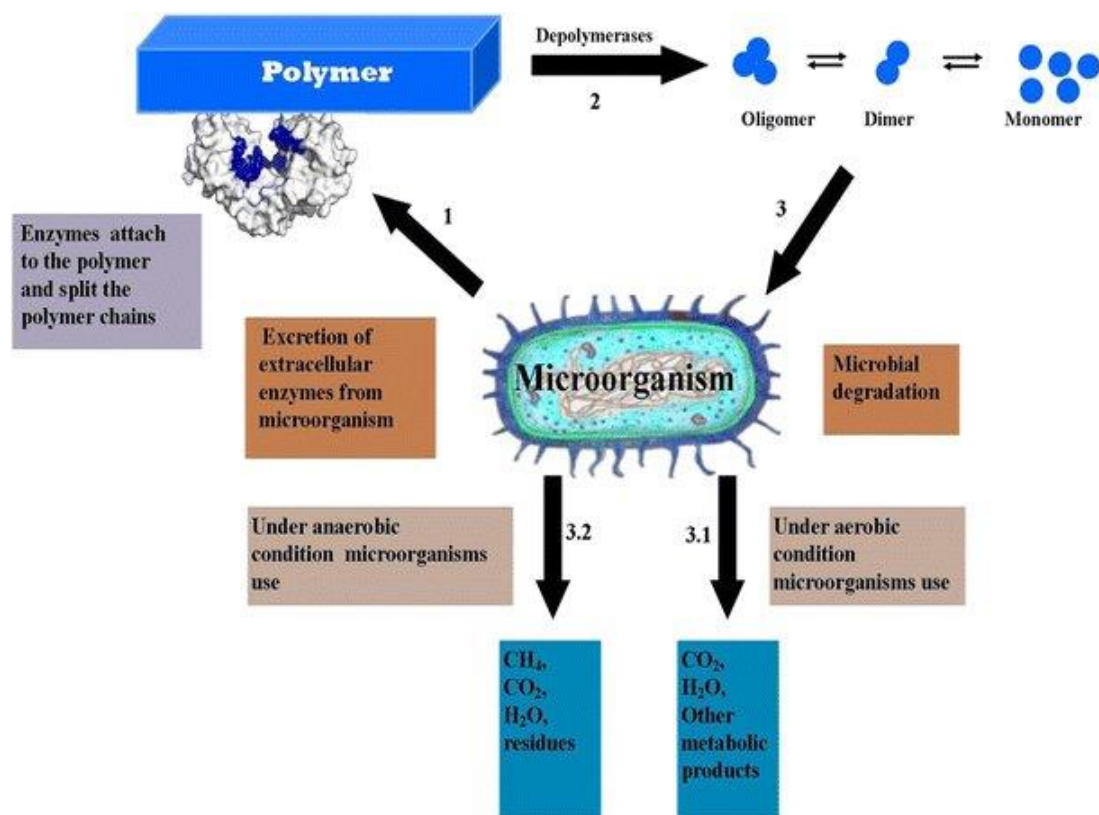

Figure 12 : Mechanisms of plastic biodegradation (26)

Factors influencing biodegradation

The factors influencing the degradation of polymers can be classified into three categories that define the whole degradation system : the polymer properties, the environmental conditions, and the microbial or enzymatic characteristics.

- *Environmental conditions*

Moisture

Ho et al. (1999) (27) has suggested that the polymer degradation rate is enhanced by the surrounding moisture and humidity. Indeed, those factors are crucial for the development of microbes which then have an enhanced degradational behavior. Moreover, wet conditions support the rate of hydrolysis, responsible for chain scission within the polymer before the bio-deterioration. Hydrolytic degradation is completely compatible with biodegradation and even accelerate it. This degradation mechanism is often associated with various biodegradation processes as for example the enzymatic hydrolysis. Seas and oceans propose ideal moisture environment for biodegradation and microbial development.

Temperature

The temperature is one of the state variables responsible for the activity of microbes in an environment. Certain temperatures are more ideal to certain microbial developments and hence, this variable defines the microbial population of its environment.

Oxygen presence

As described earlier, aerobic, or anaerobic environment has an impact on the microbial activity and thus on the degradation process. Aerobic microbes cannot survive in anaerobic environment and vice versa. The presence of oxygen is often essential to the biodegradation of a polymer.

- *Microbial & enzymatic characteristics*

Enzymes have specific roles and impact on the decomposition of polymers. Kale et al. (2007) (28) suggested that fungal species *A. flavus* and *A. niger* produce efficient enzymes for the degradation of straight chain polyesters. Yamada-Onodera et Al. (2001) (29) suggested that the extracellular enzymes degrading polyhydroxybutyrate (PHB) has multiple degradation mechanisms depending on the various polymerases produced by microbes. The large diversity of microbes and enzymes related to them offers a wide selection of degradation mechanisms, with some being more appropriate or even exclusive to certain polymers. As such, Skariyachan et Al. (2016) (30) suggested that a microbial consortia of *Pantoea* spp. and *Enterobacter* spp. are capable of degrading low density polyethylene (LDPE). Additionally Kowalczyk et Al. (2016) (31) indicates that a recently discovered bacterial strain, *Achromobacter xyloxidans* shows degradation potential on HDPE. Finally, aromatic compounds, that are known to be stable molecules, therefore hard to biodegrade seems to have a particular sensitivity to the bacteria *Anoxybacillus rupiensis* that uses those molecules as a carbon source according to Mahdi et al. (2016) (32).

- *Polymer nature & properties*

The properties of a polymer play a preponderant role in the understanding of its the biodegradation process. Yet, those inherent properties are not the only factors that affect the biodegradation. As additives are commonly used in the polymer industry nowadays, they also play a significant role on biodegradation.

Polymer nature

The composition of a polymer is deeply connected with its degradation process and as described earlier, determines the nature of the enzymes and

thus the microbes that affect it. Some polymers are more easily degradable by microbial action due to their structure and composition. As a result, some polymers like polypropylene take years to biodegrade in aqueous environment while some others, usually manufactured in an ecological purpose can completely disappear within a matter of days or even hours for the most extreme cases like *Algopack* produced by the company of the same name (33). On the other hand, Yamada-Onodera et Al. (2001) (29) and Vijaya and Reddy (2008) (34) suggested that petrosourced polymers are not readily degraded in the environment because of their inherent hydrophobicity and structure. Non-biodegradable polymers include a wide range of the most used synthetic polymers nowadays like PVC, PP, PE, polyethylene terephthalate (PET) and polystyrene (PS).

Molecular weight

The molecular weight of a polymer is probably one of the most important factors influencing the biodegradation rate. The degradability is inversely proportional to the molecular weight. As such, Tokiwa et al. (2009) (23) suggested that high molecular polycaprolactone (PCL) degraded at a slower rate than low molecular weight PCL by a lipase created by *R. delemar*. Additionally, Auras et Al. (2004) (35) suggested that a low molecular weight substrate is convenient for microbial enzymes to degrade.

Polymer morphology

The global aspect of the polymer also has an impact on the degradability of the polymer. Stevens (2003) (36) then Kijchavengkul and Auras (2008) (37) both noticed that the surface area of a polymer is highly connected with the rate of degradation. As such, the larger the surface area, the more interaction there is with the environment and the faster is the degradation. The morphology and dimensions of a polymer piece for biodegradation is framed

by the standard criteria presented by the American Society for Testing and Materials (ASTM) under the regulation ASTM 2004.

Melting Temperature

Enzymatic impact on degradability is regulated by the melting temperature of the polymer. In fact, the enzymatic degradability can evolve inversely with the melting temperature. As an example, Tokiwa and Calabia (2004) (38), then Tokiwa et al. (2009) (23) showed that a purified lipase of *R. delemar* have efficiently hydrolyzed polyesters, especially PCL that exhibit low melting temperatures.

Additives

Additives can be seen as non-polymeric components encapsulated within the material composition. There are plenty of different additives with as many functions for the polymer that can affect its degradability. Some additives are specialized in chemically stabilizing a polymer, like fillers, rendering the biodegradation very hard. On the other hand, some others help the material to be naturally degraded in nature like the d_2w masterbatch from Symphony environmental which received in 2014 an ecolabel regulated by the International Standard Organization (ISO) under the regulation ISO 14020 (2002) and more recently the ISO 14024 (2004). More commonly starch and pro-oxidants are used as additives to promote biodegradation. Those polymers that are of usual composition but with a lifetime regulated by the additives, they are commonly called oxo-biodegradable. Pro-oxidant additives usually are transition metal ion complexes able to accelerate the oxidation of polymers (39). The oxidation reduces the molecular weight of the polymer which hence facilitate biodegradation. It is the combined actions of oxidation and microbial alteration that form the so-called oxo-biodegradation (40–42). Thanks to multiple studies about the oxo-biodegradation of polyolefins, it has

been proved that pro-oxidants are easily biodegradable (21). Other additives can impact the biodegradability indirectly, like the ones that influences the thermal stability and hence, the melting temperature or the UV stabilizers that prevent photo-oxidation to occur and thus to initiate the first step of the biodegradation.

Biosurfactants

Biosurfactants are compounds sometime used in polymer manufactures as additives that are displaying an amphiphilic behavior. It means that these molecules are made out of hydrophilic (thus polar) and hydrophobic (thus apolar) chemical groups. As a result, such species react particularly to aqueous environment, often leading to molecular rearrangement like micelles, liposomes and bilayer sheets shown on Figure 13.
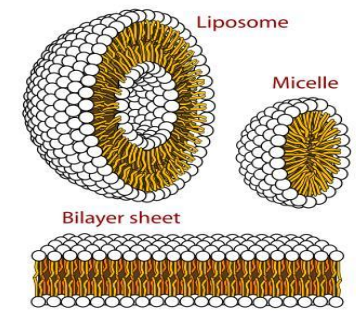
Figure 13 : Cross section views of amphiphiles species rearrangement in aqueous environment

According to Orr et Al. (2004) (43), those amphiphile compounds present the characteristics of having a low toxicity and being highly biodegradable resulting in an enhanced biodegradation of polymers (even for petrosourced ones) when added to it. Additionally, Kawai et Al. (2002 & 2004) (44,45) explained that the specific functional groups of amphiphilic species allows the bioactivity of microbes under extreme conditions of temperature, salinity and pH.

Overall, the estimation of the lifetime of polymers at sea is complex. Nowadays, there is no scientific proof showing that certain polymers can last hundreds of years at sea. This is due to the complexity of studying the degradation in such variable environment (and therefore variable degradation factors). Also, we only have a recent overview of the plastic interaction in seas and oceans as plastic utilization is still relatively recent. As an example, the development of plastic bottles, which nowadays represents the major pollutant of seas and oceans originates from the 1970s. Moreover, it is certain that polymer materials found in sea greatly differ in their composition. Especially considering the wide range of additives commonly found in polymeric products nowadays. Some of them make the polymers more resistant to degradation like phthalates while some others accelerate the phenomenon like oxo-biodegradable additives. Recently, some additives have been created in order to render polyolefins completely biodegradable within a maximum period of 42 months (SPtek ECLIPSE by SmartPlastic (46)). Yet, those additives need to obtain certification regarding the biodegradability of the polymer afterwards.

Moreover, most of the studies focusing on the ageing of polymers are made for industrial purposes. They usually evaluate the degradation of polymers up to a certain point corresponding to a loss of properties necessary for the usage of the product. The level of degradation studied greatly vary from one application to another but very few actually monitor the entire degradation process as it does not serve industrial purposes. This makes it difficult to estimate the lifetime of a polymer at sea, based on the present knowledge on polymer degradation.

Yet, thanks to these studies, it is possible to predict the environmental factors that are responsible for polymer degradation.

c. Marine degradation factors

Chemical interactions :

- *Hydrolysis*

Polymer hydrolysis is a chemical reaction between the polymer and water. It is described as the breaking of a polymeric bond caused by the intricating of water. The degraded polymers form eventually monomers. During this process, the water molecule is consumed, and energy is liberated. This phenomenon can be accelerated by the presence of catalysts like ions and enzymes within the polymer (47). Without water surrounding the polymer, hydrolysis cannot happen. This justifies the enhanced sensitivity to hydrolysis by hydrophilic polymers.

There are multiple factors that can affect the effective rate of hydrolysis of a polymer including its structure, its chemistry and the presence of external substances that can function as catalysts or inhibitors.

The rate of diffusion of water within the polymer is also a factor influencing the hydrolysis. Therefore, the fastest hydrolysis degradation in water environment is related to high rate of diffusion and permeability of the polymer.

Moreover, the molecular arrangement can also affect effective rates of hydrolysis : hydrophobic molecules or crystalline structures can isolate molecules susceptible to react with water from H_2O molecules. Typically, carbonyl bonds (-C = O) are highly reactive materials for hydrolysis and they are fairly common within polymer structures. Yet not all carbonyl polymer displays a degradative behavior in immersion. Anhydrides, esters, and carbonates do have a strong tendency to degrade but urethane, imide and amide carbonyl groups are stable when exposed to water. Those particular chemical groups are illustrated on Figure 14 and 15.
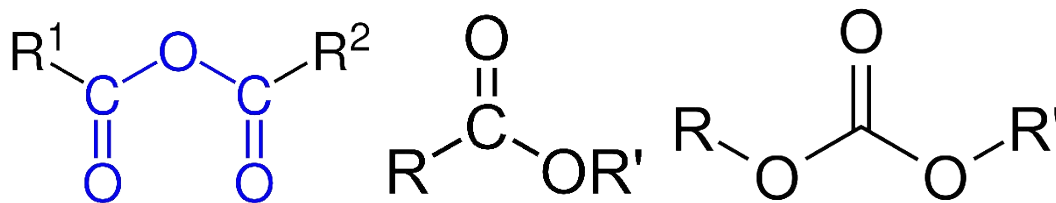
Figure 14 : anhydride, ester and carbonate chemical groups (from left to right)
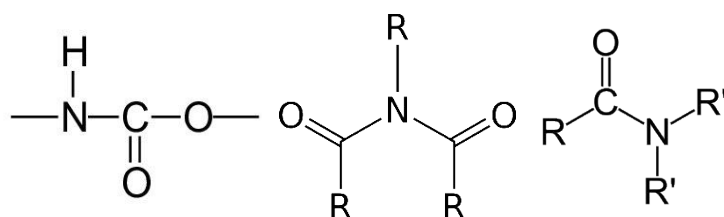

Figure 15 : urethane, imide and amide chemical groups (from left to right)

When those groups are surrounded by hydrophobic molecules, hydrolysis does not occur. Cross linking of the polymers can also prevent or impede the hydrolysis.

The morphology of the polymer material also bears a consequence on the rate of degradation. A structure with high ratio of surface area to volume presents more opportunity for water molecules to interact with the polymer, resulting in an accelerated hydrolysis. Its porosity and surface area also make a difference : A highly complex surface with cavities and rugosity increases the probability of interaction between the polymer and water molecules. It is therefore possible to qualify the rate of hydrolytic degradation by monitoring the evolution of molecular weight. A sample become lighter as hydrolysis occur by losing matter.

- *UV alteration*

There are multiple polymers that are sensitive to UV. The degradation can take different aspects : some polymers change or lose their color, some loose matter or see their properties altered. The propensity to degradation can vary from negligible to extreme. J.H Botkin proposed that UV interaction leads to chain scission which

induces enhanced crystallization. This crystallization then cascades in various effects such as the appearance of cracks and voids and global embrittlement of the polymer (48).

The principal responsible for the degradation to UV are species called chromophores that absorbs UV light. The term chromophore refers to conjugated multiple bonded atoms of a molecule that is able to absorb UV (49). When they absorb the light, they release energy from the absorbed UV which generally results in chemical interaction with itself or with surrounding molecules, causing bond breakings. This process creates de facto free radicals within the polymer that are unstable and therefore highly susceptible to react with its environment. Michael Tolinski in *Additives for Polyolefins* (50), describe typical chain reactions that creates a degradation cycle of the Polyolefins :

- Affected by UV, Polyolefins creates radical that interacts with oxygen, creating peroxy radicals and hydroperoxides.
- The hydroperoxides reacts with the polymer and create additional free radical species such as hydroxy and alkoxy radicals

This cycle results, depending on the polymer in either a chain scission (for polypropylene) or cross-linking interactions (for polyethylene). Naturally, because the degradation processes vary from one polyolefin to another, some additives are more appropriate and hence more effective to one polymer and vice versa (48,51,52). The degradation phenomenon observed by the combined action of UV light and oxygen elements is called photo-oxidation. This process generally occurs at the surface of the polymer materials, but it can also affect the bulk of the material if UV has the opportunity to reach it, i.e., if the surface of the material does not properly dissipate the UV energy. As a result, without additive protection, P. Solera assured that a 1.5mm thick plaques of high density polyethylene (HDPE) can lose up to 80% of their impact resistance in 2000 hours of direct UV exposure (accelerated ageing) (53). It has been proved that the structure of the polymeric chains affects the photo-oxidation rate. As such, some polymers do not undergo any photo-oxidation. Indeed,

highly branched monomers like LDPE are more susceptible to interact with UV light than with linear polymers like HDPE. Moreover, like for hydrolysis, the amorphous phases of the polymer are more sensitive to photo-oxidation than the crystalline phases.

Without chromophoric species, photo-oxidation cannot apply. Those substances are not necessarily inherent to the polymer composition. Indeed, in some cases, chromophore molecules can originate from residues of catalysts from the production of the polymer or from additives used to modify the properties like pigments and processing aids. It has been evaluated that molecules containing conjugated double bonds tend to be chromophores. As illustrated on Figure 16, Polyamide 11 (PA11) naturally has a double bond (C = O) in its radical, which makes it quite sensitive to UV photo-oxidation.
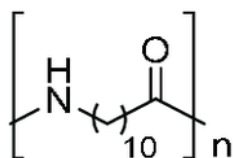
Figure 16 : Polyamide 11 Rilsan chemical structure (54)

- *Water uptake influence*

The water uptake of the polymer plays a preponderant role in its natural degradation. As discussed previously, the amount of water absorbed by a material is a factor enabling the process of hydrolysis. Polyolefins naturally have small water uptake due to the fact that some part or the whole monomer is hydrophobic, preventing the incursion of water within the bulk of the material. According to INEOS data (55), after 24h of immersion in a water at 25°C, polypropylene has absorbed less than 0.01% of its mass while high density polyethylene has absorbed 0.03% of its mass. Such a small absorption makes it hard for hydrolysis to happen.

Physical interactions :

- *Hydraulic fluxes*

Fluxes are omnipresent in seas and oceans, it can exist locally like swells, baïnes and riptides or at a large scale like the oceanic currents illustrated on Figure 17 and gyres. Those fluxes are caused by various external forces such as the Coriolis effect resulting from the Earth rotation and the wind. It can also be the result of physical state variables of water : Temperature and salinity variation creates density variations within water, which creates huge inherent fluxes like the thermohaline circulation (THC). It is a deep ocean flux in a closed loop (also called the conveyor belt) occurring at a world scale. The cold waters leaving from the poles heats at various locations across the globe before returning to the poles where it cools and starts the process again.

Figure 17 : Map of the oceanic currents (56)
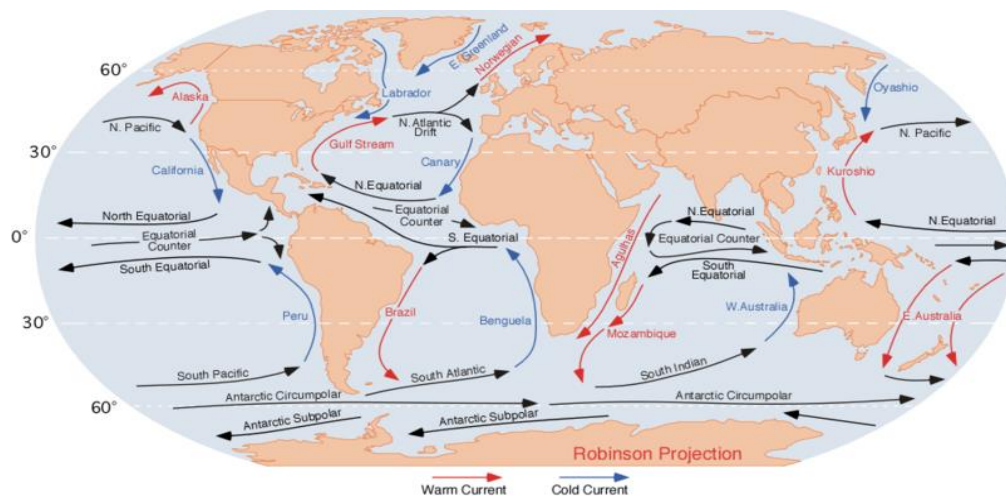
Fluxes cannot be separated from the sea and ocean environments. Therefore, it is important to characterize the impact of hydraulic currents on the degradation of polymers. It has already been shown that currents enhance the rate of hydrolysis (57). Moreover, sufficient currents in coastal environments are susceptible to carrying sediments that can hit and abrade the polymers.

- *Sediment abrasion*

Abrasion of polymers is highly dependent on the mechanical properties of the polymer material. Hasan Muhandes et al. (58) has shown that the abrasive sensitivity of polymers is in direct relation with the dimension less numbers retrieved from the equations of the material mechanical properties such as the elongation at break (%), the yield stress, the compressive and flexural stresses (MPa) and the Young's Modulus (GPa). From an experimental setup using a containing system with gravel and loamy soil-based slurry that spins around a rotating shaft at speeds around 2 lm/s, he studied the abrasion evolution of PA6, Ultra High Molecular Weight PolyEthylene (UHMWPE) and PLA samples. It has appeared that tensile related characteristics have a larger impact on abrasion than compressive and flexural properties.

Nonetheless, we could argue that sediment abrasion would not be a principal factor of degradation. Indeed, floating sediment caused by agitation and hydraulic fluxes does not necessarily have high velocity when impacting polymers at sea. As displayed on the Hjulström diagram (Figure 18), particles equivalent to the size of sand grain requires at least between 5 and 200 cm/s water. Yet those particles can eventually reach higher velocity in eroded areas, up to 1000 cm/s. At such speed, we can argue that a polymer material might degrade.
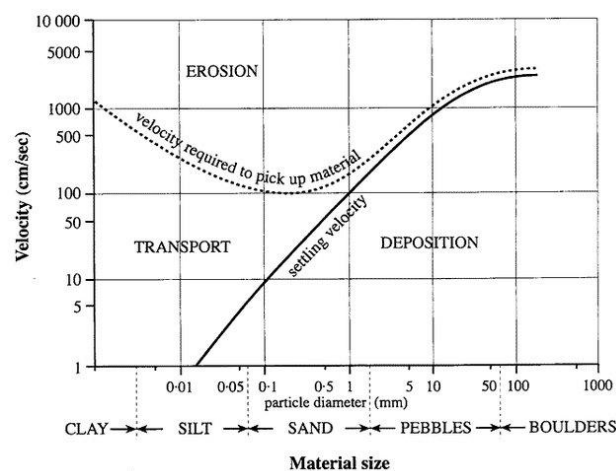

Figure 18 : Hjulström diagram (59)

Moreover, polymers are also floating and they are not strictly physically constrained like in Hasan Muhandes experiment (58). The combined low velocity of sediment and the ability to move for the polymer material reduces the impact and probability of a sediment to actually abrade a polymer surface. However, as we previously discussed the ability of hydrolysis and auto-oxidation to alter physical properties of polymers, there is a legitimate probability that aged polymers can be affected by sedimented particles.

We previously described the hydrolysis and photo-oxidation phenomena and their ability to alter the properties of polymers. Hence, it is reasonable to consider a degradation of the polymer from the sand particles that intervenes after some chemical alteration by hydrolysis and photo-oxidation. It could be a secondary actor of the degradation that participate in the late period of the ageing of the polymer. Inversely, abrasion is susceptible of increasing the surface area of the polymer, therefore increasing the reactivity in hydrolysis and photo-oxidation.

Biological interactions :

- *Bacterial degradation*

As described previously in the biodegradation subchapter, there are multiple microbes, all with distinct functions, that can, eventually, transform polymers into biomass and gases. Those microbes are often bacteria and fungi that create extracellular enzymes. The degradation of the polymers is undergone by various enzymatic mechanisms

III.   Methodology

Nowadays, the majority of plastics that forms ocean waste is PE, PA and PP. Those polymers are considered as waste because they are unable to degrade in sea environment. Actually, few polymers degrade rapidly in sea water and even fewer of them are bioassimilable. The majority will degrade in the form of microplastic that will not be assimilated by organic species to be transformed into gases and biomass.

Currently, 80.7 % of the ocean plastic waste is of one of the following nature : Polyethylene (54.5%), Polypropylene (16.5%) and Polyesters & Polyamide (9.7%) (1). Not only these plastics are the most widely used today for their industrial convenience, their low price as well as their versatility but they were found to be very resilient in marine environment.

Therefore, it is hard to qualitatively define the degradation of those polymers into sea because experiments take years. Moreover, most of the literature that treat of the degradation of polymers sea water only seek the endpoint of the degradation when the polymer is either completely fragmented in microplastic or completely assimilated by the environment.

Within the frame of the RESTCOAST and Prospère projects, this thesis aims to qualitatively defines the point where a *Roselière* will no longer holds its necessary properties (mechanical and structural) for its purpose in order to define a lifetime of the product. This will avoid *Roselières* to lose strands by mechanical rupture therefore, adding waste to the sea in the form of macro-plastics. It will also prevent the deployment of toxic elements to the sea like microplastics and additives.

a. Sample definitions

The studied polymer is a classic polypropylene treated with HALS for UV stabilization. This study focuses on 7 samples taken from various sites within France. They have been labelled S1 to S7. Figure 19 shows information about the samples including their exposition time to water and various observations made about their immersion sites.

Label	Location	Age	Ageing environment
S1		New	Unaged and conserved in sealed bag
S2	Harbor of Marseille	7 years	At a 4m depth (protected from UV)
S3	Harbor of Marseille	7 years	At a 1m depth (exposed to UV)
S4	Harbor of Agde	3 years	Least exposed location (in terms of hydraulic fluxes)
S5	Harbor of Agde	3 years	Most exposed location (in terms of hydraulic fluxes)
S6	Bay of Arcachon	11 months	Inter-tidal location (High UV exposition, high temperature variations, high abrasion potential)
S7	Bay of Arcachon	11 months	Inter-tidal location (High UV exposition, high temperature variations, high abrasion potential)

Figure 19 : Table of samples description

It is interesting to see that all samples present a great variability in the degradation environment. The comparison of the results will help to understand the role of each degradation factor. As an example, by comparing S2 and S3, it is possible to understand the role of UV degradation. On the other side, by comparing S4 and S5, it is possible obtain information on the potential impact of mechanical forces exerted by hydraulic fluxes. S6 and S7 samples have been retrieved from the Bay of Arcachon which is a singular degradation environment since the Roselières were placed in an inter-tidal zone. This environment presents a particularly harsh environment for the

polymer since the UV exposition will be intense at low tide and particle abrasion might get intense during tide turnings. Moreover, especially in summer, the temperature variations can also be particularly important which may accelerate the ageing of the Roselières.

Sample geometry

The morphology of the samples has proven to be an essential subject for the study of the degradation of polymers, greatly influencing the rate of degradation. As discussed before, the surface area in contact with the environment is a predominant factor for hydrolysis.

It is essential in order to make a coherent comparison of the results to have similar samples. As such, the samples are full strands of Roselières. Those strands are made of multiple twisted flattened thinner strands. As a whole, the assembled strand has a diameter of 4 mm and a length of 1 m whereas the thinner strands that composes it are of 1 mm diameter. Overall, this geometry is radically different from a classic slab (a commonly found geometry of retrieved plastic waste). The surface area is incomparably superior. Therefore, it is expected to degrade faster than regular polymer waste.

Yet, there is an existing industrial constraint to this geometry. Because the polymers have the shape of thin elongated strands, those are necessary manufactured using extrusion process. This means that the used polymers can only be extrusion grade ones. This problematic may seem anecdotic, but it can prevent the use of some grades of PA11 (like the BMNO) that have the particularity to be biosourced and without containing any additives while displaying durable behavior. Unfortunately, this grade is only compatible with injection process.

b. Analysis

The analyses made on the samples will allow to characterize the aged polypropylene from different angles. As such, mechanical, chemical, and morphological testing will be done in order to better understand the degradation mechanisms involved. Beforehand, an attempt at cleansing the samples from biofouling will be made to ensure that surface of samples will be visible and that macrofouling won't provide mechanical resistance during the traction tests.

Morphological analysis

Morphological analysis allows to precisely measure the mass and the dimensions of the samples. The results will be compared to standard measures made on an unaged PP Roselière strand. If samples are lighter than the unaged strand, it will imply that matter has been lost by the samples. This lost matter will be caused by micro or macro fragmentation of the polymer into the water. On the other hand, if samples are heavier than the standard measure, it will be because of residual biofouling and also because of remaining humidity within the samples.

Visual analysis by scanning electron microscopy

All the samples will be degraded, even a little. Those samples will be analyzed using a scanning electron microscope (SEM). The optical data retrieved will characterize the physical state of the surface of the samples. By comparing pictures of aged samples and new samples, we aim to establish the degradation causes and mechanisms (sand abrasion, chemical fragmentation, UV degradation, bacterial degradation…) of the polymer immerged.

Chemical analysis by infrared spectroscopy

It is interesting to do chemical analysis of the samples using infrared (IR) spectroscopy. It will help us understanding the chemical alteration of ageing polymers. It will provide information about the degradation mechanisms by revealing the absence of molecules or the presence of newly formed molecules.

In the case of polymer samples containing additives, we will be able to quantify the freeing of additives within the water and therefore qualifying the potential danger that the polymer degradation represents for the marine environment. With the help of ecotoxicity analyses and bibliographic research, it becomes possible to show at what extend those polymers can be toxic for marine wildlife.

Mechanical analysis by traction tests

The traction measurements will describe the basic mechanical behaviors of the polymers. We will compare the mechanical properties of aged polymers and new polymers so we can qualify the loss of structural properties due to water environment. These results will be a direct indicator for the lifetime estimation of *Roselières*. We will essentially look at the evolution of the Young's Modulus (E) and of the strain (ε) and stress (σ) to rupture.

We might also be able to see how the polymer first plasticizes (enhanced flexibility) because of water absorption, then rigidifies because of hydrolysis. Plasticization is a phenomenon describing the blending of small molecules with a glassy polymer (when the temperature is below the glass temperature (T_g)). This natural or artificial blending enhance the mobility of the chemical groups and hence the polymer flexibility. It has also been shown that this process decrease the T_g and the elastic modulus of the polymer (60). It has been shown that water molecules can be responsible for the plasticization of a polymer and alter its properties (61,62). This data could help *Seaboost* anticipating the elastic behavior of immerged polymers,

adding, or retrieving flexibility to the material. That way, they will be in a better position to avoid plasticizing agents and additives that are usually put in polymer compounds for obtaining better mechanical properties. It will significantly reduce the potential toxicity of those polymers for the marine environment caused by the leaking of those additives into water.

IV.   Results & discussion

As derived from the protocol, characterization tests have been done on naturally aged Roselières made from PP that were immerged for various periods in sea environment. Those samples have first been physically characterized (weighted and measured). Then, they have been studied with an SEM using 3 different magnifications (x23, x200 and x2000) in order to optically qualify the state of degradation of the strands. After that they have undergone mechanical traction tests. Finally, an infrared spectroscopy of the samples has been made. The results were compared to a new strand of Roselière made from that same PP in order to characterize the natural evolution of the polymer properties

a. Comparative study of naturally aged Roselières

Cleansing of the samples, attempts at removing biomass

The samples retrieved from the different sites were for the majority of them entirely covered in biomass. Before proceeding to physical measurements of samples, the

biomass needed to be removed. Figure 20 present the different steps and attempts made in order to cleanse the samples. At every step of the cleansing process, a mass measurement was made to analyze the mass of removed biomass.

Steps	Mass of sample (g)	Observations
1. t = 0	12.9	Presence of Balane, macrofouling, macroalgae and microalgae
2. Mechanical cleansing with freshwater	9.4	Presence of macrofouling, macroalgae and microalgae
3. Drying at 105°C for 60 min	2	Separation of the strand in 2 macro strands
4. Mechanical cleansing with freshwater	1.9	Withdrawal of macroalgae at the surface, remaining of macro and microfouling between the filaments constituting the strand
5. Drying at 105°C for 60 min	1.8	Very few remaining organic matter remaining but hardly accessible

Figure 20 : Table presenting the different cleansing steps

Figure 21, 22 and 23 displays the results of the cleansing method. Figure 21 shows the sample before cleansing (step 1) where Balane can be seen (agglomerate shape), Figure 22 shows the sample after step 2 and Figure 23 shows the final result.

Figure 21 : Sample before cleaning at step 1

Figure 22 : Sample after step 2

Figure 23 : Sample after the final step of cleaning

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These different steps of sample cleansing have been made as an experimental attempt for removing the biofouling. The results are encouraging and seems to comply with the necessity to preserve the polymer integrity. However, it has not been scientifically assessed that this protocol does not degrade the polymer. Therefore, it has not been applied on the samples for the next steps of the protocol. A proposition can be made to enhance the cleansing protocol as described by Phuong et al. (2018) (63). It consists of cleaning the samples using a solution of potassium hydroxide (KOH 10%) at 25°C for 24h. This technique could remove up to 99% of the organic matter without degrading the material.

Morphological measurements of the samples

The results of the physical characterization are displayed on Figure 24.

	S1	S2	S3	S4	S5	S6	S7
Length (cm)	50	43.183	39.283	44.740	46.720	50.960	55.650
Weight (g)	2.120	7.066	13.333	4.500	6.120	6.420	7.375

Figure 24 : Table displaying the physical measurement results

It is clear that there are some great variations of weight and length. Length variations have two origins. The first one is the degradation of the polymer leading to a shortened strand. The gradual degradation of the structure can lead to bits of strands being ripped of by agitation. The second one is more of a human cause. Indeed, the strands had to be retrieved from underwater by professional divers. Yet, the harsh conditions of samples collection have induced some irregularities regarding the cutting of the samples from the Roselières. The appearance of samples longer than 50 cm is due to the Roselières strands gliding from its original position. Indeed, the specimen of the Roselière is manufactured as follows : a strand of 1 m long is trapped

between two entangled inox bars at half length (that is, 50 cm). As such, a strand of 1 m long makes up for two strands of 50 cm long. It can happen during the use of the Roselières that the strand glides and derives from its original position.

Referring to the weight measurements, two factors can describe their variation. The first one is explained by the length variation of the samples may it derives from degradation cause or cutting precision. The second and the most important one is due to the biofouling which has occurred to be significant in some cases. As an example, biofouling is presumably the cause for the excessive weight of S3 (13.333 g) compared to that of S4 (4.5 g). After multiple attempts, it has been evident that it was impossible to remove all the biofouling without degrading the strand's integrity and this has a direct effect on the results.

SEM analysis

After weighting and measuring the samples, SEM images have been provided to better understand the surface degradation of Roselières strand during immersion. The equipment used is the SEM Jeol JSM IT500-HR/LA. Figure 25 to 31 shows the images of all seven samples. Respectively, Figure 25 shows S1 and Figure 31 shows S7.
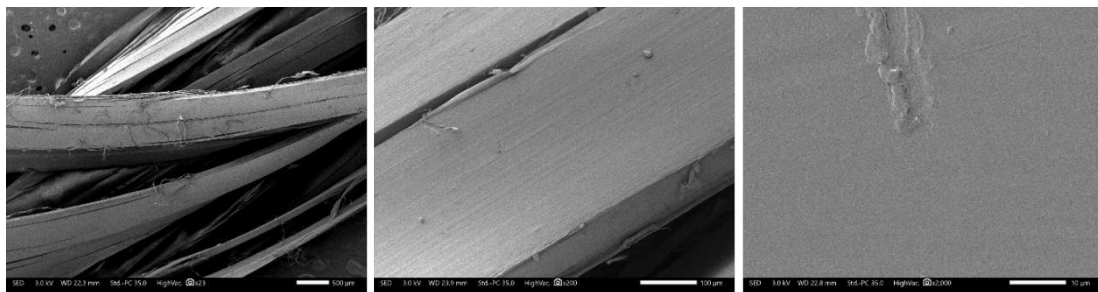

Figure 25 : SEM Image of S1 sample at zoom x23 (left), x200 (center) and x2000 (right)
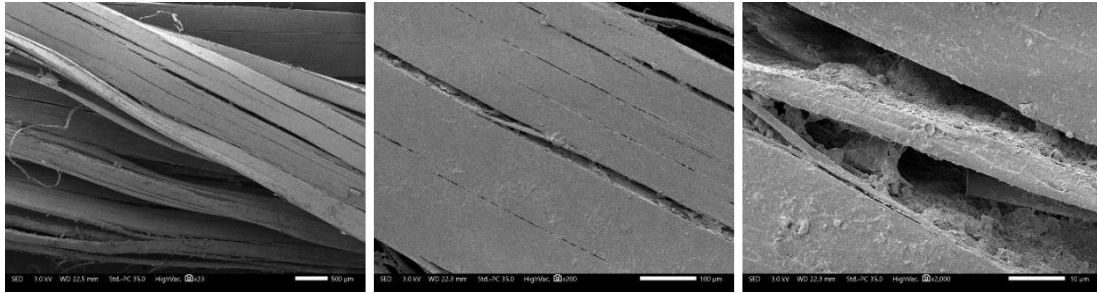
Figure 26 : SEM Image of S2 sample at zoom x23 (left), x200 (center) and x2000 (right)

Figure 27 : SEM Image of S3 sample at zoom x23 (left), x200 (center) and x2000 (right)

Figure 28 : SEM Image of S4 sample at zoom x23 (left), x200 (center) and x2000 (right)

Figure 29 : SEM Image of S5 sample at zoom x23 (left), x200 (center) and x2000 (right)
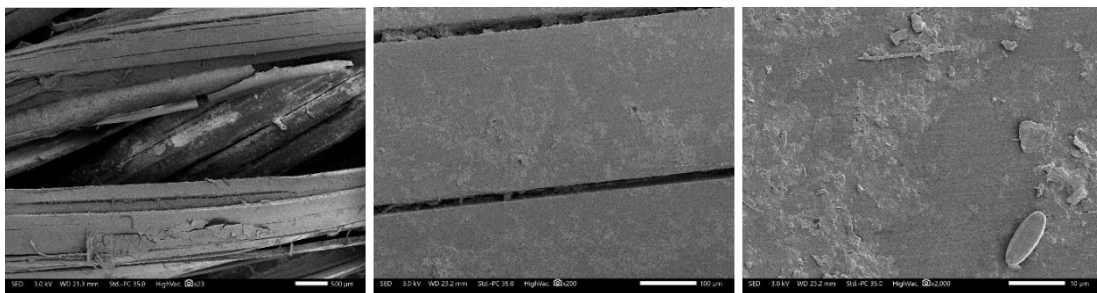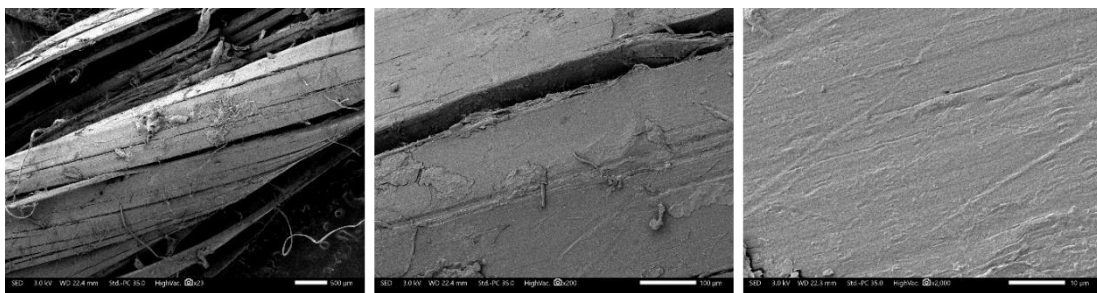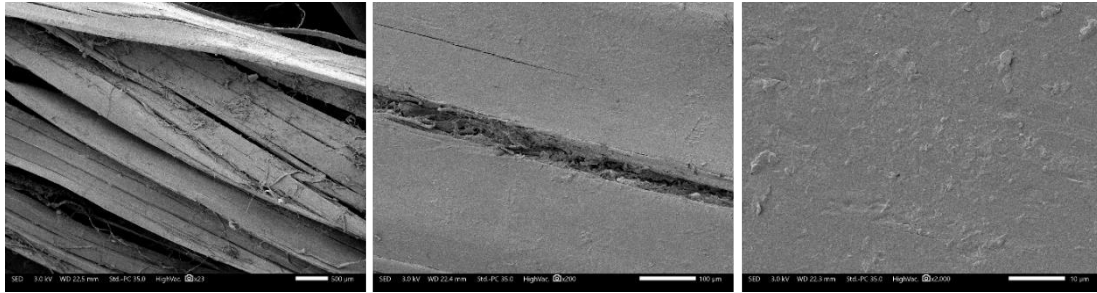
Figure 30 : SEM Image of S6 sample at zoom x23 (left), x200 (center) and x2000 (right)
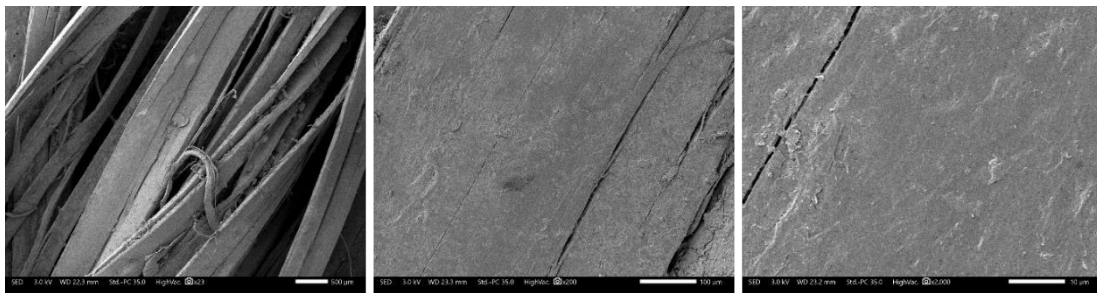

Figure 31 : SEM Image of S7 sample at zoom x23 (left), x200 (center) and x2000 (right)

Looking at the images, it is evident that S1 samples shows no visible surface degradation. At x23 magnification, we see the different filaments that are not all cohesive with each other. Zooming more, the surface looks smooth and unaltered.

At x23 magnification, S3, S5 and S6 (Fig. 27, 29, 30) each displays evident signs of biofouling. At the same scale, all the aged samples also show signs of global structural disorder with unbraided filaments and hazardous positioning. This is mainly due to the hydraulic fluxes applying forces on the filaments and to the continuous degradation of the adhesive between the filaments. The degradation of the adhesive is due to all the degradation phenomenon described earlier (Fluxes, abrasion, hydrolysis, UV, microbial attack). As unaged filaments already show evidence of occasional non cohesion, such structural degradation could be hindered by an optimized cohesion between the filaments.

At x200 magnification, it becomes clear that samples S3, S4, S5 and S7 are greatly covered by biofouling (Fig 27, 28, 29 and 31). While S3 and S5 samples shows bacterial colonization in cracks, S4 and S7 displays a different biofouling in the form of thin

layer covering the surface. On the bottom left of the Figure 28, there appears to be a microplastic piece stuck within the filament, possibly due to its rugosity. On the structural side, all the samples are damaged by cracks formed in the length of the filament. S3, S5 and S6 are the ones with the larger cracks. These cracks originate from the accumulation of mechanical fatigue and hydrolysis and UV interactions fragilizing the structure.

At x2000 magnification, except for S2 and S7, there is no proof of structural degradation. It is because the zoom is so large that it is possible to picture the sample between two cracks. Yet, as S2 is a sample aged for 7 years in the harbor of Marseille, there are obvious signs of bacterial colonization within the cracks which can imply that the cracks appeared sufficiently long ago for the bacteria to deposit. However, a common result from the x2000 images of all samples is the presence of light scratches all over the surface. It is especially observable for samples S3 and S5 (Fig 27 and 29). These scratches can be interpreted as abrasion marks from sand or any other particles. Curiously, the scratches on samples S6 and S7 are not very preponderant, despite the fact that the Roselières evolved in inter-tidal zones with lots of sediment turbidity during tides. The three hypothesis that can explain it is that either the tides are not strong enough to carry the sediment at sufficient speed (refer to Fig. 18), or the polymer has not aged enough since it has only been immersed for 11 months. Another highly unlikely yet possible reason may lie in the problem of acquiring representative images by microscopy : the images may have been taken on particular zones non exposed to abrasion (potentially due to a superposition of another strand). During the experiment, an important number of images were done; the selected ones are therefore supposed to be representative of the situation.

Overall, the images indicate the obvious surface interactions and phenomena occurring to the PP filaments immersed in sea water. The microbial interaction is omnipresent and takes two forms : a powdery aspect covering the surface and a denser accumulation proliferating more favorably in cracks. Traces of mechanical efforts and abrasion are visible as well. S6 and S7 samples do not show evident sign of advanced degradation as expected. This might be due to the immersion period

being too short and the presence of anti-UV additives doing their part and protecting the filaments. It would be interesting to make new images of samples in a year or two to see the progression of the degradation in such a demanding environment. By comparing the two samples retrieved from the harbor of Marseille S2 and S3, it seems that the deeper one is less colonized by bacteria than the one at 1m depth. It might indicate that biofouling is more efficient in low depth environment. In parallel, by comparing S4 and S5 samples, higher exposition to fluxes seems to enhance biofouling the same way low depth environment is doing on Marseille's samples. By agitating water, fluxes might increase the probability for bacteria to encounter and fix on the polymer surface.

Mechanical analysis

This analysis has been made using an Instron 5566 A equipped with grip specific for filaments. The traction tests provided data about 4 qualities that are the Young's modulus, the strain (ε_b), the stress (σ_b) and the force (F) to rupture. The measured diameter of the filaments was constant and equal to 4000 µm. Figure 32 displays all the results of the mechanical analysis.

Sample	Diameter (µm)	Young's Modulus (MPa)	σ_b (MPa)	ε_b (%)	F (N)
S1	4000	947.2 ± 61.7	64.7 ± 4.5	9.5 ± 0.9	813.5 ± 56.4
S2	4000	787.4 ± 123.5	61.7 ± 8.4	9.5 ± 1.3	775.8 ± 105.0
S3	4000	819.9 ± 146.3	58.6 ± 18.3	10.0 ± 1.1	736.5 ± 230.5
S4	4000	1028.8 ± 74.3	69.8 ± 2.6	9.1 ± 0.8	877.3 ± 33.0
S5	4000	991.1 ± 39.3	59.1 ± 11.2	8.5 ± 1.0	743.0 ± 141.3
S6	4000	1011.1 ± 83.3	72.0 ± 4.1	9.7 ± 0.8	904.3 ± 51.8
S7	4000	1130,8 ± 47,8	76,6 ± 9,7	9,7 ± 0,7	962,5 ± 122,4

Figure 32 : Table of traction tests results

The hypothesis stated earlier in this document that polymer first plasticize after immersion then rigidify because of hydrolysis is contradictory to these results, or at least, not visible by the results. Indeed, the Young's modulus tends to evolve by first increasing : S6 and S7 are the samples that aged less timewise and they have the highest moduli of 1011.1 and 1130.8 MPa, respectively. The second less aged samples are S4 and S5 which display a Young's moduli of 1028.8 and 991.1 MPa, respectively. Those values are higher than the one retrieved form the unaged sample S1 (947.2 MPa). It indicates that the aged samples are more rigid than the unaged PP. However, the most aged samples S2 and S3 have given moduli of 787.4 and 819.9 MPa, respectively. Therefore, sample aged for 7 years proves to be more flexible than new sample. Looking at these results, it is incoherent to justify this by polymer degradation prior to plasticization. Plasticization must occur during the first months of immersion which makes it indetectable with the current samples. Subsequently, hydrolysis would rigidify the polymer. What is displayed here might be the sign of continuous degradation that at term involves a loss of rigidity from the polymer which decrease its Young's modulus. This degradation must have fragilized the integrity of the structure rendering it less rigid. Figures 33 and 34 illustrate these explanations by displaying the tendency of evolution of the Young's modulus. Figure 34 shows the descending evolution of the Young's modulus.
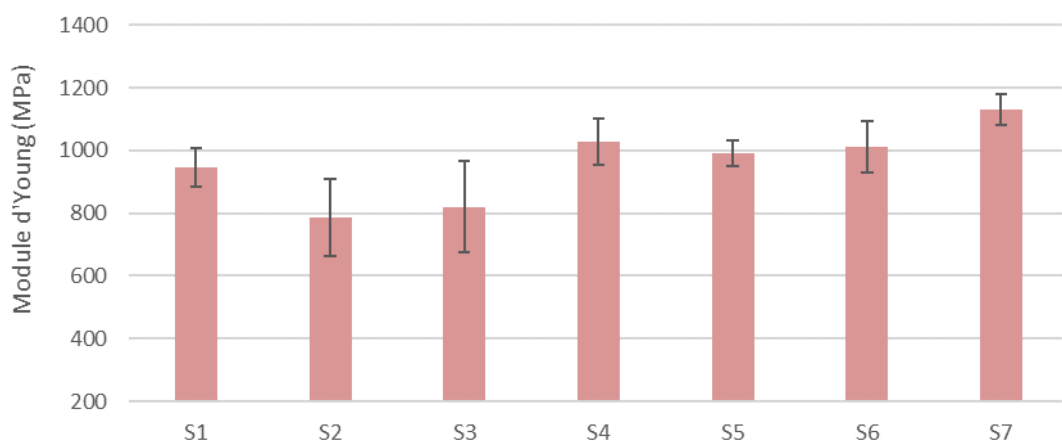

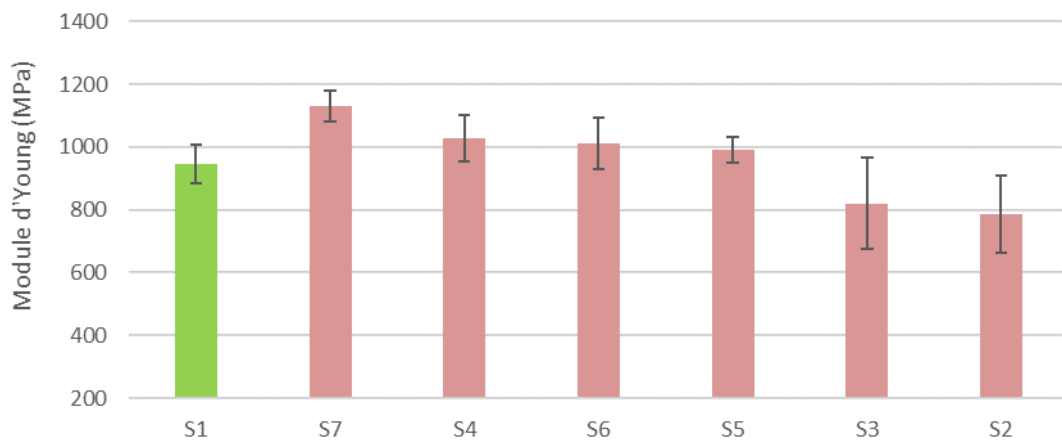*Figure 33 : Histogram representing the Young's modulus measured*

Figure 34 : Histogram representing the Young's modulus classified from highest to lowest

It is also possible to question the role of the biofouling in the mechanical degradation of the samples. Surely, macroscopic biofouling must have some impact on the samples. Since the samples originate from various locations with different biomes and environment, it is not possible to accurately assess the impact of bacterial presence. More importantly, the samples used for the traction tests are not completely dried as the standard sample S1 is. The presence of water must have an impact on the results. More analysis should be done with fully dried samples in order to obtain more conscientious results.

Overall, it seems that the mechanical properties of the polymer have not been altered to a great extent. The results indicate that the PP is sufficiently resilient in sea environment for its inherent characteristics to be conserved, even after 7 years of immersion. The greatest difference in Young's modulus was between S1 and S7 from the Bay of Arcachon with a 183.6 MPa difference (19.38 % increase). Similarly, the stress to rupture difference between S1 and S7 is a 18.39 % increase (from S1 to S7). This can be explained since a small difference is seen for the strain to rupture of samples (2.1 % increase from S1 to S7). Obviously, as $E = \sigma\varepsilon$, it is coherent to obtain approximately the same variation.

It is a good sign for Seaboost to see this relative low dispersion of the mechanical properties of their product. It proves that the Roselières is already able to sustain its

mechanical functions for at least 7 years in a relatively unexposed area. There is still an interest to see how the Roselières from Arcachon would evolve during the following years as it is still believed to present the highest number of degradation factors for the polymer.

Infrared spectroscopy analysis

IR spectroscopy is a strong analytical technique for studying the chemical composition of a component. Therefore, by comparing results with various samples, it gives information about the potential apparition of new species due to the ageing of PP. The spectroscopies have been made using the Bruker Vertex 70.

Figure 35 shows the spectroscopy of S1 sample, proving that the samples are indeed made of PP. Indeed, polypropylene is made of a rather simple structure shown on Figure 36 which make it identifiable studying only 3 peaks. The position of the peaks on the graph allow to identify the chemical groups of the sample studied. The red arrows on the specter exhibits the peaks in question. By using standard tables containing the known position of the peaks it is possible to identify the nature of the material :

- Peaks at 2950 cm^{-1} and 2920 cm^{-1} is a sign for the elongation of the $C-H$ bond originating from the alkyl groups - CH, - CH2 and - CH3.
- Peaks at 1458 cm^{-1} is a sign for the deformation of the $C-H$ bond originating from the alkyl groups - CH, - CH2 and - CH3.
- Peaks at 1376 cm^{-1} is a sign for the deformation of the $C-H$ bond originating from the alkyl group - CH3.

The presence of these peaks on the specter clearly shows that the samples are made of PP.
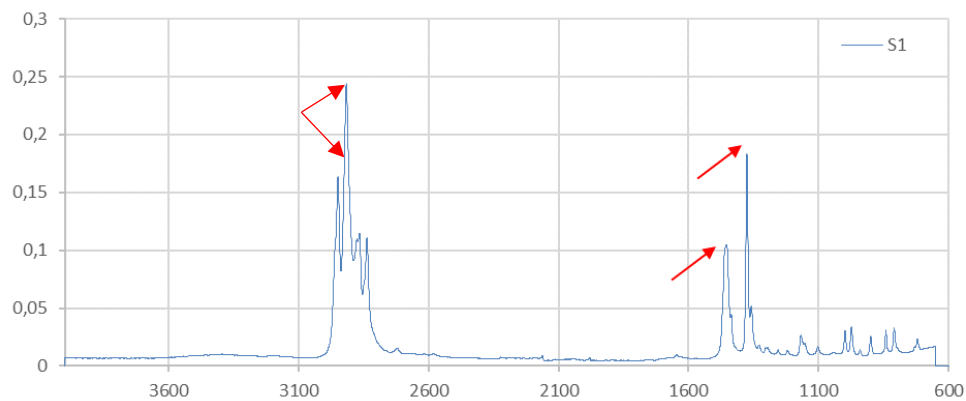
Figure 35 : IR spectroscopy of S1 sample
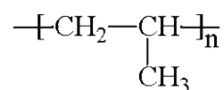
Figure 36 : Polypropylene formula

Figure 37 below shows the comparison of the specters of samples S1 and S2. The specters are significantly different. Undoubtedly, these differences are mainly caused by the remaining humidity in the sample S2 (and subsequently to all other samples except the standard one). This hypothesis is strongly supported by Figure 38 where the differences between sample S2 and S7 (aged in different environments) are less marked because they both have residual humidity.

Figure 37 : Superposed IR spectroscopies of S1 (blue) and S2 (red)

Figure 38 : Superposed IR spectroscopies of S2 (red) and S7 (green)

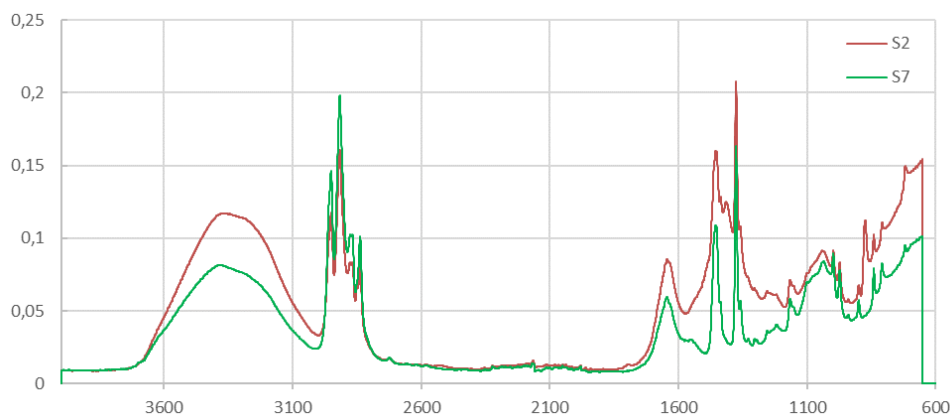Globally, the IR spectroscopies did not meet their expectations since they did not allow to conclude about the formation of new chemical groups originating from a potential degradation. Ensuring that the samples are all dry is a necessity to obtain exploitable results.

b. Outlook to the accelerated ageing on plastic samples

This suggestion of protocol for accelerated ageing of polymers could help to better understand the behavior of polymers in seawater in parallel to the results presented in this document. The objective is to participate to the elaboration of a model for the prevision of resilient polymers lifetime expectancy at sea. Comparison between the results presented here and the ones that may emerge from this protocol could indicate how good is the protocol in reproducing the natural ageing environment. The following protocol has been elaborated to study the polymer degradation while trying to consider most of the environmental factors for a plastic evolving at sea.

Protocol :

Certain polymers like polyethylene and propylene can last a long time before disappearing in an environment. As far as we know, this could take hundreds of years to integrally be assimilated by an ecosystem. Some actors of the protection of seas and oceans already retrieved polymer products that used to be sold 60 to 80 years ago (10), proving that these polymers degradation in sea water is extremely slow.

It has been shown that the degradation of polymers in hydraulic environment is significantly faster in distilled water because the sea water represent a complex environment of minerals, salts and microorganisms that hinder the physical and chemical degradation strictly due to the water presence (64). Therefore, it is interesting to immerge the samples in distilled water tanks to accelerate the ageing process.

The most key factor of degradation for accelerated ageing of polymers is the temperature of the environment. It has been proven many times that a higher environment temperature lead to a faster degradation (64). Elevating the temperature of the water around the polymer samples will accelerate the ageing process. It is therefore predictable that the most degraded samples, regardless of their nature, will systematically be the one in the hotter water tank. It is suggested to age the samples in water with temperature varying from 10 to 60 °C. The temperature serves here as a reference to qualify the advancement of the degradation of the polymer throughout the lifetime of usage. However, it is difficult to precisely make the transition between lifetime in controlled distilled water tanks and lifetime in natural marine environment. Such objective requires a study based on the principle of time-temperature superposition in concordance with the Arrhenius law. Yet, the data retrieved with this protocol can be compared to one presented in this thesis. The data will allow, by comparing the values, to relatively estimate the ageing stage of the accelerated aged polymers. Indeed, if the naturally aged polymer displays better properties than the accelerated aged one, we can argue that it has a better integrity and thus, can be consider at a lesser stage of degradation. It is a

precious information for Seaboost to obtain a range of idea for the estimated lifetime of a Roselière and more generally of plastic at sea. This comparison of results implies to use the same experimental methods (traction tests, IR spectroscopy and SEM) on the accelerated aged samples.

The samples will be immerged separately into water tanks presenting different controlled temperature. They will stay in immersion for 6 months with periodic checkpoints on the polymer state. The samples will periodically be taken out of the water tanks, dried and directly exposed for a certain amount of time to UV light in order to reproduce the tides period where *Roselières* will be out of water (if placed in inter-tidal zones). Similarly, the samples will periodically be exposed to sand abrasion in a compartment rotating on itself. The samples will be exposed to moving sand particles hitting the plastic surface. Subsequently, the samples will be immerged again in their respective water tanks.

After 2 months and 4 months, bits of samples will be taken and will undergo various tests to monitor the evolution of the degradation of the polymers. The overall time of ageing might vary according to the degradation kinetics of the samples. That way, it is expected to see an evolutive behavior of the samples as the ageing process goes. In parallel, one sample of each polymer will be tested after a natural ageing in free air after 6 months. This will provide us to compare the natural and inherent degradation of a polymer with any other sort of accelerated ageing.

It is suggested to add a gravimetrical analysis during all the ageing period. Gravimetrical analysis allows to precisely measure samples' masses. A series of measurements are made from the beginning to the end of the ageing period. The evolution of the sample's mass will indicate a quantity of lost matter from the polymer. This lost matter will be caused by micro or macro fragmentation of the polymer into the water. Additionally, mass difference will help to understand the kinetics of the water absorption phenomenon which is the cause of polymer degradation by hydrolysis. Therefore, a relation with the rate of hydrolysis can be studied. Moreover, by knowing the exact composition of the samples, it will also be

possible to see through the gravimetrical analysis, the potential leakage of additives from the polymer to the water. It is an important aspect of the gravimetrical analysis as it will be possible to assess the potential polluting threat that the immerged polymer can represent for the marine environment. A tree structure scheme can be found in Appendix 1 to help visualize the roles and objectives of each analysis.

Critical observations about this protocol :

Critically looking back at the protocol established for accelerated ageing of polymers, it is evident that the environmental conditions of ageing could be enhanced. To make it better, it would require to focus around the following problematic : what would be the best model conditions to reproduce ocean environment for the polymer degradation. Indeed, the study of the degradation of polymers in the sea requires to implement an ageing environment as representative as possible to the average natural conditions. Despite all the efforts made to duplicate this environment as precisely as possible, the samples would not age like they would normally do in the ocean. The equipment and machinery required would make the experiment difficult to make. It would require applying simultaneo usly all the degradation factors. For this reason, it is difficult to replicate the usual degradation middle that plastics in ocean have. The periodic cycle of exposure to UV should comply with the daily sunshine exposure outdoor. Similarly, the abrasion from sediment can happen continuously in a natural environment and is even more probable during tides. Additionally, the protocol in itself does not allow to study the influence of microbial degradation. As discussed previously, the water quality and the environmental variables defines the microbiotic population and efficiency. For many reasons including the non-salinity of the water, the absence of minerals and other molecules in the water (distilled water) and the temperature, implanted microbiomes would have abnormally behaved, thrive or in contrary, perish. This would have completely distorted the results of the experiment. A suggestion would be to establish a protocol

focused entirely on the study of the microbial impact in a separate tank containing water collected from a sea or an ocean. Yet, this would lead to an exceedingly long study as the ageing wouldn't be accelerated.

The additives leaching study could also have been enhanced by analyzing the water tanks after the ageing using gas phase pyrolysis. It would have allowed to precisely identify and quantify all the substances that have leached from the samples.

The chemical analysis could also have been improve using other analysis either complementary to the IR spectroscopy or in replacement. The use of both chromatography and mass spectroscopy like Matrix Assisted Laser Desorption Ionization - Time of Flight (MALDI-TOF) would have been interesting to identify and monitor not only the presence of chemical groups but also of the exact molecules and species composing the sample.

V. Conclusions

This thesis has presented experiments to better understand the longevity of polypropylene (PP) in sea water. Through various analyses including traction tests, IR spectroscopy and SEM imagery, the continuous degradation of PP in sea water has been studied under chemical, physical, optical, and mechanical scopes. Results from prolonged exposures spanning up to 7 years showed that PP is particularly resilient in European oceanic environment. However, even the most inert polymers will eventually degrade in marine environment. This justifies the importance of analyzing the polymeric chains that have been separated from the coarse polymer during the degradation in order to assess their toxicity for the marine biodiversity. There is also an interest in looking for additives molecules that might have been freed from the polymer during its degradation. These can also be toxic.

As temperature is a crucial factor for the degradation rate, there is an inherent need to provide data on the degradation of polymers in tropical waters. To partly answer this challenge, this thesis suggests an experimental protocol for accelerated ageing of polymers in water with the ability to adjust the water temperature. This suggestion does not act as a life expectancy model of polymers in water, but it can help to elaborate one by using and comparing the results found in this experiment with the one retrieved by the accelerated ageing protocol.

The retrieved data will, eventually, allow to propose durable and ecological solutions for the manufacturing of Roselière strands and can, more broadly, justify the seemingly contradictory idea that plastics might be used for the benefit of marine ecological engineering.

VI. References

1. ub. A scientific study reveals the most abundant type of microplastics in Mediterranean coastal waters - Universitat de Barcelona [Internet]. [cité 24 sept 2022]. Disponible sur: https://www.ub.edu/web/ub/en/menu_eines/noticies/2019/02/048.html

2. Dayton PK. Ecology of Kelp Communities. Annual Review of Ecology and Systematics. 1985;16:215-45.

3. Jones DL, Darrah PR. Role of root derived organic acids in the mobilization of nutrients from the rhizosphere. Plant Soil. oct 1994;166(2):247-57.

4. Dayton72_Understanding.pdf [Internet]. [cité 24 juill 2022]. Disponible sur: http://daytonlab.ucsd.edu/Publications/Dayton72_Understanding.pdf

5. Dayton75_amchitka.pdf [Internet]. [cité 24 juill 2022]. Disponible sur: http://daytonlab.ucsd.edu/Publications/Dayton75_amchitka.pdf

6. Ellison AM, Bank MS, Clinton BD, Colburn EA, Elliott K, Ford CR, et al. Loss of foundation species: consequences for the structure and dynamics of forested ecosystems. :8.

7. plastic pollution - Plastic pollution in oceans and on land | Britannica [Internet]. [cité 24 juill 2022]. Disponible sur: https://www.britannica.com/science/plastic-pollution/Plastic-pollution-in-oceans-and-on-land

8. The History of Ocean Pollution [Internet]. Ocean Generation. [cité 24 juill 2022]. Disponible sur: https://www.oceangeneration.org/blog/the-history-of-ocean-pollution

9. Heinrich-Böll-Stiftung B. Plastikatlas: Daten und Fakten über eine Welt voller Kunststoff. Heinrich-Böll-Stiftung, Berlin. 2019;

10. The Great Pacific Garbage Patch • The Ocean Cleanup [Internet]. [cité 24 juill 2022]. Disponible sur: https://theoceancleanup.com/great-pacific-garbage-patch/

11. Introduction - Global Plastic Navigator [Internet]. [cité 24 juill 2022]. Disponible sur: https://plasticnavigator.wwf.de/#/en/stories/?st=0&ch=0&layers=surface-concentration

12. Eriksen M, Lebreton LCM, Carson HS, Thiel M, Moore CJ, Borerro JC, et al. Plastic Pollution in the World's Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea. PLOS ONE. déc 2014;9(12):1-15.

13. Lebreton L, Andrady A. Future scenarios of global plastic waste generation and disposal. Palgrave Commun. déc 2019;5(1):6.

14. Lebreton L, Van Der Zwet J, Damsteeg JW, Slat B, Andrady A, Reisser J. River plastic emissions to the world's oceans. Nature communications. 2017;8(1):1-10.

15. Arthur C, Baker JE 1959-, Bamford HA. Proceedings of the International Research Workshop on the Occurrence, Effects, and Fate of Microplastic Marine Debris, September 9-11, 2008, University of Washington Tacoma, Tacoma, WA, USA. United States NOService Office of Response and Restoration, éditeur. 2009; Disponible sur: https://repository.library.noaa.gov/view/noaa/2509

16. Collignon A, Hecq JH, Glagani F, Voisin P, Collard F, Goffart A. Neustonic microplastic and zooplankton in the North Western Mediterranean Sea. Marine Pollution Bulletin. avr 2012;64(4):861-4.

17. Lithner D, Larsson Å, Dave G. Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. Science of The Total Environment. 15 août 2011;409(18):3309-24.

18. Shah AA, Hasan F, Hameed A, Ahmed S. Biological degradation of plastics: A comprehensive review. Biotechnology Advances. 1 mai 2008;26(3):246-65.

19. İpekoğlu B, Böke H, Çizer Ö. Assessment of material use in relation to climate in historical buildings. Building and Environment. 1 févr 2007;42(2):970-8.

20. Sivan A. New perspectives in plastic biodegradation. Current Opinion in Biotechnology. 1 juin 2011;22(3):422-6.

21. Bonhomme S, Cuer A, Delort AM, Lemaire J, Sancelme M, Scott G. Environmental biodegradation of polyethylene. Polymer Degradation and Stability. 1 janv 2003;81(3):441-52.

22. Ghosh SK, Pal S, Ray S. Study of microbes having potentiality for biodegradation of plastics. Environ Sci Pollut Res. 1 juill 2013;20(7):4339-55.

23. Tokiwa Y, Calabia BP, Ugwu CU, Aiba S. Biodegradability of Plastics. International Journal of Molecular Sciences. sept 2009;10(9):3722-42.

24. Priyanka N, Archana T. Biodegradability of Polythene and Plastic By The Help of Microorganism: A Way for Brighter Future. J Environment Analytic Toxicol [Internet]. 2011 [cité 24 juill 2022];01(02). Disponible sur: https://www.omicsonline.org/biodegradability-of-polythene-and-plastic-by-the-help-of-microorganism-a-way-for-brighter-future-2161-0525.1000111.php?aid=2984

25. T A. R63 La dégradation des plastiques en mer, par C. Dussud et J-F. Ghiglione [Internet]. sfecologie.org. [cité 24 juill 2022]. Disponible sur: https://sfecologie.org/regard/r63-plastiques-en-mer-dussud-et-ghiglione/

26. Ahmed T, Shahid M, Azeem F, Rasul I, Shah AA, Noman M, et al. Biodegradation of plastics: current scenario and future prospects for environmental safety. Environ Sci Pollut Res. 1 mars 2018;25(8):7287-98.

27. Ho KLG, Pometto AL, Hinz PN. Effects of Temperature and Relative Humidity on Polylactic Acid Plastic Degradation. Journal of Polymers and the Environment. 1 avr 1999;7(2):83-92.

28.   Kale G, Kijchavengkul T, Auras R, Rubino M, Selke SE, Singh SP. Compostability of bioplastic packaging materials: an overview. Macromol Biosci. 8 mars 2007;7(3):255-77.

29.   Yamada-Onodera K, Mukumoto H, Katsuyaya Y, Saiganji A, Tani Y. Degradation of polyethylene by a fungus, Penicillium simplicissimum YK. Polymer Degradation and Stability. 1 mai 2001;72(2):323-7.

30.   Skariyachan S, Manjunatha V, Sultana S, Jois C, Bai V, Vasist KS. Novel bacterial consortia isolated from plastic garbage processing areas demonstrated enhanced degradation for low density polyethylene. Environ Sci Pollut Res. 1 sept 2016;23(18):18307-19.

31.   Kowalczyk A, Chyc M, Ryszka P, Latowski D. Achromobacter xylosoxidans as a new microorganism strain colonizing high-density polyethylene as a key step to its biodegradation. Environ Sci Pollut Res. 1 juin 2016;23(11):11349-56.

32.   Mahdi M, Ameen R, Ibrahim H. International Journal of Advanced Research in Biological Sciences Study on Degradation of Nylon 6 by thermophilic bacteria Anoxybacillus rupiensis Ir3 (JQ912241). 1 janv 2016;200-9.

33.   Accueil [Internet]. Algopack. [cité 24 juill 2022]. Disponible sur: https://www.algopack.com/

34.   Vijaya C, Reddy RM. Impact of soil composting using municipal solid waste on biodegradation of plastics. INDIAN J BIOTECHNOL. 2008;5.

35.   An Overview of Polylactides as Packaging Materials - Auras - 2004 - Macromolecular Bioscience - Wiley Online Library [Internet]. [cité 24 juill 2022]. Disponible sur: https://onlinelibrary.wiley.com/doi/abs/10.1002/mabi.200400043

36.   Stevens ES. WHAT MAKES GREEN PLASTICS GREEN? 2003;4.

37.   Compostability of polymers - Kijchavengkul - 2008 - Polymer International - Wiley Online Library [Internet]. [cité 24 juill 2022]. Disponible sur: https://onlinelibrary.wiley.com/doi/abs/10.1002/pi.2420

38.   Tokiwa Y, Calabia BP. Review Degradation of microbial polyesters. Biotechnology Letters. 1 août 2004;26(15):1181-9.

39.   Reddy MM, Deighton M, Gupta RK, Bhattacharya SN, Parthasarathy R. Biodegradation of oxo-biodegradable polyethylene. J Appl Polym Sci. 5 févr 2009;111(3):1426-32.

40.   Albertsson AC, Andersson SO, Karlsson S. The mechanism of biodegradation of polyethylene. Polymer Degradation and Stability. 1 janv 1987;18(1):73-87.

41.   Chiellini E, Corti A, D'Antone S, Baciu R. Oxo-biodegradable carbon backbone polymers – Oxidative degradation of polyethylene under accelerated test conditions. Polymer Degradation and Stability. 1 nov 2006;91(11):2739-47.

42.   Scott G, Wiles DM. Programmed-life plastics from polyolefins: a new look at sustainability. Biomacromolecules. 2001;2(3):615-22.

43.   Orr IG, Hadar Y, Sivan A. Colonization, biofilm formation and biodegradation of polyethylene by a strain of Rhodococcus ruber. Appl Microbiol Biotechnol. juill 2004;65(1):97-104.

44.   Kawai F, Watanabe M, Shibata M, Yokoyama S, Sudate Y. Experimental analysis and numerical simulation for biodegradability of polyethylene. Polymer Degradation and Stability. 1 janv 2002;76(1):129-35.

45.   Kawai F, Watanabe M, Shibata M, Yokoyama S, Sudate Y, Hayashi S. Comparative study on biodegradability of polyethylene wax by bacteria and fungi. Polymer Degradation and Stability. 1 oct 2004;86(1):105-14.

46.   Our Performance Additives | Smart Plastic [Internet]. [cité 24 juill 2022]. Disponible sur: https://www.changetheplastic.com/additives

47.   Plastics in Medical Devices for Cardiovascular Applications - 1st Edition [Internet]. [cité 24 juill 2022]. Disponible sur: https://www.elsevier.com/books/plastics-in-medical-devices-for-cardiovascular-applications/padsalgikar/978-0-323-35885-9

48.   Botkin JH. Light stabilization of polypropylene: an independent perspective. In: Society of Plastics Engineers International Polyolefins Conference, Houston, TX. 2007.

49.   Young A. Chromophores in human skin. Physics in medicine and biology. 1 juin 1997;42:789-802.

50.   Tolinski M. Additives for Polyolefins: Getting the most out of Polypropylene. Polyethylene and TPO. 2015;177-82.

51.   Mara J, Kim S, Jung DS, Bayer J, Keck K. Benzoates as UV stabilization strategies for polyolefins. Society of Plastics Engineers - International Polyolefins Conference - FLEXPACKCON 2008. 1 janv 2008;1:581-95.

52.   Fay JJ, King RE III. Degradation and Stabilization of Polyethylene. In: Handbook of Industrial Polyethylene and Technology [Internet]. John Wiley & Sons, Ltd; 2017 [cité 24 juill 2022]. p. 751-69. Disponible sur: https://onlinelibrary.wiley.com/doi/abs/10.1002/9781119159797.ch25

53.   Solera P. Weathering and light stabilization of select plastic materials. Annual Technical Conference - ANTEC, Conference Proceedings. 1 janv 2007;3:1318-22.

54.   Soutelo-Maria A, Dubois JL, Couturier JL, Cravotto G. Oxidative Cleavage of Fatty Acid Derivatives for Monomer Synthesis. Catalysts. oct 2018;8(10):464.

55.   Porte L. Battleground Manufacturing Complex. :3.

56.   PhysicalGeography.net Welcome Page [Internet]. [cité 24 juill 2022]. Disponible sur: http://www.physicalgeography.net/home.html

57.   Min K, Cuiffi JD, Mathers RT. Ranking environmental degradation trends of plastic marine debris based on physical properties and molecular structure. Nat Commun. 5 févr 2020;11(1):727.

58.   Muhandes H, Kalácska Á, Székely L, Keresztes R, Kalácska G. Abrasive Sensitivity of Engineering Polymers and a Bio-Composite under Different Abrasive Conditions. Materials. janv 2020;13(22):5239.

59.   de Jager M. An analysis of soil properties associated with badland and gully erosion in rural catchments of the Ngqushwa District, Eastern Cape Province. 2015.

60.   Allin SB. Introduction to Physical Polymer Science, 3rd Edition (Sperling, L. H.). J Chem Educ. 1 nov 2001;78(11):1469.

61.   Chen T, Fowler A, Toner M. Literature Review: Supplemented Phase Diagram of the Trehalose–Water Binary Mixture. Cryobiology. 1 mai 2000;40(3):277-82.

62.   Hancock BC, Zografi G. The relationship between the glass transition temperature and the water content of amorphous pharmaceutical solids. Pharm Res. avr 1994;11(4):471-7.

63.   Phuong NN, Poirier L, Pham QT, Lagarde F, Zalouk-Vergnoux A. Factors influencing the microplastic contamination of bivalves from the French Atlantic coast: Location, season and/or mode of life? Marine Pollution Bulletin. 1 avr 2018;129(2):664-74.

64.   Deroine M. Étude du vieillissement de biopolymères en milieu marin. 2014;255.

VII.   Appendice

Appendix 1 : Tree structure of the analysis objectives and roles