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INSIGHTS INTO THE NATURAL DEGRADATION RATE OF PLASTICS IN THE SEAWATER ENVIRONMENT AND THEIR DEGRADATION BY-PRODUCTS

(PHTHALATES AND BISPHENOL A)

BY

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ABSTRACT

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Title: Insights into the Natural Degradation Rate of Plastics in the Seawater Environment and their Degradation By-Products (Phthalates and Bisphenol A)

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Most plastics end up in the oceans. Their chemical additives that leach out into the ocean can be detrimental to humans and animals. This study investigates the degradation-fragmentation of different plastic types for 140 days in extreme environments, using fourier-transform infrared spectroscopy and scanning electron microscopy with energy-dispersive X-ray analysis along with weight loss and degradation rate calculations. Seawater samples used for the investigations were analysed using gas chromatography–mass spectrometry to examine three different phthalates and bisphenol A (BPA). Findings showed that microplastics degraded faster than macroplastics. The degradation behaviour of plastics varied depending on type and size. High-density polyethylene and polyethylene degraded faster under outdoor onshore conditions, while other types showed higher degradation under outdoor marine conditions. Dibutyl phthalate (DBP), Bis(2-ethylhexyl) phthalate (DEHP), and BPA were detected in seawater samples. Wave abrasion promoted the leaching of DEHP and DBP, while temperature and light promoted the leaching of DEHP.

DEDICATION

This thesis is dedicated to my parents, Nejib Dimassi and Monia Bouzouita Dimassi, my continuous source of strength, support, and encouragement. This work is also dedicated to my beloved brothers, Ala and Yassine Dimassi, who have always loved me unconditionally.

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CHAPTER 1: INTRODUCTION

Plastics are one of the most fundamentally used materials worldwide due to their attractive physicochemical properties and characteristics, which include resistance to resistance, levity, and inexpensive transparent material. In addition, it does not require high maintenance. All these valuable properties help in facilitating the implementation of plastics into various activities including agricultural, mercantile, and industrial activities (Ali et al., 2021; Amobonye et al., 2021; Jenkins and Harrison, 2008). Unlike other types of solid materials, plastics have gained the ultimate attention due to their extreme durability and stability, which are generated mainly by their polymeric structure (Rivard et al., 1995). Nevertheless, like any material, plastics have their disadvantages. The main challenge in using this desired material is its degradability since the majority of plastics are non-degradable and their complete decomposition in landfills may take centuries to occur. These previously mentioned facts elucidate the global current situation of plastic waste (PW) accumulation in the environment (Ali et al., 2021; Barnes et al., 2009; Matjašič et al., 2021). In addition, conventionally used monomers for synthesizing polymers of plastics such as propylene and ethylene are usually invented from fossil hydrocarbons. Moreover, their polymeric properties boost their resistance to being degraded microbially, and even their short-term existence in nature obstructs the production of innovative enzymes, which may have the capability to degrade common polymers (Amobonye et al., 2021; Mueller, 2006).

In the 1940s and 1950s, plastics production started blooming due to the dramatic increase of industrialization, leading to a tremendous universal annual production which was projected to reach 367 million metric tons by 2020 (Tiseo, 2021). However, due to Coronavirus (COVID-19), plastic production declined by approximately 0.3% when compared to the previous year (Tiseo, 2021). Presently, the most dominantly used types of plastics in the market are mainly thermoplastics, such as polyvinyl chloride (PVC), polypropylene (PP), high-density polyethylene (HDPE), and low -and linear low-density polyethylene (LDPE and LLDPE). Besides, other commercially demanded plastics such as polystyrene (PS), polyurethane (PU), and polyethylene terephthalate (PET) (Ali et al., 2021; Gewert et al., 2015; Hahladakis et al., 2018; PlasticsEurope and Group, 2008). Plastics including PVC, polyethylene (PE), PP, and PS are generated from C-C backbone polymers, which exemplify 77% of the global market share. On the other hand, heteroatomic polymers (e.g., C-O backbone polymers), which are mainly PU and PET account for around 18 % of the total sales in the plastics market (Ali et al., 2021; Danso et al., 2019; Gewert et al., 2015). The major universal challenge regarding the C-C backbone polymeric structure is its resistance to biodegradation, hydrolysis, and vulnerability to thermal oxidation (Ali et al., 2021; Krueger et al., 2015). However, polymers, which are heteroatomically structured can be possibly degraded via hydrolysis, photo-oxidation, and biodegradation (Gewert et al., 2015). **Figure** 1 illustrates these main types of plastics and their structure-based classification.

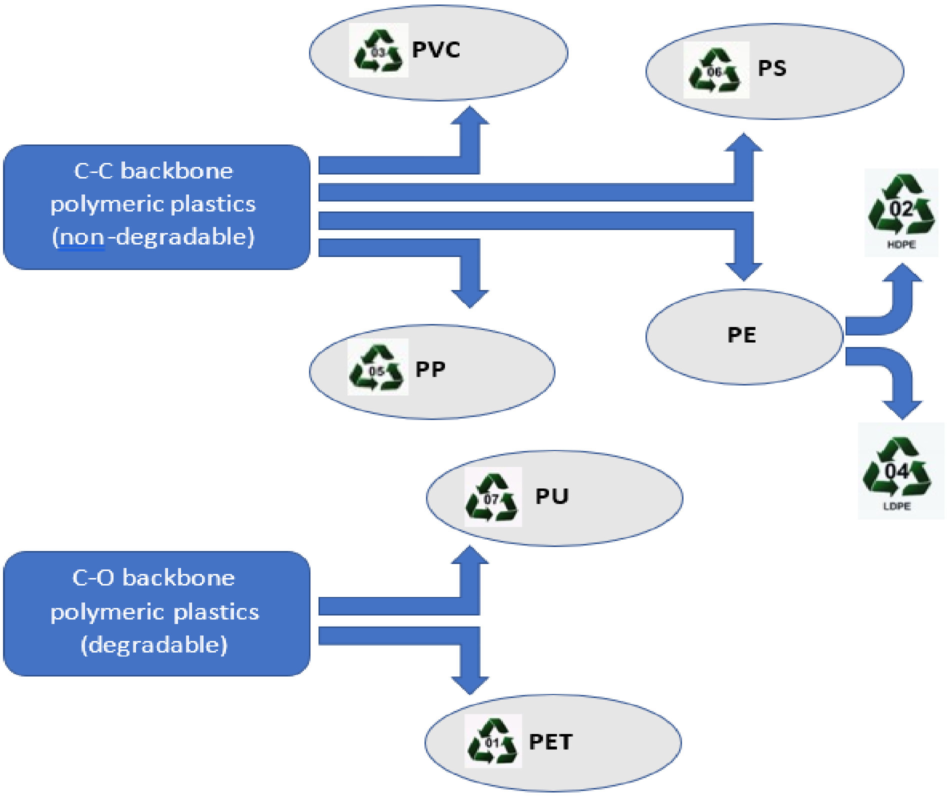


Figure 1. Most Utilized Plastic Types and their Structure-Based Categorization.

Plastic polymers (PPos) usage is not restricted to commercial consumer products but is also used in plentiful applications such as foams, synthesized fibers, adhesives, and coatings (Engelhart, 2010); Hahladakis et al. (2018). The usage of plastics in Europe is generated from various sectors, predominantly from the packaging process, then the construction sector, followed by automotive, electronics, and several other sectors (PlasticsEurope and EPRO, 2008). The excessive use of plastics generates huge amounts of PWs. The universal plastic manufacture was projected to surpass 8.3 billion metric tons from 1950 to 2018, with an annual increase of 5%, which is around 185 million tons of plastics (Ali et al., 2021; Amobonye et al., 2021; Geyer et al., 2017; Jambeck et al., 2015). Nevertheless, about 76 % of these manufactured plastics end up as PW which will be further landfilled or emitted into the environment (72%), recycled

(14%), and combusted (14%) (Ali et al., 2021; Schulze, 2016). Thus, PWs accumulation will pollute the environment and continuously pose an environmental threat, whilst impacting public health and natural ecosystems (Shah et al., 2008). Moreover, the inadequate disposal of PWs coupled with an impoverished waste management infrastructure and insufficient implementation of recycling technologies which is mainly due to a lack of public awareness has proved PWs to be a leading component of marine debris (Hahladakis, 2020). Furthermore, there are multidimensional environmental impacts of terrestrial PWs. However, this plastic litter will eventually end up in the oceans since it is the ultimate sink in our globe (Jambeck et al., 2018; Jambeck et al., 2015).

Plastic materials may be categorized into three groups depending on the size of the particles. Plastics with a size of more than 5 mm are classified as “macroplastics” (Axelsson and van Sebille, 2017). In turn, plastics can potentially undergo degradation and fragmentation processes under various environmental abiotic conditions, e.g., UV light, pH, salinity, and temperature. These processes will lead to tinier pieces of plastics known as “microplastics” which are ranged between 50 μm and 5 mm (Andrady, 2011; Kalogerakis et al., 2017; Wang et al., 2016). The last category of plastics is the “nanoplastics” which are usually characterized by being lesser than 100 nm in particle size (Hahladakis, 2020; Koelmans et al., 2015). Microplastics (MPs) and nanoplastics (NPs) are deemed to be the most deleterious to humans and living organisms. Particularly when present under marine conditions owing to numerous complications, such as the ease of their ingestion by several species (Browne et al., 2008; Hahladakis, 2020; Steer et al., 2017; Teuten et al., 2009), and the release of chemical compounds embedded in the polymers (known as additives) that occurs during the degradation-fragmentation of bigger particles. Moreover, any potential accumulation of these fine pieces is a major concern since they are characterized as persistent organic pollutants (POPs) that will further burden humans, living organisms (especially marine), and the environment, considering the potential carcinogenicity of the chemicals they bear (Chen et al., 2019b; Hahladakis, 2020; Hahladakis et al., 2018; Koelmans et al., 2013). Currently, there is no effective environmentally friendly technique which is used to treat PW. However, various reports highlighted the prospective microbial degradation of PWs (Ali et al., 2021; Sarkhel et al., 2019; Yoshida et al., 2016; Zhang et al., 2020). The biodegradation process of plastics in the marine environment involves microorganisms since they are efficient in the degradation of several synthetic polymers such as LDPE, PP, LLDPE, and HDPE. In addition, recent studies included novel isolated microbes, which can effectively degrade PWs in the marine environment, as well as some innovative concepts in which specific enzymes can be cloned to support the degradation and enhance the efficiency (Anjana et al., 2020; Premraj et al., 2004). There are many factors, which affect the degradation and fragmentation process of PW under marine conditions including, but not limited to the polymer characteristics (e.g., high molecular weight, hydrophobicity, and structure). All of these characteristics inhibit its accessibility to microorganisms (Anjana et al., 2020; Hadad et al., 2005). In addition to the effect of the marine environmental conditions, which are biotic (e.g., enzymes which are secreted by microbes, and hydrophobic characteristics of the polymer) and abiotic factors (e.g., UV, temperature, salinity, and pH) (Ahmed et al., 2018; Anjana et al., 2020). Moreover, there are some additional dynamic factors related to the plastic additives which can influence the degradation of PW such as crystallinity, high molar mass, chain configuration, functional group types, and molecular orientation (Anjana et al., 2020; Min' et al., 2015).

OBJECTIVES

The objectives of this study are:

i) To investigate the degradation and fragmentation of plastics in the marine environment under various experimental conditions (onshore/nearshore litter condition and marine litter condition),

ii) To inspect the complication and/or leaching caused by the presence of several additives embedded in plastics, to examine the effect of the various properties of the plastic types (e.g., durability, flexibility, lightweight) on the overall degradation/fragmentation procedure, and to characterize the different plastic samples by using Fourier-transform infrared spectroscopy (FTIR) analysis and scanning electron microscope coupled with energy dispersive X-ray (SEM-EDX) analysis to compare between the degradation rates of onshore/nearshore and marine plastic litter.

iii) To characterize the different water solutions (organic leachate) used during the experiments by utilizing gas chromatography coupled with mass spectrometry (GC-MS) analysis.

RESEARCH QUESTIONS

1. How do marine environmental conditions affect the degradation and fragmentation of PW?
2. How does the size of PW affect the degradation process?
3. Which are the additives/chemical substances that leached out from PW?

WORKING HYPOTHESIS

- **Hypothesis 1:** the degradation and fragmentation of plastic materials will differ based on size, and polymer type.
- **Hypothesis 2:** there is no leachable chemical substance after the completion of the experimental period set for investigating the fragmentation of the different plastic materials.
- **Hypothesis 3:** there is a difference between the degradation-fragmentation rates of onshore/nearshore and marine plastic litter.

NOVELTY OF THE WORK

The novelty of this work is mainly investigating the natural degradation-fragmentation of macro- and microplastics under the harsh environmental conditions of Qatar. In addition, it looks at combining two different experimental factors which are onshore/nearshore conditions (e.g., natural sunlight), and marine litter conditions (e.g., natural sunlight with luminance and temperature measurement (approximately every 1 hour during the 24 hrs of the day), and mechanical stirring to simulate the wave abrasion), while taking into consideration several types of plastics (6 different PPos) with a variety of sizes, 2 major size categories were investigated with different sub-categories. While some previous studies used artificial seawater or deionized water to investigate the degradation of plastics, this work was done by, using actual seawater samples collected from Qatari seawater. All the aforementioned investigations were executed coupled with the characterization of the plastic leachate by analysing the various experimental water samples (after the experimental duration). This work provides valuable insights into the leaching behaviours of phthalates and bisphenol A from macroplastics and MPs in the seawater environment, which is currently understudied.

Figure 2 shows the relationship between the degradation of PWs and the variables of the study.

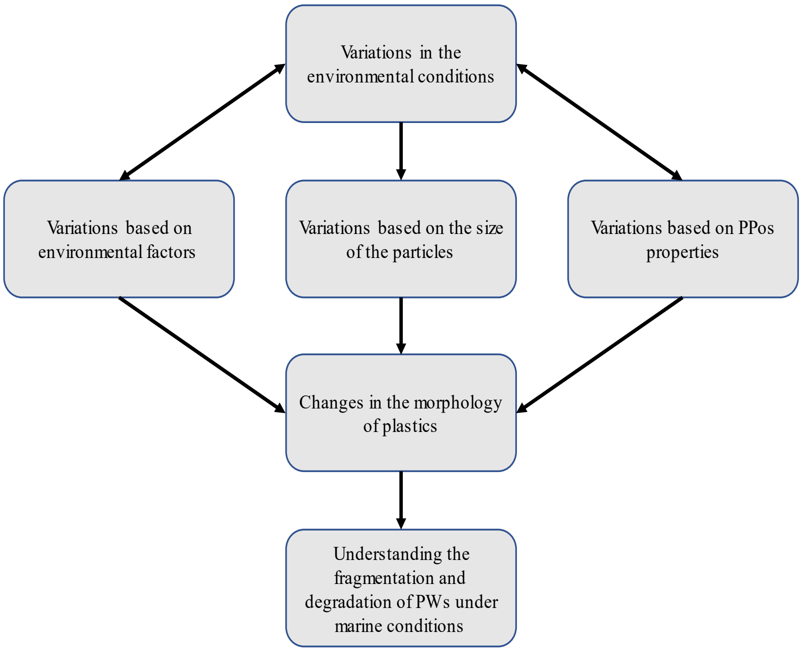


Figure 2. Understanding the Relationship Between the Degradation of PWs and the Variables of the Study.

PROBLEM STATEMENT

Nowadays, plastic materials are used in almost every single product, due to their various valuable properties of these materials including their flexibility, durability, and lightness in weight. This universal increase over the previous 60 years is mainly due to the global need of the economy. Nevertheless, the inappropriate disposal of these products, the poor waste management strategy, and the lack of recycling techniques have created extremely large amounts of PW littering the terrestrial and marine environment, leading to multidimensional impacts. In the past decade, the marine PW challenge has gained considerable attention. There are multiple reports and ongoing projects, which render this problem to be misinterpreted regarding the environmental and marine impacts of plastic litter, leading to misinterpretation of their associated human health impacts, which needs scientific and critical reasoning. Evaluating the duration in which a plastic material can resist before its degradation is one of the major challenges in this century. Therefore, the proper disposal needs to be in an acceptable condition. Once PWs go into the marine ecosystems, the behaviour of this plastic material is mainly determined through its density compared to the seawater density which determines whether these PW sink or float. PPos degradation depends on the nature of the polymers and the environmental conditions to which they are exposed (Karamanlioglu et al., 2017; Oliveira et al., 2020). In addition to the leaching of chemical plastic additives and substances from marine PW such as endocrine-disrupting chemicals (EDC), bisphenol A (BPA), and phthalates which can be found in plastic containers, all can potentially result in adverse effects and harm all living organisms including human especially if these chemicals are carcinogenic (Chen et al., 2019a; Hahladakis et al., 2018). The extensive use of these plastics creates enormous amounts of PWs in the terrestrial environment, which eventually end up in marine ecosystems (Jambeck et al., 2018; Jambeck et al., 2015). As a result, impact marine biota and human health via food chains due to the bioaccumulation of these additives and harmful chemical substances embedded within the plastics, which end up in marine organisms (Shah et al., 2008). In addition, the marine environmental conditions (e.g., sunlight, temperature, oxygen availability, mechanical string) can highly influence the PWs and lead to their fragmentation and degradation.

CHAPTER 2: LITERATURE REVIEW

2.1 Major sources of marine PW

PW can be originated from various pathways, but it ends up in seas. **Figure** 3 illustrates the main sources of marine PW. Plastic waste can be either dumped from ships, disposed of directly into oceans, driven by wind, or tapped into fishing nets (Hahladakis, 2020). In addition, rivers are deemed to considerably contribute to the carrying process of plastic litter. Since projections show that around 8Mt of the total annual quantity of plastics flows into the oceans, approximately 80% of this amount is driven from land sources (Jambeck et al., 2015). Some research papers mentioned that, in 2015, about 6.2 Mt of macroplastics and around 3.0 Mt of MPs were mainly discharged into the environment due to the mismanagement of the solid waste collected by the municipality (Ryberg et al., 2019). A recent research paper approximated a computation of the quantity of plastic litter which is carried by 57 distinct universal rivers (Schmidt et al., 2017). The findings illustrated that approximately 10 rivers could be responsible for 88 to 95 percent of this transportation, which are the Indus, Amur, Ganges, Yellow, Hai he, Pearl, Mekong, Nile, Niger, and Yangtze (Schmidt et al., 2017). However, this does not certainly mean that 90% of the entire amount of plastic litter, which exists in the ocean water, originates from the aforementioned rivers. The result of this study indicates the huge impact of rivers on the marine plastic waste challenge around the globe. It can also be helpful by the fact that these regions need to be targeted due to the absence of suitable management of the waste. Therefore, even though rivers are the main source of marine waste, there is no available scientific evidence, which supported that (Kershaw, 2016); thus, other marine polluting sources should not be underestimated or disregarded. Most of the plastics which adversely impact our oceans are influenced mainly by societal behaviors including both sea and land wastes. In addition to their impact due to the active waste-generating systems (Horton et al., 2017). Overall, each sector plays a crucial role in pollution through different ways including poorly disposed of land waste, dumping sites, abandoned landfills, plastic litter generated from several activities (e.g., fishing), and leakage from ships (UNEP, 2016a). As studies, keep developing the main sources of PW in the marine environment will soon be confirmed and categorized based on the quantity of contribution. Meanwhile, actions taken by individuals are extremely necessary in addition to the governmental measures regarding this universal challenge.

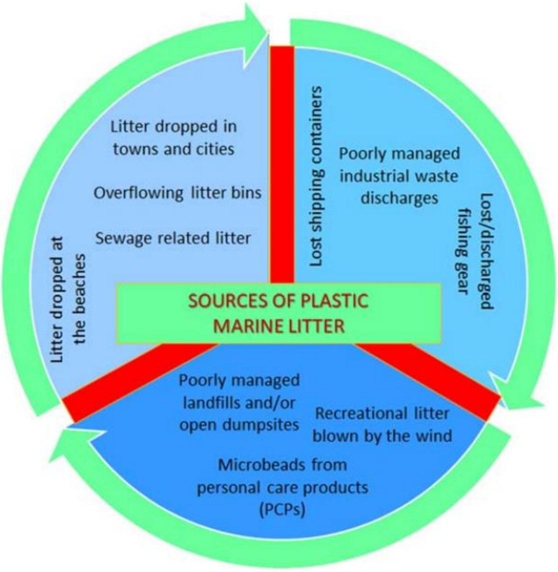


Figure 3. Various Sources of Plastic Marine Litter; Source: (Hahladakis, 2020).

2.2 Plastic accumulation and its environmental implications

2.2.1 Marine plastic litter accumulation and their overall impacts

According to several projections, starting from 2020, over 400 Mt of PW will be generated annually, and the production of plastics which are estimated to reach double by 2035 with an amount of 800 Mt and reach 1600 Mt by 2050 (Barra and Leonard, 2018). In addition, the production of plastics generates massive quantities of destructive gaseous into air such as dioxins, carbon monoxides, hydrogen cyanides, and nitrogen oxides, which creates a critical threat to human well-being and the environment. For instance, it was stated that the trace gases generated from the LDPE's increased in their intensity while incubating for 212 days and it reaches around 5.8 nmol of CH_4 per g per day, 3.9 nmol of ethane per g per day, 9.7 nmol propylene per grams per day, and 14.5 nmol ethylene per grams per days. In addition, findings show that the emission rates of LDPE's are approx. 2 times more for CH_4 and 76 times more for ethylene while incubating samples in the air rather than water (Royer et al., 2018). Therefore, it is important to emphasize that plastics could be a hidden source, which contributes to climate change due to these trace gases, which are estimated to rise with the increase of plastic fabrication and its environmental accumulation.

Regarding the disposal of plastics (**Figure** 4), from 1950 to 2018 around 6.3 billion metric tons of overall plastic manufacturing were discarded as trash, and over 4 billion tons have been only single utilized before its elimination (Geyer et al., 2017). Furthermore, around 4.5 billion tons of the overall produced PWs end up landfilled and/or released into the environment. Thus, it will adversely affect the soil microbial diversity since it was reported that landfills are potentially affecting soil infertility due to the extremely long duration (e.g., over 500 years) required for the complete decomposition of plastics (Chamas et al., 2020). In addition, the degradation of PW can potentially lead to the release of various contaminants (Webb et al., 2013). In the biodegradable plastics case, there are several microorganisms (e.g., Pseudomonas sp. and flavobacteria), which can effectively speed up the biodegradation of these PW when they are landfilled by breaking down their structure using various enzymes (Negoro, 2000).

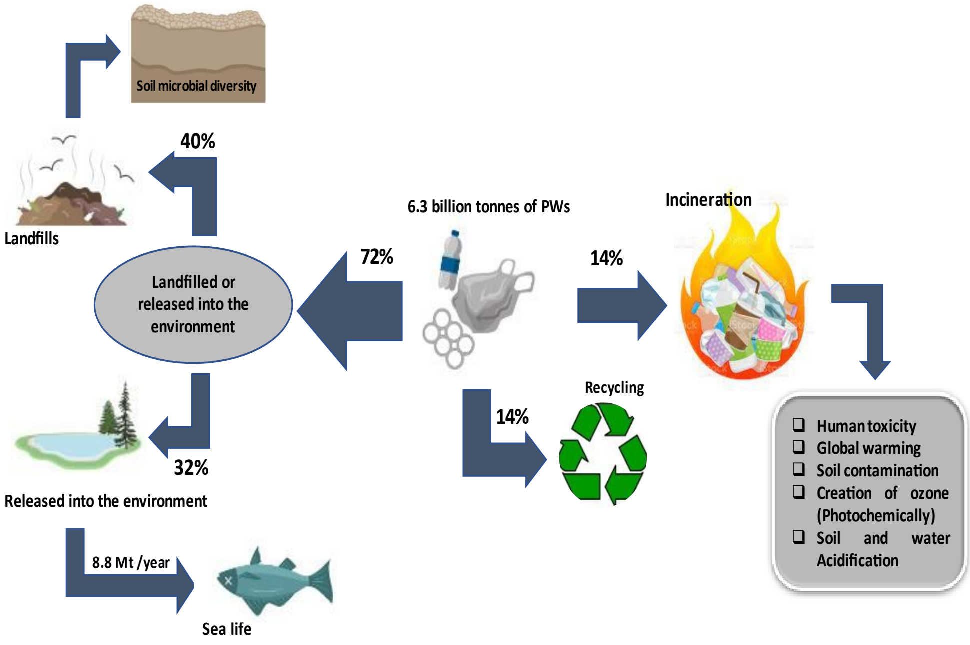


Figure 4. PW and their Environmental Impact.

Due to industrialization, plastics production started blooming in the mid-50s, leading to a huge universal annual production which was projected to reach 367 million metric tons by 2020 (Tiseo, 2021). Plastics are suitable for several applications including being an excellent packaging material because of their various properties such as lightweight and potentially transparent material, their low cost, and their outstanding property as oxygen and/or moisture barrier. Other common materials including glass, paper, and metal are being substituted by cost-efficient packaging made of plastic. Almost a third of the generated plastics are thus transformed into packaging materials including single-use items which are generally found in beach litter (Andrady, 2003). Many types of plastics are utilized in packaging such as PET, PS, PE, PVC, and PP. Their high utilization is well reflected in their manufacturing percentages as shown in **Table** 1, and therefore, these plastic types particularly will, potentially, end up in aquatic ecosystems. Moreover, overfishing, and recreational uses of the sea, as well as the demographic variations by immigrating to the coastal zones, will potentially rise the flow of PWs into the marine environment (Ribic et al., 2010). PW, which is mainly land sourced, contributes around 80% of the overall plastic debris. All universal fishing fleets are using plastic gear nowadays (Watson et al., 2006), and most of this gear is consistently lost or even carelessly disposed of in oceans during their usage. The most used plastics in fishing gear applications are polyolefins mainly; PE and PP, in addition to nylons (Klust, 1982; Timmers et al., 2005). Therefore, around 18% of the PW which is found in aquatic ecosystems is mainly generated from fishing activities, as well as aquaculture which can considerably contribute to the PW in marine ecosystems (Hinojosa and Thiel, 2009). The rest of the plastic litter is generated from land-based sources including beach waste. The quantification of the floating plastic litter does not reflect the real amounts of PWs in the ocean since the plastic debris which is located in the sediment and the middle of the seawater is not included by using this method. The debris' visibility while floating needs the plastic to be buoyant in the seawater. Nevertheless, only some of the plastics, which are utilized in marine, have a specific gravity, which is less than the seawater (the average specific gravity of seawater is approximately 1.025). In addition, the specific gravidities of these various plastics products can be altered due to the fillers and other additives. Therefore, denser plastics including nylons have the tendency to be submerged in the water columns and sometimes even reach the coastal sediments (Andrady, 2011).

Table 1. Plastics that are Frequently Found in the Aquatic Ecosystems.

Plastic-type	Production (%) *	Products and conventional origin
LDPE, LLDPE	21%	Bottles, plastic bags, nets, straws
HDPE	17%	Jugs (for milk, juice, and water)
PP	24%	Nets, ropes, bottle caps
PS	6%	Containers for food, plastic equipment, and tools
PET	7%	Bottles for beverages
PVC	19%	Cups, bottles, films

* % of the universal production of plastics in 2007 (Andrady, 2011; Brien, 2007)

It should be noted that the transport of the PW is considerably affected by the shape, density, size of the fragments, and the type of polymers used (Castillo et al., 2016; Isobe et al., 2014; Wright et al., 2013). PW which are discarded are ubiquitous in the oceans and they are found as sunken debris on seafloor sediments (Galgani et al., 2000; Schulz et al., 2015), floating on the surface of seawater (Barnes et al., 2009; Barnes and Milner, 2005), and abandoned on the coastal shores (Barnes and Milner, 2005; Thiel et al., 2013). It has been reported that almost 60% of the plastic material generated is lesser in density than seawater (Andrady, 2011). In addition, buoyant plastics can be easily moved by winds and currents once introduced into marine ecosystems (Kako et al., 2010), and consequently captured again by coastlines (Kako et al., 2014; Lavers and Bond, 2017). In turn, these plastics will be degraded into tinier pieces under several environmental conditions including sunlight, waves, and changes in temperatures (Andrady, 2011). However, some of these buoyant PW will be carried offshore and go into the oceanic gyres (Eriksen et al., 2019). A significant amount of PW (buoyant) was discovered in the North Pacific Subtropical Gyre mainly in the eastern part, renowned as the Great Pacific Garbage Patch (Chu et al., 2015; Wong et al., 1974; Young et al., 2009), where a comparatively high concentration of PW in the oceans occurs in the region (Eriksen et al., 2014; Law et al., 2014).

Owing to the intrinsic nature of the PW (e.g., durability, slow rates of degradation, and water insolubility), plastic litter has become a challenging, persistent, and significantly abundant material in marine ecosystems (Barnes et al., 2009; Browne et al., 2007; Castillo et al., 2016). It was illustrated that PW abundance (e.g., MPs) in the marine ecosystems has correlated positively with the density of the human population in the contiguous coastal zones. Usually, the increase in human population in the coastal regions results in a higher PW generation and, subsequently, their frequent occurrence in the coastal seawater (Castillo et al., 2016; Depledge et al., 2013).

Although the Middle East region is responsible for around 7.3% of the universal plastic generation, only a few studies investigated MP pollution in the region (Castillo et al., 2016). Qatar is a country, which is located in the middle of the western coast of the semi-enclosed Arabian Gulf. The aquatic ecosystem is highly vulnerable to PW because of the continued economic expansion of this nation, where the economic zone increased to around 32,000 km^2, which accounts for approximately 15% of the gulf and comprises a 563 km lengthy shoreline (Castillo et al., 2016; Jones et al., 2002). Nevertheless, the marine environmental ecosystem of the country is a precious resource, which provides tourism, fisheries, and recreation activities, as well as the expanded petrochemical industries which are located in the coastal area (e.g., oil and gas rigs and other facilities), are considered anthropogenic activities. This leads to several environmental impacts which will eventually increase the plastic litter levels in the seawaters (Jones et al., 2002). Furthermore, Qatar’s marine environment conditions are extremely affecting the size and quantity distribution of the PW in the ocean where the sea temperatures during the summer may reach up to 35 °C, as well as the elevated evaporation rates. This leads to higher salinity levels, which may reach 39 ppt to 41 ppt (Castillo et al., 2016; Jones et al., 2002).

2.2.2 Environmental impacts

In 2020, it was expected that around 400 Mt of PW will be generated in 195 countries, and around 8.8 Mt will end up in the aquatic ecosystems (Koller and Braunegg, 2018; Serrano-Ruiz et al., 2021). The southeast Asia countries mainly the Philippines, Sri Lanka, Indonesia, Malaysia, Thailand, Bangladesh, China, and Vietnam, are classified with the highest rank in the mismanagement of PWs, as such 88% of these wastes end up in the ocean (Ali et al., 2021). PW has the potential to carry several organic pollutants, pathogens, chemicals, and toxic metals (Chamas et al., 2020; Chen et al., 2019a; Cregut et al., 2013; Galloway and Lewis, 2016; Tang et al., 2021). In addition, PW degradation via abiotic factors releases extremely toxic compounds, which leads to the deterioration of the water and soil quality (Chen et al., 2019a). Since oceans keep loading with extreme amounts of plastic debris of various sizes, for instance, it was reported that around 5.25 trillion macro-, micro-, and nanoplastics were found in the ocean with an overall weight of 269 t (Eriksen et al., 2014). Numerous types of PW are hydrophobic by nature, which boosts the aggregation procedure with other pollutants including organic pollutants, polychlorinated biphenyls, and polyaromatic hydrocarbons (PAHs) (Liu et al., 2016). Since the reactivity is highly contingent on the hydrophobic nature of the PW type and the proportion between the surface areas to volume, this directly leads to the efficient sorption property of the PW. Furthermore, the long-term buildup of MPs can influence the food chain due to the ingestion of these particles by animals (Frias et al., 2010). A study identified the histopathological destruction in the fish tissues due to the plastic litter and illustrated the abundance of MPs in fish's gut with a range of more than 1mm to 3mm and the amount of these particles was projected by 2.3 items/g to 15.8 items/g of digestive tissue (Li et al., 2020). Unquestionably, water pollution due to PW is an extreme challenge for biota, including various water bodies in which the waste is discarded such as rivers, ponds, lakes, etc. Several studies have indicated that PW is found universally in many seas and different locations including the Atlantic Ocean, Baltic Sea, Pacific Ocean, Mediterranean Sea, The United States, and Southwest England, depending on different mechanisms (e.g., currents, winds, Man-made factors, as well as the geography of the coastline) (Li et al., 2016). The PW presence acts as a disturber of the natural flow, restricts the reproducibility of the fish, and thus destroys the vital organisms. In fact, MPs were found to be present in raw, as well as treated drinking water. A study showed that MPs were found in all tested water samples, with an average occurrence range of 1473 ± 34 particles/L to 3605 ± 497 particles/L in raw water samples and from 338 ± 76 particles/L to 628 ± 28 particles/L in treated water samples (Pivokonsky et al., 2018). These findings explain the urgent need for novel PW adsorption techniques, as well as new strict and efficient policies to reduce the amounts of MPs and NPs. Furthermore, another study showed that MPs were present in the drinking water of various freshwater sources in Belgium (Semmouri et al., 2022). Moreover, MPs were found to be polluting commercial salt (Karami et al., 2017; Peixoto et al., 2019), which is a crucial universal ingredient. Studies illustrated that microplastics were found in 128 different brands of commercial salts originating from 38 various countries (Peixoto et al., 2019). The presence of such tiny plastics (MPs and NPs) in natural resources and food for human consumption including seafood sources, drinking water, and salt will eventually have harmful effects on humans. In addition, PWs contribute to global warming due to their shade creation which hinders the growth of plankton (Proshad et al., 2017). Consequently, they disturb the balance of the ecosystems and the natural environment, which in turn affects human health. There are several types of PWs, which can potentially contaminate the soil via surface settlement or by the penetration of the soil layers through various methods including irrigation by utilizing wastewater, bio-solids, landfills, or other sources (Darwesh et al., 2021; Horton et al., 2017). The PW fragmentation into MPs on the surface of the soil occurs mainly due to photo-oxidation and temperature (Horton et al., 2017). These fragments/particles can end up in the deep soil layer, contaminate the groundwater and thus deteriorate the soil properties (Scheurer and Bigalke, 2018; Zhu et al., 2018).

Numerous scientists have studied the effects of macroplastics and MP wastes on soil bodies and these investigations demonstrate that the accumulation of these particles can cause histologic damage (Bråte et al., 2016; Bravo Rebolledo et al., 2013; Diepens and Koelmans, 2018). Moreover, a study illustrated that those added microfibers to the soil can extremely impact the soil community and biodiversity which will eventually influence the balance of the ecosystems (Lozano and Rillig, 2020).

Lastly, the incineration of PWs emits various pollutants into the atmosphere, and thus it is deemed a major source of air pollution. The major impacts which are initiated due to incineration are illustrated in **Figure** 4. These pollutants are metals, nitrogen oxides (NOx), aldehyde (-CHO), volatile organic compounds (VOCs), carbon dioxides (CO_2), carbon monoxide (CO), PAHs, methane (CH_4), furan (C_4H_4O), particulate matter (PM), and several other compounds, which rise the heavy metals level in the environment (Sabiha et al., 2008; Sharma et al., 2013). Some of them are the main contributors to the photochemical ozone creation process.

2.3 Impacts on human well-being

PW can have considerable direct and indirect impacts on human health via inhalation or digestion or dermal exposure as illustrated in **Figure** 5. Particularly, the persistency of the MPs can potentially lead to many biological responses (e.g., genotoxicity, inflammation, necrosis, oxidative stress, and apoptosis) (Prata et al., 2020; Proshad et al., 2017). Yet, various critical outcomes can be developed when continuously exposed such as fibrosis, cancer, and tissue damage (Wright and Kelly, 2017). The composition of the polymers can have a sequence of chemical impacts due to the leaching of the chemicals which are not bounded and/or the residues of monomers and/or the combined hydrophobic organic contaminants, all leading to the deterioration of human well-being (Wright and Kelly, 2017). The ingestion of MPs and NPs by animals and humans can possibly permit the cellular entry of endogenous pollutants (Khan et al., 2015; Prata et al., 2020; Wright and Kelly, 2017). In addition, PMs may potentially result in oxidative stress because of the inhalation and consequently end up in intestinal fibrosis and acute inflammation (Nel et al., 2006). Concerning the harm that PMs can cause, a study investigated the PMs which are generated via vinyl or the incineration of plastics and reported that high concentrations of toxic pollutants were released, including the fine particle with a combination of additional harmful compounds which were detected such as benzene, acetone (Barabad et al., 2018). Furthermore, all types of plastics comprise oxygen species, which are reactive where their concentration can drastically rise because of the light interaction and/or the transition metals presence (Wright and Kelly, 2017), which leads to the formation of free radicals through dissociating C-H bonds (Gewert et al., 2015; White and Turnbull, 1994). Moreover, a study illustrated that specific plastic types including PVC, PU, and PS may produce harmful monomers which can potentially be mutagenic and/or carcinogenic monomers (Lithner et al., 2011).

How MPs and macro-PW can be transferred into the food chain? Regarding the transfer of macro and micro- PWs in the food chain, a study investigated the transfer of low-density polyethylene microplastics (LDPE-MPs) through earthworms and chicken, and it demonstrated that these MPs show high concentrations of 129.8 MPs/g in chicken feces and 10.2 MPs/gizzard (Huerta Lwanga et al., 2017). Unlike seabirds, the transport of plastic additives directly to humans has not been proven yet (Tanaka et al., 2013). In general, the exhaustion of PW per year could be projected as 840 plastic fragments per individual (Huerta Lwanga et al., 2017). Therefore, and by considering the PWs' mismanagement of the universal plastic environmental effects, and human health impacts, there is a crucial necessity for novel technologies for PW disposal and treatments.

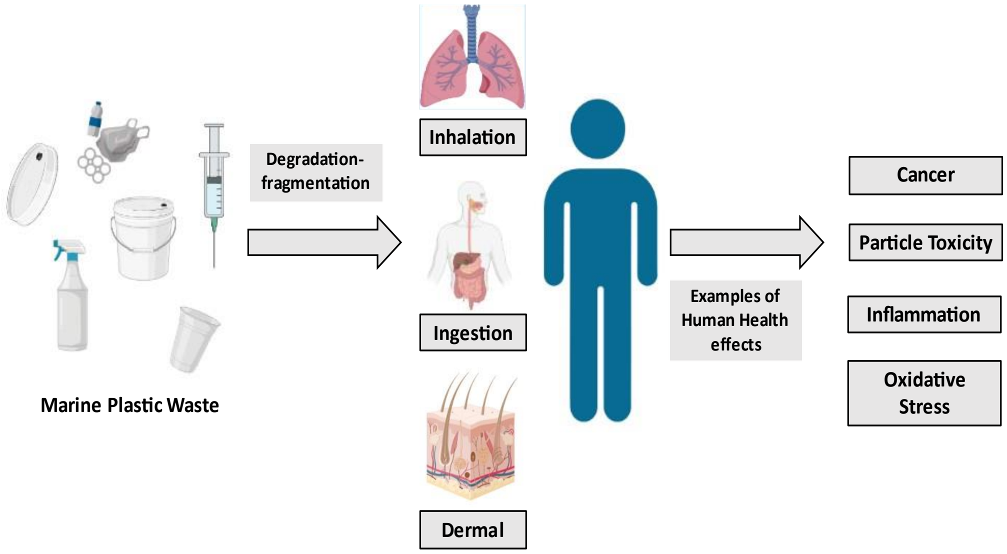


Figure 5. Marine Plastic Waste Degradation-Fragmentation and Its Human Health Impacts.

2.4 Marine plastic degradation - fragmentation and factors affecting the process

PW can be degraded via physicochemical degradation also known as abiotic degradation, and through biodegradation in which the physical forces of the polymers are primarily broken down (Kyrikou and Briassoulis, 2007). There are several plastic degradation mechanisms in the environment which have been reported, mainly including thermo-oxidative degradation, photodegradation, biodegradation, and hydrolytic degradation (Andrady, 2011). Naturally, the degradation of PWs begins with photodegradation, then by hydrolysis process, and it goes through a thermo-oxidation process. All these reactions result in breaking the PWs into compounds with lower molecular weight (MW), which may be consequently degraded through the activity of microbes (Andrady, 2011; Webb et al., 2013). Yet, this mechanism is extremely slow and it may require centuries to take place completely (Chamas et al., 2020).

2.4.1 Degradation based on the characteristics of the plastic polymer

The plastic degradation process is defined by several environmental circumstances, as well as the physicochemical polymeric characteristics of the PWs as illustrated in **Figure** 6. The physicochemical features of PPos play a crucial role in the process of degradation. The vulnerability of PWs to degradation biotically and abiotically depends on the polymer chain length and the backbone composition of the PPos, as such longer carbon chain (e.g., PP), is able to give the polymer more resistance to degradation (Fotopoulou and Karapanagioti, 2019; Huerta Lwanga et al., 2016). Nevertheless, incorporating heteroatoms as in PU and PET in which oxygen is integrated into their polymers gives the plastic the susceptibility to degrade thermally and biologically (Singh and Sharma, 2008). In addition, the hydrophobic property of the polymer highly influences the efficiency of the degradation process, as the rate of degradation rises with the increase of the hydrophobicity (Padsalgikar, 2017). Moreover, the degradation rate varies depending on the crystallinity of the polymer (Jenkins and Harrison, 2008), which means the more crystalline the structure of the polymer, the more O_2 and H_2O are required to degrade the plastic. Thus, the higher the

MW and/or the crystallinity degree, the lower the rate of degradation (Jenkins and Harrison, 2008). In contrast, attacking an amorphous structure of polymers is via oxygen and water. In addition, the amorphous regions of the polymers are considerably affected by thermal oxidation (Li et al., 2019). In this regard, the MW of the polymer may easily influence the rate of degradation, the higher the MW of the polymer, the slower the rate of degradation owing to its relatively low surface area (Singh and Sharma, 2008). It is also interesting to mention that the production techniques of plastics and the types of additives utilized extremely influence the rate of degradation of plastic products. For example, PP which is manufactured via Ziegler-Natta catalyzation or bulk polymerization is distinguished by its high photodegradation susceptibility compared to PP which is co-polymerized (Tang et al., 2005). Moreover, various additives including stabilizers are mainly utilized to reduce the chromophores which are the hydroperoxide and the carbonyl group and to lower the rate of degradation (Aldas et al., 2018). As such, the presence of these chromophores results in the photochemical creation of radicals, which helps in the initiation of photodegradation due to the availability of several photooxidative sites. In addition, the existence of metal-to-metal bonds can enhance the process of photodegradation due to the cleavage of the homolytic bond when irradiated (Daglen and Tyler, 2010). Furthermore, the morphological characteristics of the PW have the ability to increase the rate of degradation based on the favorable surface type for biofilm creation. Rough surfaces are found to be the most suitable types of surfaces for creating a biofilm. Thus, the rate of PW degradation increases whenever a rough surface appears (Booth et al., 2018).

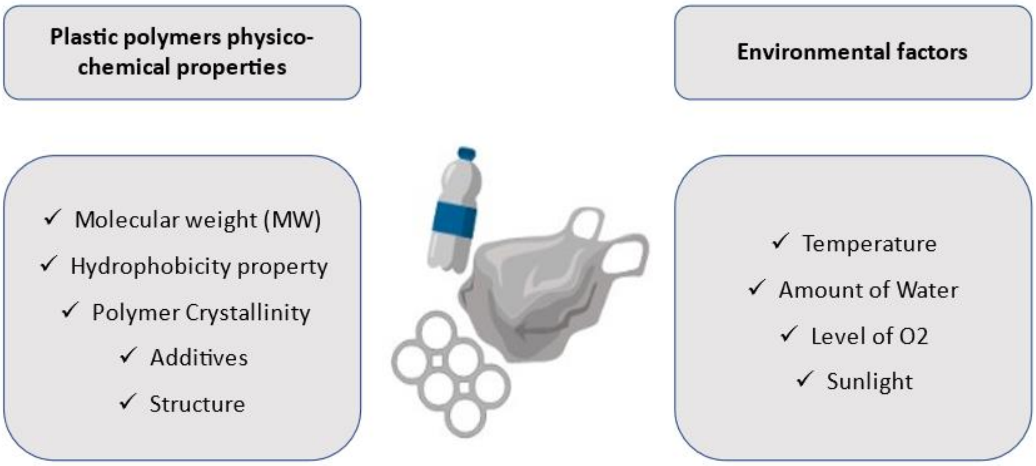


Figure 6. Factors Influencing the PWs Degradation Rate.

2.4.2 Degradation based on Environmental factors

The climatic conditions, the geographical positioning, and the various pollutants can potentially influence the techniques and degradation rate of plastics (Andrady et al., 2003). Sunlight is one of the most crucial factors, which affect plastic degradation. When the intensity of light increases the rate of the photooxidation process also increases, and thus the rate of plastic degradation increases (Kitamoto et al., 2011). Moreover, the abiotic degradation rate also rises with the elevation of temperature (Pischedda et al., 2019), with a duplication of the process rate per 10°C of increase. The temperature has the ability to influence the mobility of the polymer chain, which will consequently influence its enzymatic activity through microbial degradation, in addition to its effect on the rate of hydrolysis reaction due to influencing the creation of the free radicals, humidity, and the rate of oxygen diffusion (Booth et al., 2018). A previous study shows that a PET chain separation was much greater in 100% humidity and 60 °C conditions by around 500% compared with 45% of relative humidity (Edge et al., 1991). In addition, the photodegradation of PP was improved by the increase in humidity (Fernando et al., 2009), as well as in PE (Jin et al., 2006), and PVC plastic-type (James et al., 2013), coupled with the increase of the concentration of hydroxyl radicals. Nevertheless, a decrease in the intensity of the UV light in the sea will cause a reduction in the rate of photodegradation. However, the increase in humidity level at the surface of the sea will boost the photodegradation reaction due to the solubility of particular photo-stabilizers in the seawater, which leads to efficient degradation (Booth et al., 2018). Moreover, the accessibility of O_2 has an influence on the rate of plastic degradation through biodegradation and photodegradation (Queste et al., 2013). It was stated that the degradation process of polymers is speeded up when high levels of oxygen are present due to the swift process between the O_2 and carbon radicals, which are released from the products which are initially degraded (Price and Horrocks, 2013). Furthermore, the presence of water is crucial during the degradation process due to the hydrolysis which results in the cleavage of functional groups and thus leads to the polymeric chain cleavage (Pitt, 1992).

2.5 Degradation and fragmentation of plastics under marine conditions

2.5.1 Plastic waste degradation

It is appealing to realize that extensively utilized plastics do not naturally degrade to a huge extent whenever it is discarded into the environment (Bonhomme et al., 2003; Marqués-Calvo et al., 2006; Yamada-Onodera et al., 2001; Zheng et al., 2005). This is maybe predictable since one of the major reasons for the extensive application of several polymers is mainly the exceptional properties including extreme durability and stability (Yamada-Onodera et al., 2001; Zheng et al., 2005).

“Degradation” is the most utilized term for the description of the processes which result in the deterioration of the polymer properties (Yousif and Haddad, 2013). The polymeric structure of plastics can be degraded via either biotic or abiotic pathways (Strlic and Kolar, 2005). For instance, polymers can be completely or partially broken down due to oxygen attack, UV radiation, and/or biological effect, leading to changes in properties (e.g., fragmentation, surface cracks, and discoloration) (Maes et al., 2021). The smaller the fragmented polymer through abiotic degradation, the easier it can pass via the cellular membranes and thus it can pass through biodegradation by the cellular enzymes within the cells of the microbes. Nevertheless, some of the microbes have an extracellular excretion of enzymes, which can potentially degrade a variety of PPos (Shah et al., 2008). The degradation of plastics is mostly initiated at the polymer surface level since it is mainly exposed and thus, it can be easily enzymatically or chemically attacked. Consequently, the MPs degradation is much swifter than the macroplastics due to its larger surface-to-volume ratio. Initially, the degradation of the polymers can be visually observed due to some visual effects such as the surface crazing and the color changes) (Vasile, 2000). When the surface of the plastic is cracked, the further degradation of the interior of the plastic material will be easier, leading to fragmentation and embrittlement (Vasile, 2000). Generally, PWs in the environment are subjected to various conditions, which can stimulate the weathering process.

Yet, a question that usually comes up is: are all types of polymers being degraded effectively? The answer is simply no! Not all types of degradation pathways can degrade all types of polymers in an efficient way. The plastic degradation challenge has been investigated by several authors. The degradation of the most common polymer types was identified to investigate the degradation pathway of the plastics, which are mainly floating in the marine environment. Several findings were found while reviewing the degradation of plastics studies, thus speculative extrapolations of these findings were done in this review. Yet, due to the fact that the smaller the plastic particle, the higher its probability to sink and be unobserved. This leads to a challenge in the investigation, testing, and quantification of these plastic fragments, which are facing much more pressure leading to their further fragmentation. Therefore, most of the literature findings mainly report evidence related to the PWs, which are floating in the marine environment. These plastic particles, which are floating on the surface of the oceans are mainly subjected to several conditions including solar radiation (with a λ of 300 nm and above), oxidizing circumstances, and moderate temperature. The most crucial factors which initiate abiotic degradation are mainly sunlight and oxygen availability since the temperature level is moderate (Pritchard, 1998). Moreover, few PPos can undergo a hydrolysis process (Gewert et al., 2015).

The degradation process is a chemical alteration, which significantly decreases the average MW of the PPos. Any extent of considerable degradation can potentially diminish the plastic product due to the high dependence of the plastic mechanical integrity consistency on the elevated average MW. Thus, the extensive degradation of the plastics will lead to brittle plastic material, which will eventually be converted to powdery fragments. The more the MW of the PPos is decreased, the more the plastic material gets brittle! (Summers and Rabinovitch, 1999). In addition, it provides a larger surface area for additional reactions, which makes its fragmentation susceptibility much higher. Those smaller fragmented particles may not be even visible to the naked eye due to their tiny size, which creates difficulty in their collection and investigation. The degradation process is usually categorized into several classifications based on the main cause of the degradation, such as biodegradation, which is mainly caused by living organisms (e.g., microbes), and thermo-oxidation degradation which is caused by the slow breaking down of the PPos through oxidation reactions at moderate temperatures, hydrolysis, which is caused due to water reacting, the degradation thermally. This is caused mainly due to high temperatures, and photodegradation which is usually due to outdoor exposure to light. Generally, the UV-B sunlight radiation is the main initiator for the photo-oxidative degradation of the commonly used PPos including PP, HDPE, nylons, and LDPE, which are under marine environmental conditions. Then, the degradation process keeps proceeding with the thermo-oxidative process for a while without being exposed to more UV radiation. In addition, the catalytic reaction of polymer degradation will keep progressing in the presence of oxygen. The degradation process leads to a big decrease in the MW of the polymer in addition to the generation of oxygen-rich functional groups. While comparing light-induced oxidation and other types of degradation processes, light-induced oxidation was found to be swifter. Moreover, the hydrolysis mechanism is not a largely considered process in seawater. All types of biomaterials (e.g., plastics) can be invariably degraded under marine environmental conditions; however, the rate of degradation is slower. This is applicable to benthic sediments as well. In contrast to the oxidative degradation which is induced by light. PW degradation, which is initiated by UV sunlight, was found to be an extremely effective process when compared to plastics which are exposed to air or discarded onshore/nearshore. However, while comparing an identical PW which is exposed to UV-radiation (sunlight) at the same location, when placing it in seawater, the degradation rates were found to be extremely slower (Andrady, 2011). It should be noted that PW degradation in the marine environment is slower due to the unoptimized conditions for the degradation of polymers. Yet, biodegradation and abiotic degradation are still most likely to happen but on a large timing scale (Gewert et al., 2015).

Usually, the degradation of plastics is initiated via photodegradation, leading to thermo-oxidative degradation. The UV light produced by the sun has a crucial effect since it provides the needed energy. This helps in initiating the integration of O_2 atoms into the polymer (Andrady, 2011; Raquez et al., 2011), and leads to the brittleness of the PWs. This eventually causes its fragmentation into smaller pieces and tinier pieces until reaching an extremely low MW of these polymer chains, which then can be metabolized via microorganisms (Andrady, 2011; Webb et al., 2013; Zheng et al., 2005). The microbes have the ability to convert the carbon, which is located in the polymer chain into CO_2, or it can be also incorporated into the biomolecules (Andrady, 2011; Webb et al., 2013; Yamada-Onodera et al., 2001). Nevertheless, the whole process is extremely slow, and it may take over 50 years for plastic materials to be completely degraded (Müller et al., 2001). Moreover, photodegradation is drastically declining in seawater conditions owing to the oxygen availability, the lesser temperature, and the hydrolysis rate of the PPos in the ocean which is extremely inconsequential (Andrady, 2011; Webb et al., 2013). Usually, UV-B sunlight radiation is the main initiator of photo-oxidative degradation in the marine environment, especially with the commonly utilized polymers which include PP, HDPE, and LDPE (Andrady, 2011).

PW degradation is mainly depending on the rate of chemical, biological, and physical conditions to which plastics are exposed, where they start to lose their original characteristics. The plastic degradation phenomenon involves 6 main mechanisms categories: hydrolysis, thermal degradation, physical degradation, biodegradation, photodegradation, and thermo-oxidative degradation (Maes et al., 2021; Mattsson et al., 2015). In addition, most of these degradation processes occur in seawater at varied rates.

Plastic degradation via sunlight (UV-light) exposure, which is also called photodegradation, results in the “chain scission” phenomenon, which is mainly the breaking down of covalent bonds within the structure of PPos (Gewert et al., 2015).

Chain scission can happen at any place within the polymeric structure, leading to monomers. It should be mentioned that some PPos may be hazardous, bioaccumulative, and persistent pollutants, which may potentially harm our environment (Lithner et al., 2011). In other words, the photodegradation of plastics is mainly the decomposition of PPos through the absorption of energy from light to produce free radicals. It is also known as "photooxidative degradation" whenever oxygen is present. Generally, the major light source which is initiating photodegradation is near UV light, which is ranging from 290 nm to 400 nm (Singh and Sharma, 2008). By exposing plastics to this light range, and due to the high energy of the C-C bond in the polymeric chain, it starts cleaving (Ravelli et al., 2016). Compared to other techniques of degradation, photodegradation technology is advantageous due to the ability to localize and control the light spatiotemporally in a simplistic, independent, and green approach (Chatani et al., 2014). The photodegradation process is not only beneficial in the usage of natural sunlight to degrade PPos, however, it also decreases the time needed for consequent biodegradation while providing the prospect of complete plastic degradation (Zhang et al., 2021a). Photodegradation of plastics includes various mechanisms, for instance, secondary oxidative reactions and crosslinking, and chain scission, which occurs by generating and transferring free radicals (Bracco et al., 2018). There are two major techniques by which free radicals can be generated. The first method is directly irradiating the plastic with UV light without interfering with any catalysts, additives, or chromophores. The second method is based on adding photoactive substances into PPos to accelerate the production of free radicals (Zhang et al., 2021a). These photoactive substances comprise photosensitive groups and photoactive fillers, which are combined into polymeric chains. Studies showed that these photoactive additives could be categorized into two main categories, which are, additives, which sacrifice themselves during the photodegradation process in which they produce free radicals when exposed to UV irradiation through decomposition reactions, named as the additive photosensitizer. The other type of additives is mainly photoactive additives which do not sacrifice themselves while constantly producing free radicals, and are known as the additive photocatalyst (Grassie and Scott, 1988). To better understand the plastic degradation mechanism through UV- light irradiation, it should be noted that the UV-light wavelength range which helps initiate the bond cleavage of polymeric structures of C-C or C-H bonds is 280 nm - 420 nm (Pospisil and Nespurek, 2000). Since the UV wavelengths, which correspond to the dissociation process of bond energies (C-H bond 420 kJ/mol and C-C bond, 375 kJ/mol), are 290 nm and 320 nm. This leads to the breakage of C-C and C-H bonds and the formation of free radicals (Pospisil and Nespurek, 2000), as illustrated in the initiation part of the process in **Figure** 7 (A). It shows that the C-C bond was broken when exposed to UV-light radiation at a wavelength shorter than 320 nm, leading to the formation of alkyl radical $R^{\cdot}$. Afterwards, the propagation step, where the autooxidation begins, as the radical $R^{\cdot}$ reacts with the oxygen and forms $ROO^{\cdot}$. Then, a further reaction occurs between the radical $ROO^{\cdot}$ and polymer to produce hydroperoxide ROOH and $R^{\cdot}$. Subsequently, $ROO^{\cdot}$ and $R^{\cdot}$ react by disproportionation reaction or also known as radical coupling, resulting in the termination step of the photodegradation process. In the photooxidative process, ROOH groups (hydroperoxide) are considered to be the most crucial intermediates in this extremely photolabile process. Usually, the termination step of the photodegradation reaction combines peroxyl radicals or alkyl radical to produce stable products as illustrated in **Figure** 7 (A). Generally, the combined macroalkyl radicals can form branched, disproportionated, or crosslinked products, on the other hand, peroxyl radicals are ultimately undergoing the termination reaction with other free radicals, forming dialkyl peroxides, alcohol, or carbonyl species (Mark and Kroschwitz, 1985). In addition, the oxygen pressure is correlated to the type of termination step (Yousif and Haddad, 2013). In other words, whenever polymer is exposed to light with a wavelength shorter than 320 nm, PPos are supposed to be degraded. It should be noted that the stratosphere act as a filter for UV- light with higher energy, which is ranged between 280 nm – 315 nm, and only less than 2% of this UV- light is reaching our earth, which is ranged between 315 nm – 400 nm (Yousif and Haddad, 2013). Under sunlight irradiation conditions polymers, which mainly consist of C-H and C-C bonds such as PP and PE, have an extremely slow rate of degradation. However, the addition of other chemical bonds can cause a different initiation reaction which in turn can speed up the degradation of the polymer (Wang et al., 2019).

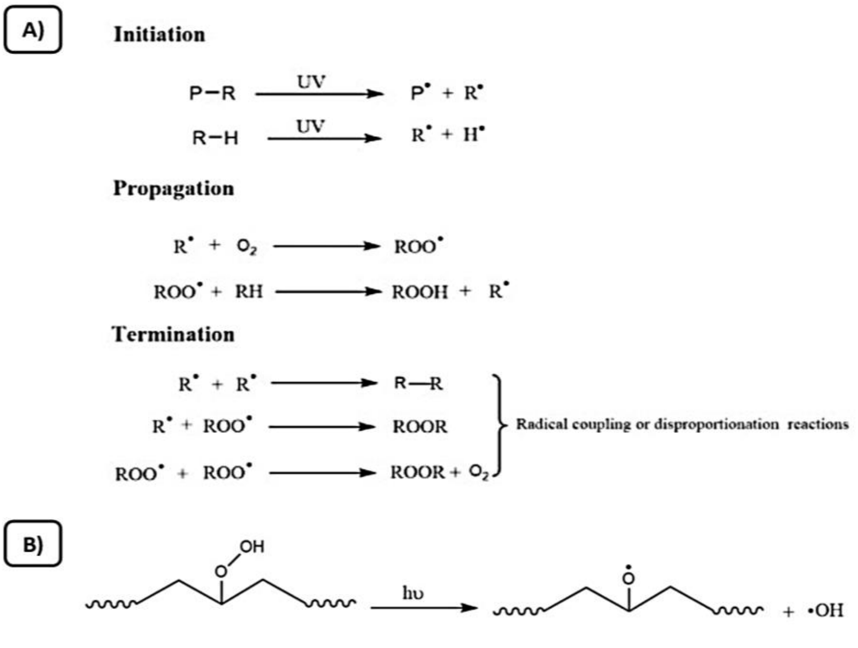


Figure 7. (A) Photodegradation Process of Polymers Via UV- Light Irradiation (Initiation, Propagation, and Termination). (B) Bond Cleavage (O-O) of Hydroperoxides Mechanism. Modified from (Zhang et al., 2021a).

It should be noted that the thermodegradation of plastics is a different process, which aims to facilitate successive microbial degradation via degrading/fragmenting macromolecular polymers into smaller particles. When comparing between pyrolysis process and the thermodegradation process, the temperature is much lower in the thermodegradation process than in pyrolysis. In addition, thermodegradation occurs in the presence of oxygen. Thus, the thermodegradation process is correspondent to thermo-oxidation degradation, which means the mechanism of thermo-oxidation degradation and photooxidation are almost similar to each other, as illustrated in **Figure** 7 (B). Where polyolefins can produce a hydroperoxide group in the presence of oxygen and heating conditions, leading to the breakage of O-O bond of the group and forming hydroxyl radicals and alkoxy groups, and then degradation continues by forming lactone and esters through the autooxidation reactions (Chiellini et al., 2006). Nevertheless, the main difference between thermooxidation and photooxidation is the instability of ketones to light, since the ketonic products are usually thermally stable, yet they are not stable to light (Wiles and Scott, 2006). A study investigated the thermooxidation degradation of PE and showed that the temperature factor is the main factor influencing the degradation rate, rather than the oxygen concentration (Jakubowicz, 2003). In addition, another study concluded that the thermooxidation degradation of plastics (e.g., PE) can improve the degradation efficiency (Khabbaz et al., 1999). It should be also mentioned that the thermooxidation technique helps in significantly reduce the temperature required for the process compared to the pyrolysis technique, thus reducing the equipment needed as well. Nevertheless, the degradation of plastics thermooxidatively requires more time, leading to further consumption of energy compared to the photodegradation process. Therefore, further research should be done focusing on developing techniques to accelerate thermooxidation degradation, as well as to reduce energy consumption.

2.5.2 Plastic waste fragmentation

The vulnerability of the structure coupled with the loss of mechanical integrity may result in breaking the parent plastics into tinier pieces of plastics (Andrady, 2011; Ekvall et al., 2019; ter Halle et al., 2016). Intrinsically, the fragmentation process of plastics results in the alteration in the size distribution of plastic debris in aquatic ecosystems. The fragmentation process does not have the capability to eliminate marine plastic litter from the environment. Yet, it is efficient in accelerating the physicochemical and biochemical processes, which occur at the surface of the marine plastic litter owing to the higher surface-to-volume ratio of tinier pieces (ter Halle et al., 2016). Moreover, the fragmentation of plastic materials may be simulated by the mechanical stress in marine environmental conditions because of the wave action (Cooper and Corcoran, 2010; Weinstein et al., 2016). Moreover, this fragmentation process may be speeded via the potential biodegradation and weathering, which makes the plastic materials more brittle over time (Andrady, 2017; Barnes et al., 2009; Kalogerakis et al., 2017; ter Halle et al., 2016). The fragmentation rate increases as the size of the particle decrease. Additionally, marine plastic litter particles which are bigger than 2mm have a morphology that looks like a sheet, which makes one face more likely to be exposed to sunlight (ter Halle et al., 2016). Therefore, the fragmentation process will be accelerated leading to the creation of cracks at the surface of the particle, which generates more cubic pieces that seem like the parent fragment (around 1 mm of thickness). Furthermore, the degradation of the cubic pieces will be much swifter due to their tendency to roll at the surface. Accelerated fragmentation may also be a valid justification for the relatively low masses of floating marine litter particles. The fragmentation of marine PW can lead to the generation of tinier particles (less than 1 µm), which are known as NPs.

The fragmentation process tends to influence the PW transport through marine systems since tinier particles are carried in a different way horizontally, as well as vertically than larger plastic pieces (Cole et al., 2011; Gerritse et al., 2020; Zhang, 2017). It should, also, be mentioned that smaller fragments have a relatively greater surface area compared to their volume, leading to increased rates of degradation, adsorption sites per unit, and decreased buoyancy. This is due to biofouling, which results in the transfer of MPs from the surface to the water sediment or column (Cózar et al., 2014; Eriksen et al., 2014; Gewert et al., 2015; ter Halle et al., 2016; Zhang, 2017). Hence, the fragmentation process creates a larger specific surface area, leading to more water contact, and thus swifter sorption and/or leaching rates for chemicals (Velzeboer et al., 2014).

Macro- and MPs are the most found PW types in the ocean, and their environmental impacts are clearly stated in many research papers. However, these plastics can also be degraded in the marine environment via several mechanisms mainly photo-oxidation coupled with microbial degradation. Consequently, the degradation of plastics in the ocean is expected to be the highest in the tropical and sub-tropical regions due to the high pollution levels where plastic marine litter is highly accumulated (Wayman and Niemann, 2021). Degradation and fragmentation mechanisms result in the transformation of larger plastics into smaller fragments, where macro and microplastics can be potentially transformed into NPs. In addition, the smaller the fragments, the higher their degradation due to the greater surface-to-volume ratio, leading to higher rates of degradation.

According to (ter Halle et al., 2016), there are two different behaviors of MPs in the marine environment due to their physicochemical properties. To understand the fragmentation of MPs, different samples (big parallelepipeds and small cubic) were analyzed through their physicochemical properties. It was noticed that the bigger sample (parallelepipeds) was floating at the sea surface while exposing only one surface to the sun as represented in **Figure** 8. During sunlight exposure, the photodegradation process will induce fragmentation due to a decrease in mechanical properties. The fragmentation process takes place because of the breaking down near cracks on the surface of the plastic samples, resulting in smaller fragments. However, the cubic samples have the tendency to roll on the water surface. It was also confirmed that the continuous rotation of the cubic appeared to prevent the biofilm growth on the surface of the cube pieces, while edge erosion seemed more likely to happen. These variations in the motion behavior of PW are undoubtedly associated with different fragmentation rates. It was concluded that the cubic sample was fragmented faster than the larger parallelepipeds. Similarly, other studies showed that smaller plastic items can degrade faster (Andrady, 2015; Kershaw, 2015b). Overall, it should be highlighted that these investigations can significantly contribute to a better understanding of the fate of the MPs in oceans.

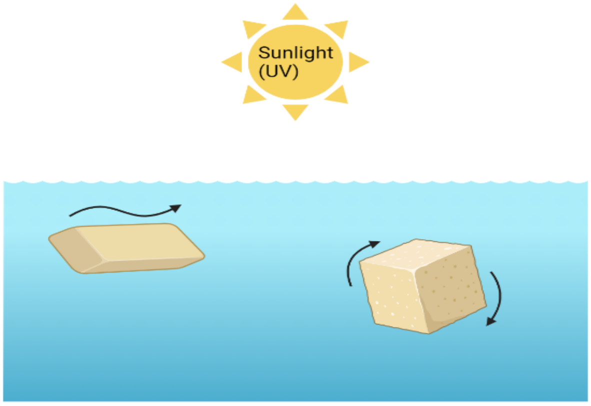


Figure 8. Seawater PW Fragmentation Based on the Shape.

Recently, the creation of MPs and NPs through fragmentation has been investigated under marine conditions in several studies through accelerated laboratory conditions (photodegradation) (Gigault et al., 2016; Lambert and Wagner, 2016a; Lambert and Wagner, 2016b). However, many plastic fragments tend to be lost in the open exposure systems, leading to an underestimation of the real numbers of plastic fragments formed (Song et al., 2017). Thus, the collection of data through the fragmentation process of plastics in marine environments is needed to estimate the number, production rate, and size of the plastic particles developed by fragmentation.

The fragmentation process can occur through different factors including UV exposure and MA. (Song et al., 2017) shows that some polymer types can be affected by MA such as PS; however, others were unlikely to be fragmented via MA only. To be fragmented, an additional factor needs to be present as well, which is UV exposure/sunlight. These findings can be confirmed by the difference in the mechanical strength of PPos, where PS has lower mechanical strength compared to PP and PE. It was concluded that with the increase of UV exposure time and MA, the fragmentation of PPos increases, despite the fact that the fragmentation rate will differ based on the type of polymer. UV light acts as a producer for initial free radicals by dissociating C-H and C-C polymer backbone bonds (Feldman, 2002), leading to chemical changes, visible fractures and cracks, and surface embrittlement. It was also confirmed that due to chain reactions and cross-linking, UV oxidation can create surface embrittlement to a depth exceeding 100 μm (Feldman, 2002). However, it is interesting to mention that the photooxidation process, alone, cannot directly cause polymer fragmentation. PPos need to be exposed to successive MA as well to be fragmented. This means that an additional physical process is needed to improve the fragmentation of PPos. Some factors and conditions were found to be critical in the rate of photooxidation and propagation of PPos such as oxygen availability, diffusion of radicals, and the depth of UV penetration (Pilař et al., 2015). Furthermore, the rate and degree of fragmentation-degradation coupled with the environmental conditions are determined mainly by the physicochemical characteristics of PPos. In addition, the degree of fragmentation is also affected by the additives (e.g., antioxidants and UV stabilizers) embedded in plastics which hinder the process.

It should be noted that paints contribute to marine plastic pollution. Due to the fact that paint pieces contain polymers combined with various additives (Turner, 2021). Nevertheless, paint fragments are usually undetected, and consciously disregarded in the pool of MPs, especially in the marine environment. Because of the extensive literature on micro-litter. A study showed that paint coatings of different commercial solar glass mirrors were degraded after being exposed to marine outdoor conditions for 3 years (Guerguer et al., 2021). Changes in some colors were observed. In addition, FTIR-ATR findings showed several changes in the intensity of several IR bands. In fact, the reason behind this degradation is not limited to UV-radiation. It is also related to other conditions including salinity, temperature, rainfall, and humidity. Nevertheless, the amounts of MPs released during the production, use, and disposal of paints are still not clear (Faber et al., 2021). Thus, further studies are needed to take measures in order to reduce emissions.

2.6 Potential leaching of plastic waste additives in the marine environment

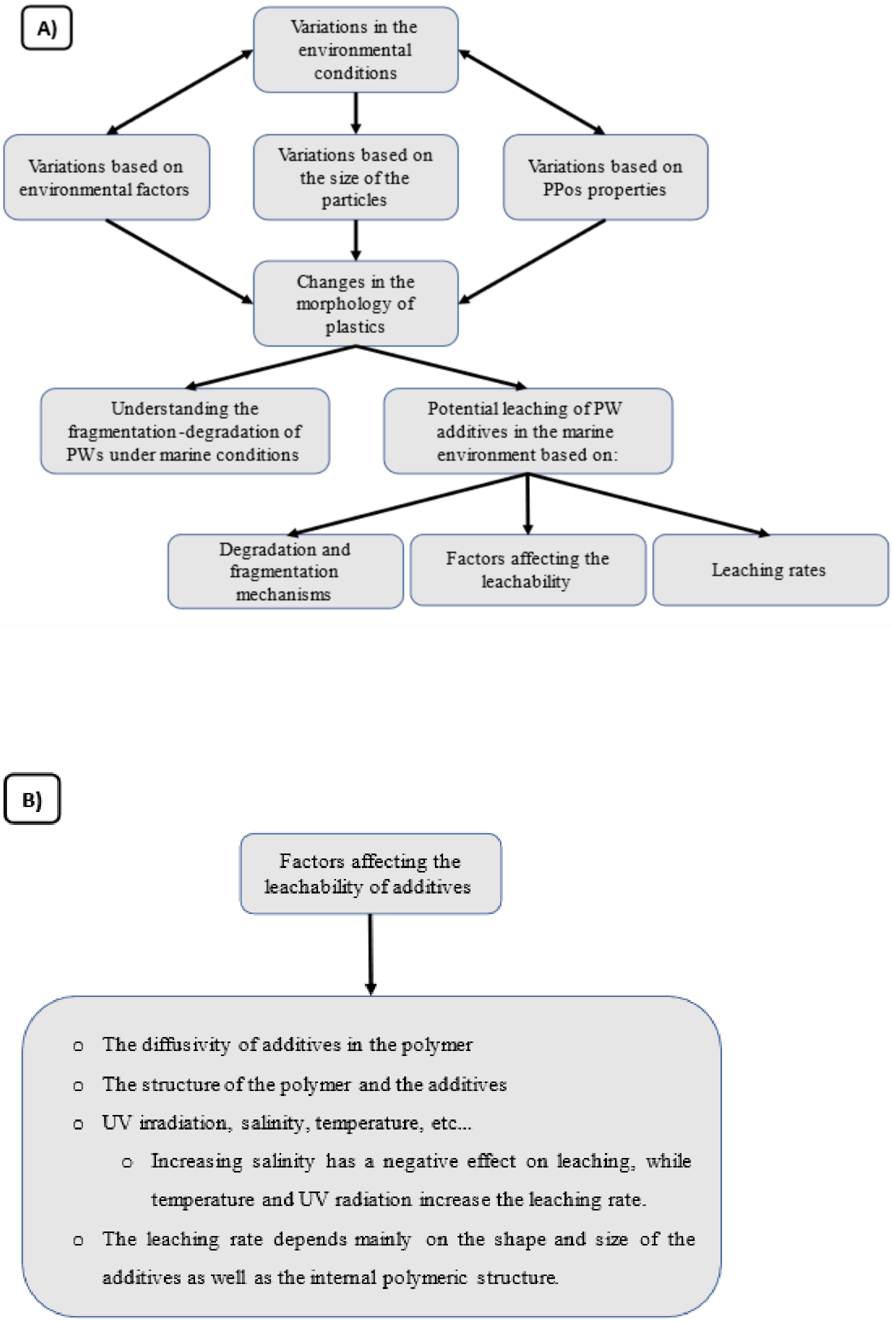
Several studies show that PW particulates in marine ecosystems contain significant amounts of various organic pollutants and additives, which can potentially leach into seawater, leading to adverse harmful effects. Many toxic substances and compounds may encompass polychlorinated biphenyls (PCBs), nonylphenol, and organic pesticides, which may comprise dichlorodiphenyltrichloroethane (DDT), PAHs, BPA, and polybrominated diphenyl ethers (PBDEs). All of the aforementioned toxic chemicals have been constantly found in a marine plastic litter (Hirai et al., 2011; Mato et al., 2001; Rios et al., 2007). While these toxic chemicals are present, the risks linked to the ingestion of plastic litter by marine organisms, and the plentiful of these chemicals can be significantly biomagnified, leading to a potential direct risk to human well-being (Hirai et al., 2011). Many studies illustrated that these toxic compounds are associated with several health issues, which may include cancer, diabetes, developmental impairments (hormonal imbalance, neurological impairment, abnormalities in growth), endocrine disruption, DNA hypomethylation, breast cancer, neurobehavioral variations, arthritis (Chung et al., 2011; Schecter et al., 2010; Trudel et al., 2011; Zhou et al., 2011).

The state of the plastic materials after being exposed to several environmental conditions could be affecting their interactions with the environment as well as influencing the potential release of the additives and chemical substances which are embedded (UNEP, 2016b). Most of the polymers are initially fabricated as thermostable materials, which means that they cannot break down easily to deliver the intended use of the product (UNEP, 2016b). Due to the non-biodegradable property of plastics, their products are considered as persistent pollutants. Biodegradable plastics are accounting for a smaller share nowadays. Yet, these products are constantly expanding in the markets. Nevertheless, not all commercial plastic products are completely, environmentally biodegradable (Kershaw, 2015a; O’Brine and Thompson, 2010). In addition, some biodegradable products can potentially change the geochemistry of the sediments in the ocean and impact the marine species as well as their co-existence (Balestri et al., 2017). To improve the performance of plastic products, several additives are added to most of the plastic materials, mainly during the formation of the polymers and their shaping, which enhance their functions and aging characteristics. There are numerous additives, which can be used for various types of polymeric products, which include, but are not limited to, antioxidants, plasticizers, pigments, slip agents, thermal stabilizers, and lubricants (Hahladakis et al., 2018). Each of these additives has a distinctive role in improving the polymeric characteristics and the functionality of the final product. For example, pigments are commonly used to deliver a diversity of colors. In addition, slip agents are utilized usually to avoid the sticking of the latter together or to the metal surface. Additives can be divided into several categories (Hansen et al., 2013), including functional additives, fillers, colorants, and reinforcements. It should be emphasized that most of these additives are not chemically bound to the polymeric plastic products, and only some additives, which are mainly organic reactive additives, will be part of the polymeric chain due to their polymerization with the plastic particles.

Toxic substances can be potentially leached from plastic products into water, air, and soil. Potentially leaching additives (PoLA) from plastic products to water, food, and air have been studied and detected through chemical analysis, which is mainly conducted in laboratories. The identification of the type and magnitude of the chemical leachate is a complicated task due to its dependence on several factors. Generally, in the short term as well as the long term, any chemical substance and/or degraded polymeric products will bioaccumulate in different environments due to their persistence, leading to potential harm to humans and the environment. The composition of the additives in the plastic products will define what can be leached from the product. Yet, there are several other factors, which are controlling the actual potential emission of these substances in any environment. The presence and/or release of PoLA and other substances in plastic products do not necessarily represent a hazard; there are many additional facets, which needs to be taken into consideration while assessing the risk posed to the receptors including human, animals, and the environment. It needs to be noted that the long-term release of potentially toxic substances into the environment is mitigated and controlled efficiently, where migration mechanisms are used to test the potential release of most of the additives. These are mostly embedded in plastic food products, as well as the leaching/release of PoLA throughout the recycling process of all plastic types (Velis and Brunner, 2013). Numerous research studies investigated the potential release of several additives from different plastic products such as BPA (Brede et al., 2003; Geens et al., 2010; Olea et al., 1996; Sajiki et al., 2007), phthalates (Rijk and Ehlert, 2001; Tønning et al., 2010), volatile organic compounds (e.g., benzene) (Skjevrak et al., 2003), bisphenol-A dimethacrylate (Olea et al., 1996), lead, cadmium, and tin (Al-Malack, 2001), brominated flame retardants (Kim et al., 2006), acetaldehyde and formaldehyde (Mutsuga et al., 2006), 4-nonylphenol (Fernandes et al., 2008; Loyo-Rosales et al., 2004), and several other volatile organic compounds including methyl tert-butyl ether (MTBE) (Henneuse-Boxus and Pacary, 2003). The concentrations of these released plastic products were found to be low in many of these research investigations when compared to legal standard/guideline limits, yet in some cases; these concentrations may be significantly higher. Conspicuously, the low levels at which EDCs can potentially generate an impact were not included in the standard/guideline values (Vandenberg et al., 2012), as well as the mixtures toxicity/harmfulness (Kortenkamp, 2007).

The degradation of plastic products produced depends highly on the type of polymer (Ravve, 2000). In addition, the amount and type of degraded plastic products can be affected by the degradation pathways, as well as the existence of polymerized impurities and/or the environmental conditions including oxygen availability and temperature (La Mantia, 2002; Ravve, 2000). It should be also mentioned that plastics, which contain nitrogen such as nylons release hydrogen cyanide during thermal degradation, as well as plastic products, which contain chlorine such as PVC, which releases dioxins and hydrogen chloride (Hahladakis et al., 2018; Lokensgard, 2004; Ravve, 2000). Moreover, several polymers can depolymerize through chain scission such as polyoxymethylene, which is capable of complete depolymerization into their initial monomers. Furthermore, there are some other polymers, which can partially depolymerize into their monomers, which include nylons, and polyesters such as polycarbonate and PET (La Mantia, 2002; Ravve, 2000).

The leachability of various chemical substances in seawater was investigated through several research studies. Recently, the leachability of EDCs associated with mesoplastics (large plastic particles which are commonly defined as 5 mm – 10 mm in range (Isobe et al., 2014)) and MPs were studied under various normal life conditions which are usually occurring during the life cycle of plastics (e.g., solar irradiation, autoclaving, microwaving) (Chen et al., 2019a). Findings showed that Estrogens were the main EDCs found on the plastic fragments, which either originated from plastic fabrication or leached out to the surrounding water. In addition, while using an average concentration, Bisphenol A showed the greatest detection frequency compared to other EDCs such as octylphenol, nonylphenol, and bisphenol S. Furthermore, it was found that smaller plastic particles (MPs) leached out larger quantities of EDCs compared to other sizes due to their higher and more efficient sorption capability of seawater. Moreover, results showed that solar irradiation has the ability to increase the concentrations of EDCs leaching out into the seawater (Chen et al., 2019a). Recently, a study investigated the leaching of six different phthalic acid esters from various commonly used commercial plastic types including LDPE, HDPE, and recycled PE. In addition, the effect of some factors on leaching was investigated such as temperature, salinity, and UV irradiation. In addition, GC-MS was used for the identification and characterization of leaching chemical substances. Generally, the leaching of various chemical substances mainly depends on the migration of the additives via the voids of the PPos. Therefore, the leaching rate of chemical substances is mainly depending on the shape and size of the additives in addition to the internal polymeric structure (Basfar, 2002; Tüzüm Demir and Ulutan, 2013). LDPE showed higher leaching rates among other used polymers (HPDE and recycled PE) (Dhavamani et al., 2022), which confirms the fact related to the diffusivity of plastic additives within the polymeric amorphous regions (Jordan et al., 2016; Satkowski, 1990). In other words, the diffusion of plastic additives is related to the ratio of amorphous regions and crystalline arrangements of the internal molecular polymeric structure of plastics. Therefore, the higher the content of amorphous regions, the more flexible and loose the polymer is, which makes the diffusivity of the plastic additives a significant factor in the leaching process. Moreover, the increase in salinity can negatively impact the leaching process (Dhavamani et al., 2022). On the other hand, the increase in UV irradiation and temperature can positively impact the leaching rate. (Dhavamani et al., 2022) found that the leaching of phthalic acid esters from recycled PE and LDPE increased as the temperature increased. It also means that additive leaching rates fluctuate based on the time of the year, where leaching rates increase in hot weather conditions rather than winter conditions. Nevertheless, the leachate dramatically increases with UV radiation exposure. **Figure** 9 illustrates the relationship between the degradation of PWs, variables affecting the process, and factors influencing the leachability of additives embedded in plastics.



- The diffusivity of additives in the polymer
- The structure of the polymer and the additives
- UV irradiation, salinity, temperature, etc...
    - Increasing salinity has a negative effect on leaching, while temperature and UV radiation increase the leaching rate.
- The leaching rate depends mainly on the shape and size of the additives as well as the internal polymeric structure.

Figure 9. Understanding the Relationship Between a) the Degradation of PWs, Variables Affecting the Process, and b) Factors Influencing the Leaching of the Plastic Additives.

Figure 10 presents the flow charts of the research methodology in this study,

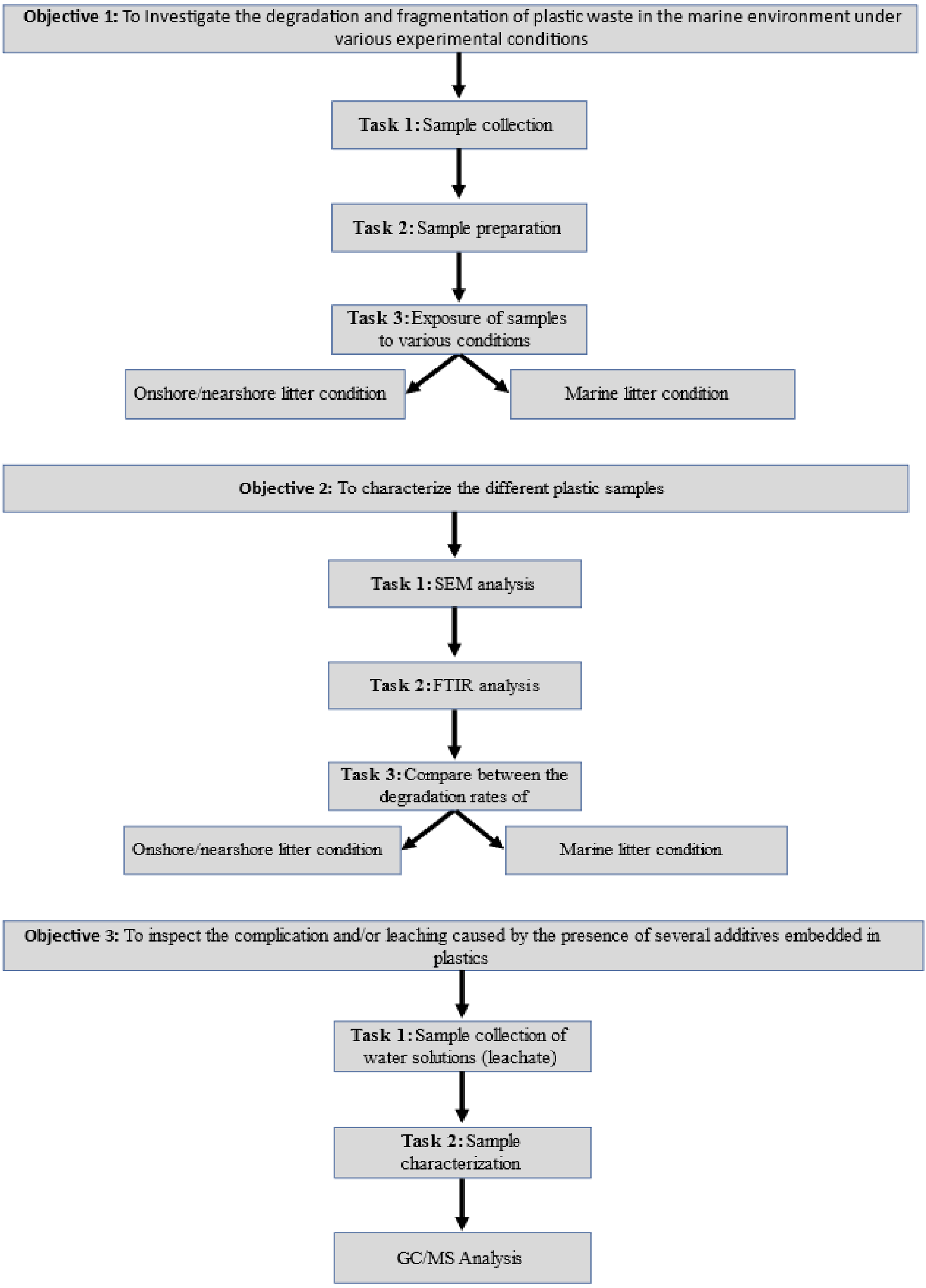


Figure 10. Flow Charts of the Research Methodology Implemented.

3.1 Sample collection and preparation of macro- and microplastics

Different commercial plastic materials were selected for the investigation of plastic degradation-fragmentation due to their crucial contribution to marine plastic litter. The different plastic products were purchased from local supermarkets. The thickness of each plastic material was measured using a manual micrometer provided by Mitutoyo, Japan (check rod size 25 mm, reading 0.01 mm, capacity 0 mm to 100 mm) as shown in **Table** 2.

Table 2. The Different Plastic Types Used in the Study and their Thickness.

Rigid			**Flexible**		
Type	Product	Thickness (mm)	Type	Product	Thickness (mm)
LDPE	Ketchup bottle	1.70 ± 0.01	PE	Hand gloves	0.02 ± 0.01
PP	Food container	0.63 ± 0.01	HDPE	Garbage bag	0.02 ± 0.01
PET	Water bottle	0.21 ± 0.01			
Foam PS	Food plate	4.37 ± 0.01			

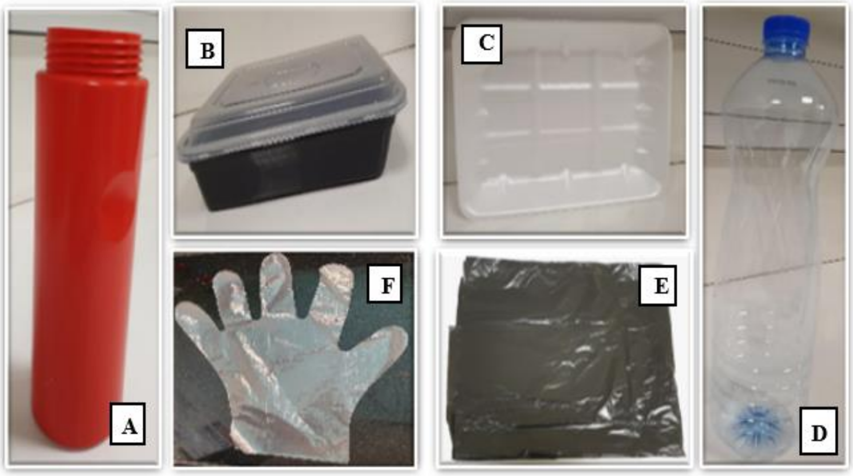


Figure 11. Plastic Materials Used for the Degradation-Fragmentation Investigation, A) LDPE - Ketchup Bottle B) PP- Food Container C) Foam PS- Food Plate D) PET – Water Bottle E) HDPE - Garbage Bag F) PE - Hand Gloves.

All plastic materials, shown in **Figure** 11, were washed with deionized water for around 3 mins to remove any dust and dried. Then, a sample from each plastic material (regardless of the size of the particle and which category it belonged to) was characterized using SEM, differential scanning calorimetry (DSC), and FTIR for prior experimental procedure analysis. Each of these plastic materials was shredded by using clean scissors (MAPED Zeno'a Fit Stainless Steel, 21 cm, France) into 2 categories, which are macroplastics: (> 5 mm), and microplastics (50 µm –5 mm). Within the microplastics category, plastic samples of 4 mm × 4 mm (± 0.01 mm) size were investigated. In addition, within the MPs category, another size of particles (less than 1 mm) was studied, and the degradation assessment for this size sub-category was based on the weight loss% and leaching investigations of bisphenol A and phthalates. On the other hand, the macroplastics category consists of 2 different sizes: Macro1 and Macro2, with a size of 5 cm × 5 cm and 8 mm × 8 mm (± 0.01 mm), respectively. The degradation investigations for Macro2 plastic sizes were mainly focused on the weight loss% assessment as well as the leaching investigations of BPA and phthalates. Sizes were determined through a manual micrometer provided by Mitutoyo, Japan (check rod size 25 mm, reading 0.01 mm, capacity 0 mm to 100 mm).

The small MP samples were sieved through a HUMBOLDT U.S.A standard sieve of 1 mm, and the particles from all 6 types of plastics, which are less than 1 mm were collected for the degradation and weight loss% investigations of this sub-category. The macro- and microplastics samples were then washed with milli-Q deionized water to remove any excess dust or tiny particles and oven-dried (50 °C - 60 °C) until sample dryness. Afterward, their weight was measured accurately through Mettler Toledo, Model: XSR105, Switzerland (± 0.00001 g) and put in small clean glass containers and stored before use in a desiccator shielded from light.

3.2 Experimental setup

The degradation of the samples was tested under two main different conditions, where all plastic samples (of all categories-sizes and types) were subjected to a 5-month simulation of:

a) Onshore litter condition (plastic samples of all types-sizes were mixed with sand collected from the Qatari shorelines, Katara Beach N^{o}1, (25^{o}21′17″N 51^{o}31′32″E) (**Figure** 12), and remain under natural sunlight), and

b) Marine litter condition (sinking or floating in Qatari seawater collected from Katara Beach N^{o}1, (25^{o}21′17″N 51^{o}31′32″E, approx. depth of 50 cm), under natural sunlight, with measurement of luminance (UV-light intensity) by using HOBO Pendant® MX2202 Temperature/Light Data Logger, total of 2 Loggers, used for the outdoor experimental setup, to monitor the light and temperature intensity on one-hour intervals throughout the duration of the experiment.

Each of the plastic samples with size categories and various types was exposed to 4 treatments, each of these treatments represent a different environmental condition, as shown in **Figure** 13:

a)- **T1 and T2**

- T1: an indoor Sand tank (Plexiglass large tank 72 L, depth 20 cm, dimensions 60 cm x 30 cm x 40 cm), where replicates of macroplastics and MPs were placed in the tank. This treatment represents the control for the onshore litter condition, where there is no sunlight exposure (under Osram Brand L18 W/765 Cool Daylight 18 W Lightbulb, 240 Volts) and a controlled laboratory temperature (20 ± 2) °C.

- T2: an outdoor Sand tank with a similar depth (20 cm), where replicates of macroplastics and MPs were placed in the tank and exposed to direct natural sunlight to simulate the onshore litter condition.

b)- **T3 and T4**

  - T3: an outdoor seawater tank (depth 25 cm, dimensions 60 cm x 30 cm x 40 cm), exposed to direct sunlight, outdoor temperature, and aerated through air pumps, NS 750, Voltage: 220 V – 240 V 50 Hz Power: 5 W, by Minjiang, China, and a Turbelle® nanostream® 6020 wave maker by Tunze, Germany, to simulate the wave abrasion, to inspect the potential degradation and fragmentation of macroplastics and MPs in the marine litter condition.

  - T4: an indoor seawater tank (depth 25 cm, dimensions 60 cm x 30 cm x 40 cm) aerated with air pumps, NS 750, Voltage: 220 V – 240 V 50Hz Power: 5 W, by Minjiang, China, and a Turbelle® nanostream® 6020 wave maker by Tunze, Germany, to mimic the real conditions, with a controlled temperature and no sunlight exposure. This treatment represents the control for the marine litter condition.

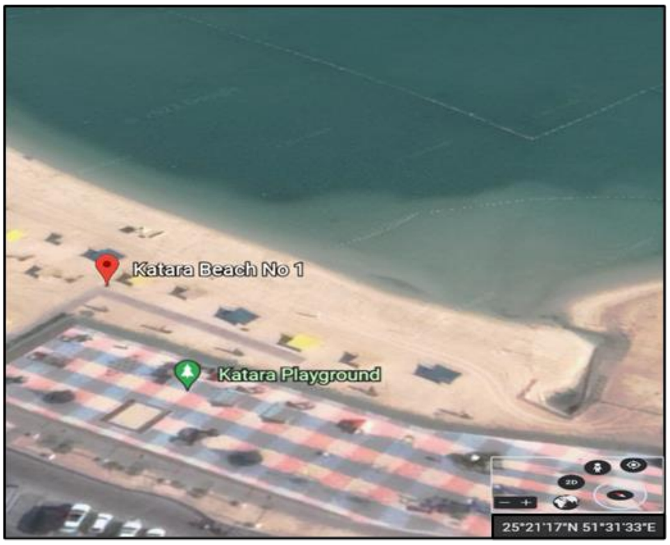


Figure 12. Geographical Location Map of Sand/Seawater Sampling in Katara Beach No.1, Doha, Qatar.

A total of 216 plastic samples from all types of plastics (PET, PS, HDPE, LDPE, PE, and PP) were placed in each tank as shown in **Figure. 13**, where 16 samples from each type were representing macroplastics (Macro2), and 16 samples from each type were representing MPs (LMPs), and 4 samples from each type represented macroplastics (Macro1). This experiment lasted a total of 5 months, from 24 Mar 2022 to 11 Aug 2022. Two different samplings were executed (week 12 and week 20), by removing a sample from each size category per treatment for all plastic types for further analysis (Weight loss% and FTIR) and examination. The GC-MS will be used to investigate the potential leachate of plastic additives from the seawater samples.

The investigation of degradation-fragmentation of small MPs (less than 1 mm) was conducted in 100 mL bottles for both onshore litter conditions as well as marine litter conditions. This facilitates the accurate recovery of MPs from sand and seawater, as an amount of 0.5 g was accurately measured for each plastic type and put in different clean glass bottles of 100 mL, in duplicates (indoor (control) and outdoor), after being washed with deionized water and oven-dried at 50°C - 60°C until complete dryness. For the outdoor set-up, glass bottles were filled with 100 mL seawater to simulate the marine condition and closed tightly to avoid evaporation during the period of natural sunlight exposure, with a periodical manual mixing to mimic the wave abrasion, as shown in **Figure** 13 (C and B). Meanwhile, the same outdoor setup was implemented for the onshore simulation, where the plastics were mixed with 40 mL of sand instead of seawater. The same setup was implemented for the indoor experiment. However, the marine litter condition samples were put, periodically, on the shaker platform to mimic the wave abrasion at a speed of 180 rpm for 5 months, as illustrated in **Figure 13** (D). In this study, the investigation of the potential degradation of this specific sub-category of MPs, which is small MPs, was performed mainly to study the percentage of weight loss (%) of these tiny particles.

Figure 13. Indoor and Outdoor Experimental Set-up, A) Indoor Experimental Setup (T1 and T4), B) Outdoor Experimental Setup (Morning) (T2 and T3), C) Outdoor Experimental Setup (Afternoon) (T2 and T3), D) Small MPs Indoor Experimental Setup (Marine Litter Condition). E) Small MPs Indoor Experimental Setup (Onshore Litter Condition – **T1**).

Experimental conditions

The pH of the seawater collected was measured by using a Jenway 3520 pH meter, Fisher Scientific, UK. It was found to be 8.56, which is slightly higher than the global average pH of 8.07 ± 0.02 (Jiang et al., 2019). In addition, the seawater salinity was found to be approximately 45 ‰, measured by the REED R9600 refractometer, China, which is much higher than the average seawater salinity (35 ‰) (Cullum et al., 2016), since the seawater salinity in the Arabian peninsula is considerably higher than other regions in the world (Li and Babcock, 2014). Moreover, Qatar is an arid country with harsh environmental conditions, where there is severe water scarcity due to a critical lack of rainfall with approximately 82 mm/year. In addition to the high evaporation rates which reach more than 2000 mm/year (Mohamed et al., 2021; Rahman and Zaidi, 2018). Thus, to compensate for the high seawater evaporation rate during the experimental work, which was calculated to be 1,744 mm/year, deionized water was added on a regular basis to keep the water level consistent at 25 cm each time a slight dropping in the water level occurred due to evaporation. This will help in maintaining the concentration of salts and substances, which are available in the seawater (potential plastic leachate). In addition, both tanks were covered with a glass lid cover. Moreover, the outdoor tank was placed on a trolley for easy movement and was left outside, to try to simulate the real seawater (SW) temperatures. The covered glass tank traps the heat and elevates the seawater temperature to more than the current SW temperature (> 35 °C) which is commonly observed around the eastern Arabian Peninsula (Torquato et al., 2022).

Furthermore, the pH and salinity of the seawater, both in the indoor and outdoor tank, were monitored during and after the plastic exposure to verify if there are any significant changes.

The degradation of macro- and microplastics under environmental marine conditions depends on several environmental conditions, such as oxygen level, luminance, temperature, as well as the properties of PPos materials and their degrading nature (e.g., MW, and additives presence). Over the experimental period, water/sand temperature and light levels (luminance) were monitored and assessed daily, mainly for the outdoor experimental setup, by using HOBO Pendant® MX2202 Temperature/Light Data Logger. Moreover, the oxygen availability factor was evaluated, where the seawater was aerated by air pumps and the tank simulating the onshore litter conditions remained under natural weather conditions (sunlight, oxygen, and temperature).

After setting up the experiment, it was observed that some plastics were floating and others were sinking to the bottom of the marine simulation tanks, where all size categories of HDPE, PE, and PET plastics were sinking to the bottom of the tanks. However, all other types, regardless of their size categories, were floating on the surface of the seawater. After a few weeks of natural sunlight exposure, some degradation and/or fragmentation signs were initiated in some plastic types such as HDPE, PE, PP, and LDPE. These signs were, mainly, fading of color, discoloration, loss of clarity, formation of cracks, and chalky appearances, **Figure** 14 illustrates some of the visual degradation signs after 3 weeks of exposure to marine litter condition (T3) compared to the plastic samples prior to the experiment (Week 0).

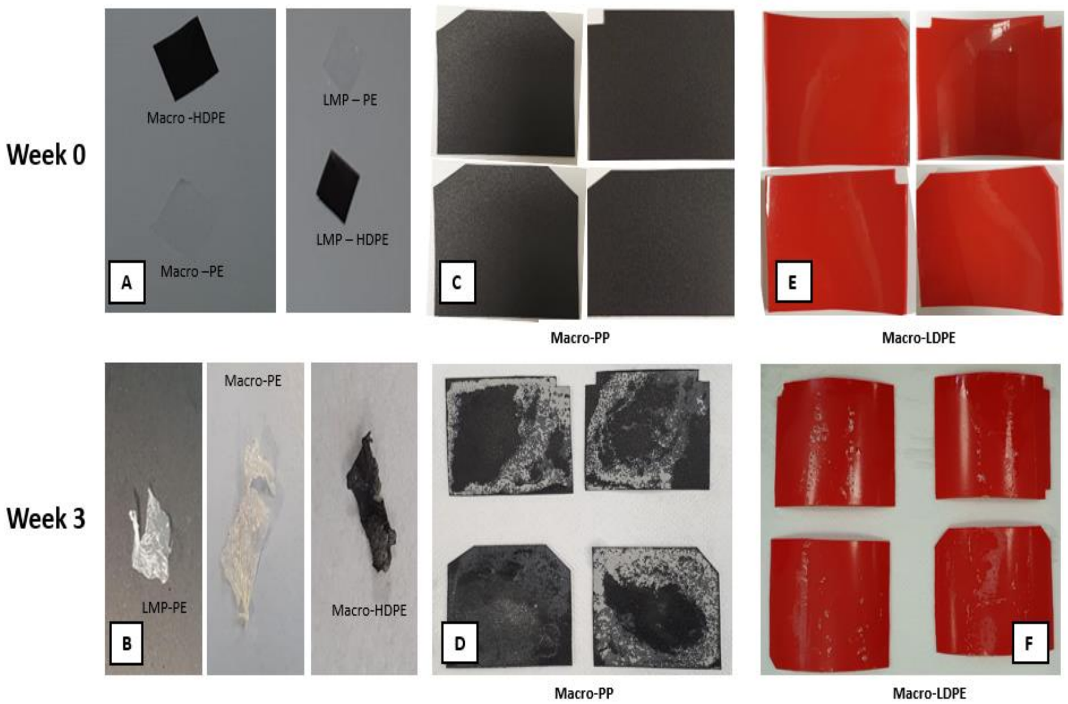


Figure 14. Degradation-Fragmentation Visual Signs of HDPE, LDPE, PP, and PE After 3 Weeks of Exposure to Marine Litter Conditions (T3). A) HDPE and PE in Macroplastics and Large MP (LMP) Size at Week 0 (Prior Exposure), B) LMP-PE, Macro-PE, and Macro-HDPE After 3 Weeks of T3 Exposure, C) Macro-PP at Week 0 of Exposure to Marine Litter Condition (T3) - (Prior Exposure), D) Macro-PP After 3 Weeks of Exposure to Marine Litter Condition (T3), E) Macro-LDPE at Week 0 of Exposure to Marine Litter Conditions (T3) – (Prior Exposure), F) Macro-LDPE after 3 Weeks of Exposure to Marine Litter Conditions (T3).

3.3 Sample characterization and experimental procedures

3.3.1 Soil Particle Size Analysis

Soil particle analysis was performed for the soil sample collected from Katara and used in this study. Sieve analysis was achieved to have a better understanding of the soil type and to determine the percentage of various grain sizes included within the soil sample. It mainly helps in the determination of the coarser and larger sand particles.

This test was performed by following the standard test method for particle size analysis of soils- ASTM D 422. Firstly, the weight of the dry soil sample was measured by using an analytical balance after being oven-dried overnight at approximately 100 °C. Secondly, the set of sieves was cleaned by using a cleaning brush, weighed by using an analytical balance and assembled in ascending order of sieve number and sizes. The pan was used as the last container to collect the rest of the fine sample particles. Then, the soil sample was poured into the top sieve and the cap was placed over it. Afterward, the sieve stack was placed in the mechanical shaker and shaken for 10 mins. Finally, the stack was removed from the shaker and the weight of soil which was retained from each sieve as well as the pan was recorded.

The analysis of soil particle size was done in this research study due to its significance in providing grain size distribution, which is necessary for soil classification. Thus, it helps in understanding how plastic pieces can be affected by the different grain sizes of soil. Since studies show that the inherent complex properties of soil have a great effect on plastics (macroplastics and MPs) and their environmental behaviour (Guo et al., 2022). In addition, the physicochemical properties of soil such as pH, pore, etc., also have an impact on the relocation of macroplastics and MPs (Guo et al., 2022). Therefore, the pH of the soil was measured before and after the experiment for both T1 and T2. The pH of the soil was determined according to the method mentioned elsewhere (Zhang et al., 2021b). pH of the soil was measured by using a Jenway 3520 pH meter, provided by Fisher Scientific, UK, where a 5:1 volume weight ratio (water suspension: soil) was used (e.g., 5 g of soil in 25 mL of deionized water). The mixture was stirred well for 1 min, and the readings were taken after 1hr of equilibration.

There are two main quantities, which are required for the characterization of the sand sample. Firstly, the effective particle size (D10) which refers to the diameter of the particle which 10% of the grains in this sample are less significant in size than it and 90% of grains are bigger compared to it. Secondly, the coefficient of uniformity, this coefficient expresses the difference in size between the biggest and smallest grains in the sample. This method is also called the particle size distribution. The coefficient of uniformity is described as the ratio of D60/D10. D60 is the size of the particle where 60% of the grain samples are less significant in size and 40% are bigger.

3.3.2 Weight loss (%) calculations

All plastic samples were accurately weighed, before and after being subjected to any experimental tests, to determine any weight loss, as part of their degradation process. The weight of the plastic samples was measured after rinsing thoroughly with demineralized water to remove, as much as possible, any traces of salts from the seawater, swept and dried in an oven at 50 °C - 60 °C for 1-2 days until complete dryness to remove the excess of water and measure their constant weight. Concurrently, FTIR analysis was carried out to assess any degradation signs (overtime), prior to and after weathering due to onshore or marine simulated exposure. During this 5-month procedure, samples were taken and examined periodically (week 0, week 12, and week 20) to compare the degradation of onshore PW and marine plastic litter.

The average weight loss% was computed for all types of plastics by using this mathematical formula:

Avg. weight loss% = $\frac{avg.Wo-avg.Wf}{avg.Wo} \times 100$; where avg. W_0 is the average initial weight of all plastic replicates and avg. W_f is the average final weight of the plastics

Although the degradation process can include chemical and physical modification in the properties, depolymerization, complete mineralization to H_2O and CO_2, and an overall loss of mass, which can be due to any mechanism, to realize the aims of this research study, the degradation definition will be limited to the overall loss of mass from the initial plastic polymer fragments. Recent research studies suggested that the ablation of plastic surfaces can be crucial for tiny particles in the marine environment (Lambert and Wagner, 2016b). Yet, it must be mentioned that this definition is found to be most suitable for larger plastic fragments. In addition, the degradation of the macro- and microplastics will reduce the initial mass without altering the overall amount of plastic present. The degradation rate of polymer (r_{deg}, g/d), is mainly the change of mass (mass loss) per unit of time (t), as it is represented in this equation:

$$r_{deg} = -\frac{\Delta m}{\Delta t}$$

To compare the two conditions (marine litter condition and onshore litter condition), the degradation rates of plastics exposed to both conditions were calculated.

3.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The plastic polymers were analysed by using FTIR, Spectrum 400 FT-IR, from PerkinElmer, using UATR, 8 scans per sample, 4 cm^{-1} resolution. The spectrum range of analysis was 4,000 cm^{-1} to 400 cm^{-1}. The concept behind FTIR is mainly the production of the transmittance or absorbance spectrum by passing the IR radiation through the sample. FTIR analysis was chosen in this study owing to its distinctive feature where the whole wavelength range could be measured at once. The spectrum created whenever an IR frequency is identical to the vibrational frequency of a bond acts as a “fingerprint” for the sample. In addition, the spectrum provides information about the molecular structure of the sample through the position of peaks, their intensity, and their shape. Plastic materials, shown in **Figure** 11, were washed with distilled water for around 3 mins to remove any dust and dried naturally for 2 days. Then, a sample from each plastic material (regardless of the size of the particle and which category it belongs to) was characterized using FTIR for analysis of the sample before being subjected to any treatments. Afterward, the various samples were analysed by using FTIR after being exposed to the different treatments. OriginPro 2018 software for scientific graphing and data analysis was used to graph the FTIR spectra.

3.3.4 Scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX)

Scanning electron microscopy is one of the high-resolution electron microscopy tools which provides information about MPs as well as NPs (Mansoureh and Parisa, 2018). This surface imaging technique analyses the samples on a very fine scale by using a high electron beam, which probes the sample and provides informative data about the micro or nanosized material. SEM technique is able to monitor the size, formation, size distribution, and morphology of synthesized micro or nanosized material (Mansoureh and Parisa, 2018). The characterization of samples using SEM coupled with energy-dispersive X-ray spectroscopy (EDX) can direct the analytical chemical composition and investigate the surface structure simultaneously. In addition, the morphology of nanosized materials which are below 10 nm can be characterized through high-resolution SEM (Rashidi, 2021). These characteristics make results simple and easier to interpret. SEM-EDX analysis was used in this study to investigate the sample information, the topography of the surface as well as the sample composition. In this study, the analysis was performed by using Nova Nano SEM 450 coupled with Bruker Energy Dispersive X-ray (SEM/EDX) Spectroscopy. Samples have been imaged at a magnification of 500x – 25,000x.

3.3.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was performed in this study to analyse the degradation of all different plastics. DSC reveals details about the interaction between the plastic components and the variation of their chemical structure when exposed to heat. The DSC curves are expected to be different depending on the type of plastic polymer to which they belong. DSC analysis has been used in various studies (Mehrotra et al., 2010; Tarrío-Saavedra et al., 2011), and the results showed that the differences in the thermal degradation of each material used for the investigation depends on the constituents of the material itself. Consequently, DSC curves can be utilised as a discriminant characteristic. This analysis was performed on a Perkin Elmer, Jade DSC under a nitrogen atmosphere. A known weight of each plastic type (HDPE, LDPE, PET, PE, PP, and PS) was analysed, where about 1.162 mg, 2.071 mg, 2.494 mg, 2.292 mg, 2.857 mg, and 1.327 mg, were heated from 25 °C to 250 °C with a rate of 10°C/min, respectively. The temperature was held at 250 °C for 1 min. Then, the instrument was cooled by using a chiller.

3.3.6 Gas chromatography mass spectrometry (GC/MS)

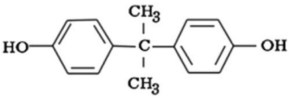
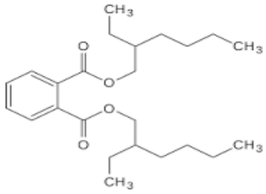
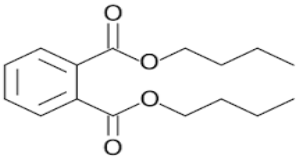
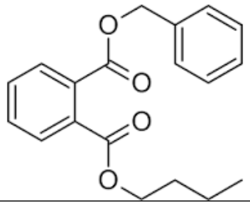
3.3.6.1 Liquid-Liquid extraction and GC/MS analysis

Three different phthalates were selected for the investigation of leachable plastic additives, which were bis(2-ethylhexyl) phthalate (DEHP), benzyl butyl phthalate (BBP), dibutyl phthalate (DBP), and BPA. All analytical standards were of high purity grade and were obtained from Sigma Aldrich, Germany.

Chemical substances are intentionally added during the manufacturing of plastics to aid with the polymerization process as well as, to improve the properties of the resulting plastic products (Hahladakis et al., 2022). However, there are also those chemical substances that are not intentionally added but arise as a result of the degradation of certain plastic products. These chemicals can be of concern (Groh et al., 2019; Leslie et al., 2016) because they migrate from these plastic products such as food containers to the food they contain (Vilarinho et al., 2019). Therefore, it is imperative that the safe limits of such chemicals are known.

In the context of this study, there are four such chemicals of interest: DEHP, BBP, DBP, and BPA. The reference dose (RfD) and specific migration limit (SML) along with the tolerable daily intake (TDI) are parameters that define the safe limits of such chemicals. The RfD according to the United States Environmental Protection Agency (USEPA), is the approximate daily dose of a substance that the human population can be exposed to safely without any serious risk. SML is the total amount of a chemical substance that can be released into the food from any packaging (Dittmann et al., 2022), while the TDI according to the European Food Safety Authority (EFSA), is the maximum amount of non-intended chemicals in food and water that can be consumed by people over their lifetime without any serious risk. The chemical structures and the international standards (RfD and TDI) of BPA, DEHP, DBP, and BBP are shown in **Table** 3.

Table 3. The Targeted Chemical Compounds and Their International Standards (Reference Dose (RfD) and Tolerable Intake Limit (TDI)). (Source: USEPA and EFSA).

Name of the compound	Chemical structure	RfD (mg/kg bw/day) [a]	TDI (mg/kg bw/day) [b]
BPA		0.05	0.04
DEHP		0.02	0.05
DBP		0.1	0.01
BBP		0.2	0.5

[a] USEPA (the United States Environmental Protection Agency)
[b] EFSA (European Food Safety Authority)

A stock solution of 100 ppm was prepared. Serial dilutions were performed by diluting this solution to 25 µg/L, 100 µg/L, 200 µg/L, 1000 µg/L, and 2500 µg/L to generate a calibration curve.

The extractions were performed in controlled laboratory conditions, at a temperature of 23 °C. All produced solutions were collected in new clean tubes. A simple liquid-to-liquid extraction (LLE) was performed to determine the presence of the four selected degradation by-products of plastics (DBP, BPA, BBP, and DEHP) in the SW samples after being exposed to two different treatments. In this method, 45 mL of each sample was transferred into a conical centrifuge tube. The sample solution was then injected with 2 mL of the solvent Dichloromethane and 50 mL of 36% Hydrochloric acid. Then, the mixture was shaken by using a vortex mixer for 1 min and then sonicated for 10 mins. After that, the sample solution mixture was centrifuged at 200 rpm for 10 mins for separation purposes. Lastly, 1 mL of the organic phase was collected in a clean Eppendorf tube and around 100 mg of sodium nitrate was added to eliminate the moisture and the remaining water droplets and injected into the GC-MS instrument for analysis. The running time of the analysis was 25 mins. The protocol was adapted following methods described elsewhere (Ajdari et al., 2018) modified and optimized for the SW used in this study.

The chromatographic analysis was performed by using GC-MS Agilent 6890N, with an inert XL mass selective detector 5975B inert XL MSD, obtained from Agilent Technologies, US. Helium was used as a carrier gas at a flow rate of 1.2 mL/min and a pressure of 11.05 psi. The chromatographic separation was accomplished on a capillary column (Agilent DB 5MS, 30m x 0.25mm, with a film thickness of 0.25 μm). The GC oven was programmed as follows; the initial temperature of 70 °C was set for 1 min, then increased at 20 °C/min until it reached 300 °C and held for 8 mins. 1 mL of each sample was injected into a splitless mode at 250°C. Data were obtained by using selected ion monitoring (SIM) to enhance the sensitivity of the targeted compounds. This can be accomplished by setting the voltage of the analyser to scan a single peak with a defined retention time. SIM helps in reducing the noise and improving the signal because the analyser can take longer time intervals to collect the specific ions. In addition, the obtained data were analysed by using Agilent MSD ChemStation software. **Table** 4 shows the retention time of the targeted chemical compounds (DBP, BPA, BBP, and DEHP) by GC-MS.

Table 4. Retention Time (min) of the Targeted Chemical Compounds (Phthalates and Bisphenol-A) by GC-MS.

Compound	**Molar Mass (g/mol)**	**Retention time (min)**
Dibutyl phthalate (DBP)	278.3	10.09
Bisphenol-A (BPA)	228.3	11.18
Benzyl butyl phthalate (BBP)	312.4	11.93
Bis(2-ethylhexyl) phthalate (DEHP)	390.6	12.64

DBP, BPA, BBP, and DEHP were quantified by dilutions of 25 µg/L, 100 µg/L, 200 µg/L, 1000 µg/L, and 2500 µg/L to generate a calibration curve. The response factor of each chemical compound was assessed from a freshly prepared standard.

3.3.6.2 GC/MS calibration and method optimization

GC/MS calibration curves were generated, and linearity was examined over five-point calibration ranging from injected concentrations of 25 µg/L to 2500 µg/L for all different chemical compounds as shown in **Figure** 15. The recoveries of phthalates and bisphenol A were computed from the spiked SW samples. The collected SW samples before and after 140 days of exposure were spiked with authentic chemical compounds with different concentrations of 50 µg/L, 500 µg/L, and 2000 µg/L to execute the recovery experiments by using the same previously mentioned GC/MS analysis procedure. All SW samples were performed in triplicates to validate the accuracy of data.

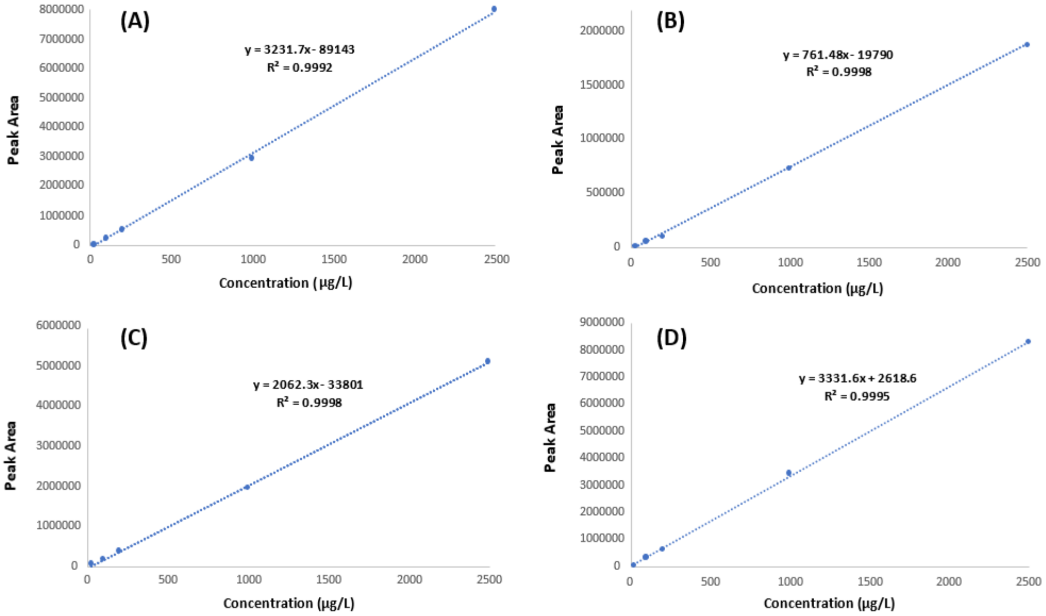


Figure 15. Calibration Curves of Phthalates and Bisphenol A (A) DBP, (B) BPA, (C) BBP, (D) DEHP.

3.4 Statistical analysis

Principal component analysis (PCA) was used as a statistical tool to compare multivariate data. This technique helps in reducing the dimensionality of the different data sets. It categorizes similar spectra together, which will increase the interpretability of the results and minimize the loss of information. This maximization of variance can be accomplished by generating new uncorrelated variables (Jolliffe and Cadima, 2016). Due to the effectiveness of this statistical analysis, it was performed to investigate the difference in the degradation-fragmentation of different plastics under marine litter conditions and onshore litter conditions. In this study, PCA and cluster analysis have been applied using FTIR spectra as input data. The effects of treatment, size, and time on all different plastic types were studied. Firstly, PCA was performed to study the effect of all four treatments at a specific time (e.g., week 20 was chosen for this analysis since it is the last experimental week where results show the highest potential degradation). In addition, this analysis was implemented on the smaller size sub-category (LMP) for this study due to its higher degradation (weight loss%) and a higher percentage of variance. Subsequently, the effect of time and size on specific treatment was studied by performing PCA for the most effective treatment at degrading each plastic type (which showed a significant difference). The most effective treatment for each plastic type was chosen based on the highest percentage variance, and correlation values. Finally, a combination of effects was performed by mainly combining the effect of outdoor treatments (T2 and T3) on various plastic types with 2 different sizes (LMPs and Macros1). OriginPro 2018 software for scientific graphing and data analysis was used to perform the statistical analysis.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Soil Particle Size Analysis

Soil particle size analysis showed that the soil sample consisted of sandy soil with more than 96% of sand (84.38% of fine sand, 12.32% of medium sand), around 2.5% of slit, and approximately 0.8% of clay, based on the unified soil classification system (USCS) as illustrated in **Table** 5. These results were obtained through calculations, where soil mass was obtained by subtracting the weight of an empty sieve from the weight of the sieve and retained soil. Then, the %retained was calculated for each sieve by dividing the retained weight of each sieve by the initial weight of the soil sample. Afterward, the %passing or also called percent finer was calculated by subtracting the value from 100% initially and then subtracting by the %retained for each sieve since it is a cumulative procedure. Finally, the semilogarithmic plot of grain size vs. percent finer was made as shown in **Figure** 16, and Cu and Cc for the soil were computed by using the following ratios:

$$Cu = {}^{D60}\!/_{D10}$$

$$Cc = {}^{D30^2}\!/_{D60 * D10}$$

Cu and Cc were found to be 0.75 and 1.09, respectively. Thus, according to these findings, the sand used for this research has an effective size of 3.85 mm, as shown in **Figure** 16. In addition, D30 and D60 were found to be 3.5 mm and 2.9 mm, respectively. Cc and Cu provide an idea about the particle size distribution of a soil sample. Moreover, these values are utilised in the classification of soil. In this experiment, Cu is closer to 1, which means that the soil is uniformly graded. On the other hand, Cc is greater than 1, which indicates that the soil sample is well-graded. Furthermore, the pH of the soil was measured before and after the experiment for both T1 and T2. Soil pH was found to be 8.34 before exposure to different types of plastics.

Afterward, the pH of the soil increased for both treatments (T1 and T2) to 8.64 and 8.88, respectively. Several studies suggested that MPs in the soil can result in changes in the physicochemical properties. These findings are consistent with other research findings, where the pH of the soil increased with MPs (Zhao et al., 2021). This confirms that MPs could affect the physico-chemical properties of soil including their pH.

Table 5. The Soil Classification Based on the USCS.

Type of Soil		**Size of Particle (mm)**
Clay		<0.002
Silt		0.002-0.075
Sand	Fine	0.075-0.42
	Medium	0.42-2.0
	Coarse	2.0-4.75
Gravel		4.75-75

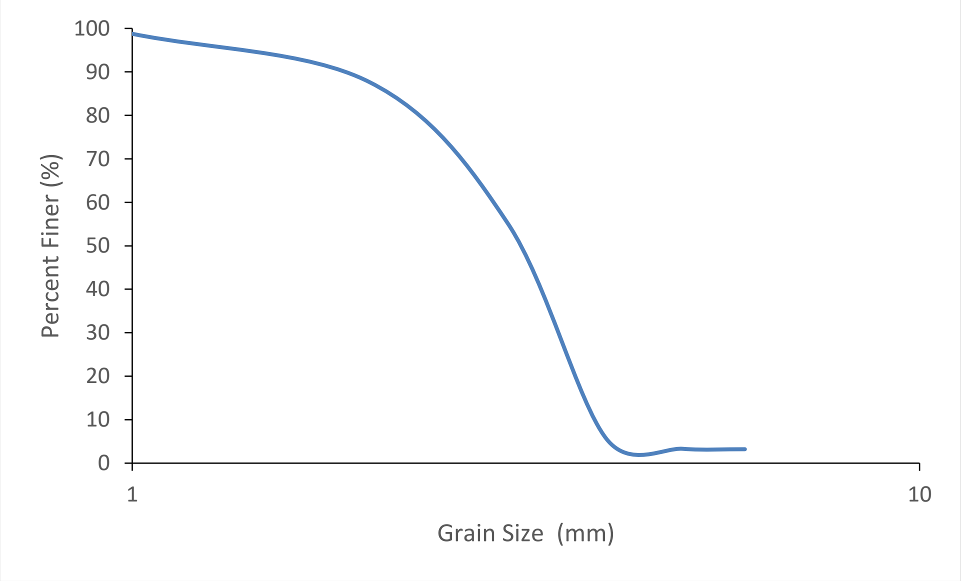


Figure 16. Grain Size Distribution Curve (Grain Size (mm) vs. Percent Finer (%)).

4.2 Environmental conditions

The degradation of plastics under environmental marine conditions depends on several environmental conditions, such as oxygen availability, luminance, temperature, as well as the properties of PPos materials and their degrading nature (e.g., MW, and additives present). Thus, water/sand temperature and sunlight levels (luminance) were monitored and assessed daily during the experimental period, mainly for the outdoor experimental setups, by using HOBO Pendant® MX2202 Temperature/Light Data Logger. Collected data showed that temperature and sunlight varied over time during the experimental duration. These variations were mainly seasonal, as temperatures decrease in winter and increase in the summertime. The maximum and minimum temperatures and sunlight intensities exposure during the experimental period for both outdoor treatments (T2 and T3) are shown in **Table** 6.

Table 6. The Maximum and Minimum Temperatures (°C) and Sunlight Intensities (lux) Exposure During the Experimental Period for Outdoor Treatments.

Treatments							
T2				**T3**			
Min Temp °C	Max Temp °C	Min light intensity (lux)	Max light intensity (lux)	Min Temp °C	Max Temp °C	Min light intensity (lux)	Max light intensity (lux)
18.62	82.92	0	100,475	18.27	59.93	0	90,644

The temperatures and sunlight intensities for T3 are consistently lower than T2 as shown in **Figure** 17. In addition, the maximum and minimum temperatures for T2 were found to be 82.92°C and 18.62°C, respectively, which are higher than T3 as illustrated in **Table** 6. Moreover, the maximum light intensity for T3, which was logged at 90,644 lux was lower than T2. It should be also mentioned that the environmental conditions of the other indoor control treatments for onshore and marine conditions (T1 and T4) were quite similar since both were put inside the laboratory with a controlled temperature (approximately 22°C) and no sunlight exposure (under Osram Brand L18W/765 Cool Daylight 18 W Lightbulb, 240 Volts).

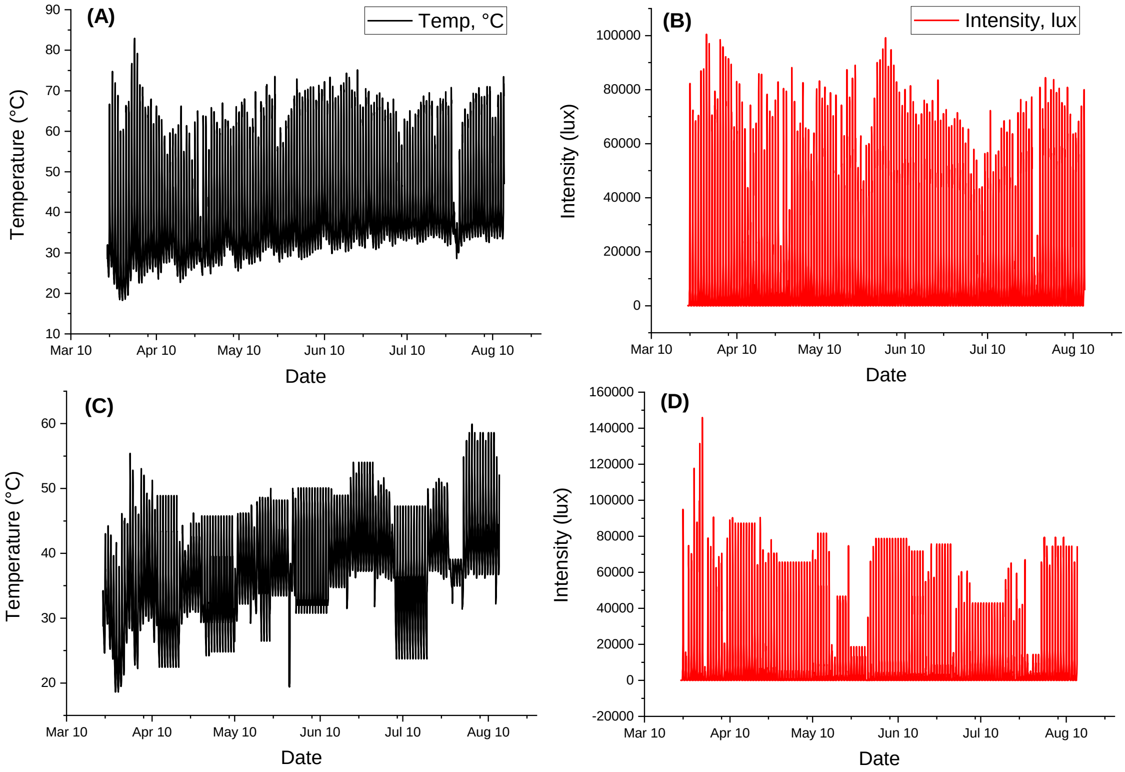


Figure 17. Luminance and Temperature Exposure Over the Experimental Period for T2 and T3: (A) Temperature (°C) Exposure Over 5 months of the Experimental Period for T2 (B) Luminance Intensity (lux) Over 5 months of the Experimental Period for T2, (C) Temperature (°C) Exposure Over 5 Months of the Experimental Period for T3, and (D) Luminance Intensity (lux) Over 5 Months of the Experimental Period for T3.

On the other hand, the outdoor treatments experienced greater fluctuations in the temperatures as well as sunlight intensities. The outdoor environmental conditions fluctuations for each month during the experimental period were shown in **Figures** 18 and 19. As expected higher light intensities and temperatures were recorded in the hot summer months especially June, July, and only a few days in August fell within the experimental period.

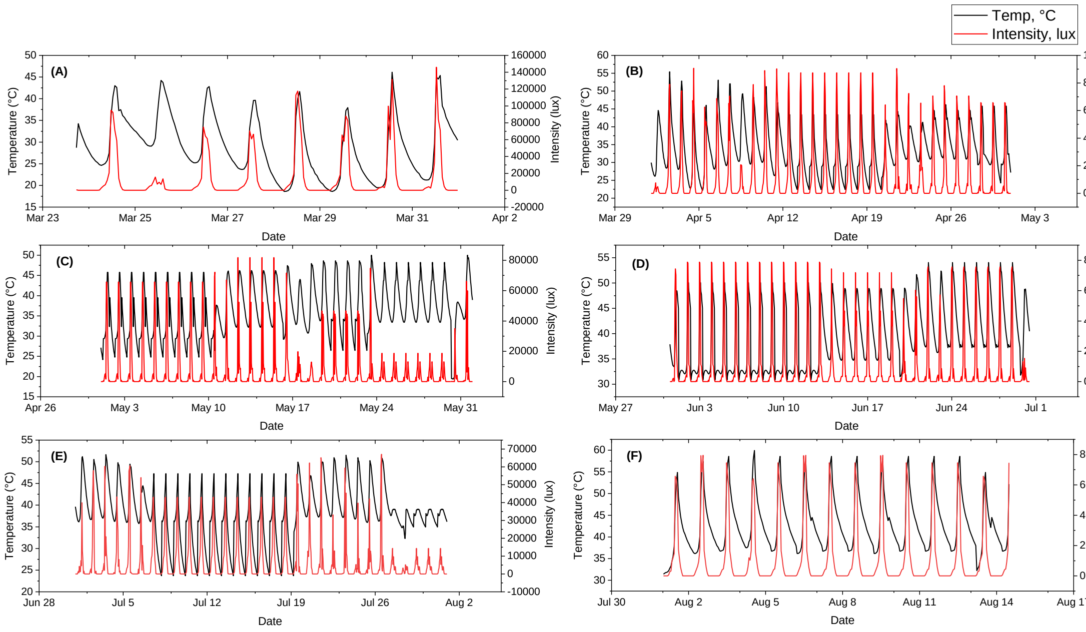


Figure 18. Environmental Conditions (Temperature (°C), and UV-Intensity (lux)) During Experimental Period (A) March, (B) April, (C) May, (D) June, (E) July, and (F) August For T3.

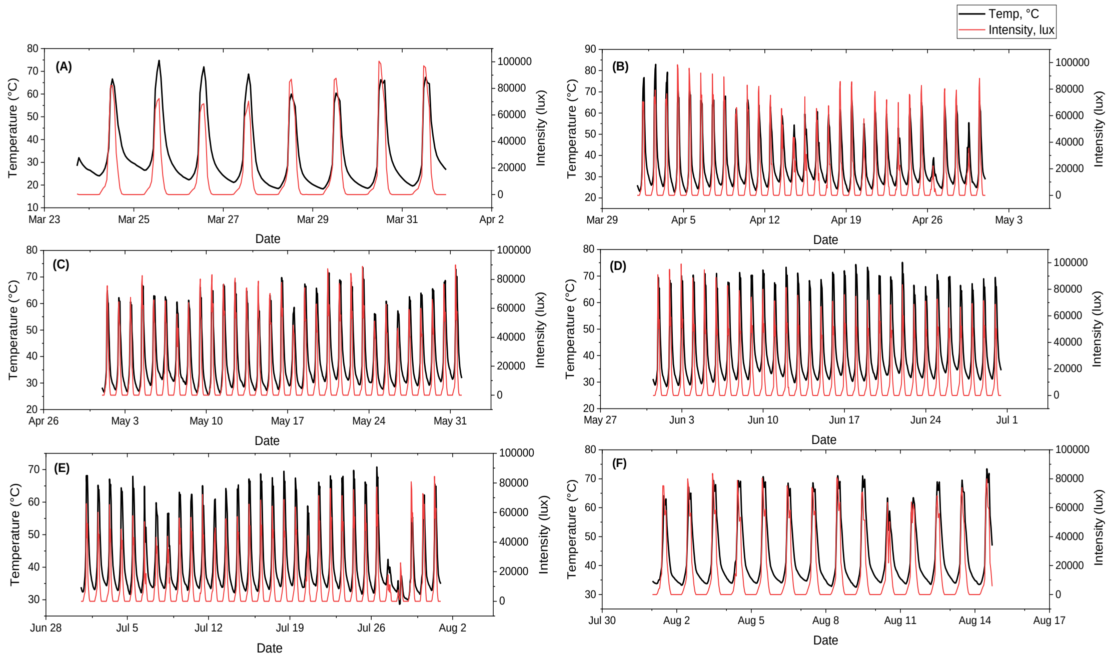


Figure 19. Environmental Conditions (Temperature (°C), and UV-Intensity (lux)) During Experimental Period (A) March, (B) April, (C) May, (D) June, (E) July, and (F) August for T2.

Furthermore, the pH and salinity of the seawater, both in the indoor and outdoor tank, were monitored during and after the plastics exposure to verify if there were any significant changes. Since evaporation is one of the main factors affecting salinity, an expected slight drop in the pH and salinity was recorded. However, since the evaporation was compensated by adding deionized water, the drop was minimal. It should be also mentioned that on Jul 28th, 2022, Doha, Qatar witnessed some rain during the day. While the tanks were covered with a lid, some of the rainwater may have found its way into the system.

After a few months of natural sunlight exposure, some growth of algae was observed in the outdoor seawater tank (T3). This algae growth was mainly due to the sunlight, temperature, air, and mixing factors. This assumption can be confirmed by the fact that the algae growth appeared only in the outdoor experimental setup (T3), and T4 (indoor marine condition) did not show any signs of algae or microalgae growth due to the absence of sunlight. Based on the literature, the main factors that determine the type of algae that grows and how dense they grow are temperature, light, nutrients availability, oxygen, and mixing (Chowdury et al., 2020). This phenomenon occurs in reality as well, where bacteria and algae in the seawater grow under marine environmental conditions. Several studies showed that marine algae and microbes (e.g., bacteria, algae, and fungi) can efficiently degrade and digest plastics and polymeric materials, especially in marine saline waters (Venkatesh et al., 2021; Zeenat et al., 2021). Thus, undoubtedly, the different marine bacterial strains and algae, which are within the Qatari seawater samples, played a role in the degradation of plastic samples. Although it would be interesting to know to what extend these marine algae and bacteria played a role in the plastic degradation process, this would be perhaps the focus of another study as the bacterial/microbial degradation of plastics is not within the scope of this study.

4.3 Weight loss (%) calculations

After a few weeks of exposure to natural sunlight, initial signs of degradation and/or fragmentation signs were observed in some plastic types such as HDPE, PE, PP, and LDPE. These signs were, mainly, fading of color, discoloration, loss of clarity, formation of cracks, and chalky appearance. Thus, the effects of marine and/or onshore conditions on plastic waste could be observed within the first few weeks. After 5 months (140 days) of exposure to different treatments, cracks and fragmentation were more visible, especially for HDPE, and PE. An example of the different signs is shown in **Figure** 20. In addition, **Figure** 21 shows the discolorations, loss of clarity as well as chalky appearance in other plastics mainly PS, LDPE, and PP. These plastics did not show any other obvious fragmentation signs. However, their materials became more fragile and susceptible to fragmentation upon being touched. Furthermore, PET samples did not show any fragmentation and/or degradation signs during the experimental period. This could be mainly due to the high melting point of the polymer. Nevertheless, based on the weight loss% findings, PET samples were also degraded after being exposed to the different treatments.

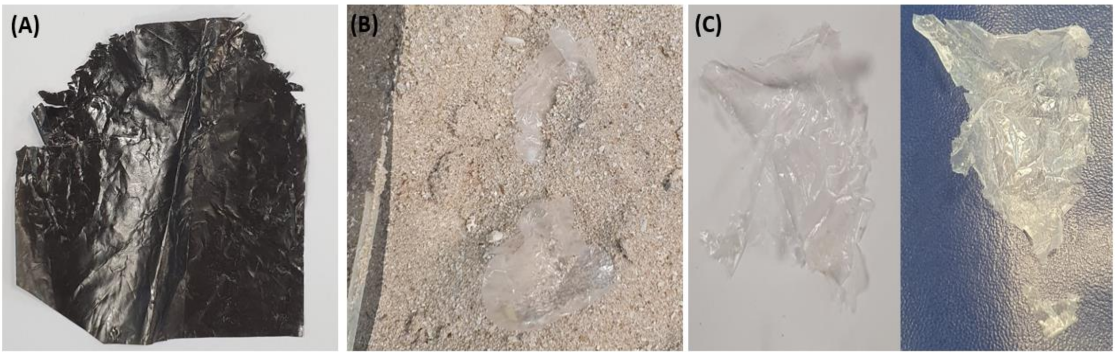


Figure 20. Fragmentation and Degradation Signs of HDPE and PE Under Onshore Conditions. (A) Macro1 HDPE After 140 Days of Exposure to T2. (B) Macro1 PE (on sand) After 140 Days of Exposure to T2. (C) Fragmented Macro1 PE After 140 Days of Exposure to T2. Picture Specifications: Resolution 12 MP, 2x Optical Zoom.

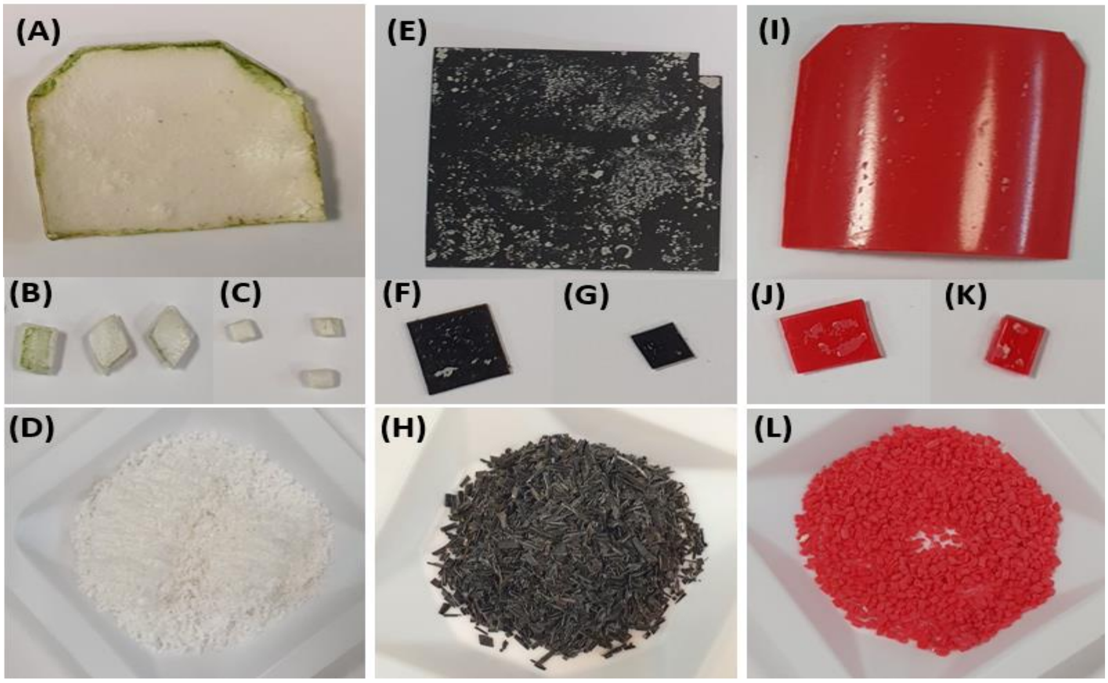


Figure 21. (A) Macro1 PS, (B) Macro2 PS, (C) LMPs PS, (D) SMPs PS, (E) Macro1 PP, (F) Macro2 PP, (G) LMPs PP, (H) SMPs PP, (I) Macro1 LDPE, (J) Macro2 LDPE, (K) LMPs LDPE, and (L) SMPs LDPE After 140 Days of Exposure To T3. Picture Specifications: Resolution 12 MP, 2x Optical Zoom.

Weight loss% findings showed great variations between the different types of plastics, the four treatments used within the same plastic-type, as well as the different size categories used in this study. The average weight loss% variations of all types and their different size categories after 140 days of exposure to four treatments are shown in the tabulated data (**Table** 7-10) as well as the Figures (**Figure.** 22-25).

Table 7. Average Weight Loss% Over Degradation Time (Days) of PP, PET, LDPE, HDPE, PE, and PS SMPs After 140 Days of Exposure to T1, T2, T3, and T4.

	Degradation time (days)	**Weight loss%**					
		PP SMP	**PET SMP**	**LDPE SMP**	**HDPE SMP**	**PE SMP**	**PS SMP**
T1	Day 0	0	0	0	0	0	0
	Day 140	0.5031	3.261	0.2680	0.1863	1.225	0.4330
T2	Day 0	0	0	0	0	0	0
	Day 140	1.040	4.335	0.3923	5.197	4.917	0.1380
T3	Day 0	0	0	0	0	0	0
	Day 140	42.83	4.384	8.734	3.335	2.303	6.840
T4	Day 0	0	0	0	0	0	0
	Day 140	2.391	0.9370	1.790	1.593	0.4199	3.167

Table 8. Average Weight Loss% Over Degradation Time (Days) of PP, PET, LDPE, HDPE, PE, and PS LMPs After 140 Days of Exposure to T1, T2, T3, and T4.

	Degradation time (days)	**Weight loss%**					
		PP LMP	**PET LMP**	**LDPE LMP**	**HDPE LMP**	**PE LMP**	**PS LMP**
T1	Day 0	0	0	0	0	0	0
	Day 140	0.6060	4.190	0.08358	0.4078	4.565	0.7106
T2	Day 0	0	0	0	0	0	0
	Day 140	0.6389	4.554	1.042	63.33	58.09	0.5930
T3	Day 0	0	0	0	0	0	0
	Day 140	48.62	8.408	11.35	2.700	7.438	8.899
T4	Day 0	0	0	0	0	0	0
	Day 140	0.7842	1.047	1.286	1.012	2.946	0.7315

Table 9. Average Weight Loss% Over Degradation Time (Days) of PP, PET, LDPE, HDPE, PE, and PS Macros1 After 140 Days of Exposure to T1, T2, T3, and T4.

	Degradation time (days)	**Weight loss%**					
		PP Macro1	**PET Macro1**	**LDPE Macro1**	**HDPE Macro1**	**PE Macro1**	**PS Macro1**
T1	Day 0	0	0	0	0	0	0
	Day 140	0.08922	0.1332	0.05108	0.01262	0.01118	0.1259
T2	Day 0	0	0	0	0	0	0
	Day 140	2.588	0.1342	0.05864	0.04991	13.78	0.1373
T3	Day 0	0	0	0	0	0	0
	Day 140	0.1793	0.1488	0.1592	0.08821	0.04176	0.1599
T4	Day 0	0	0	0	0	0	0
	Day 140	0.1955	0.1351	0.005300	0.03584	0.0173	0.1399

Table 10. Average Weight Loss% Over Degradation Time (Days) of PP, PET, LDPE, HDPE, PE, and PS Macros2 After 140 Days of Exposure to T1, T2, T3, and T4.

	Degradation time (days)	**Weight loss%**					
		PP Macro2	**PET Macro2**	**LDPE Macro2**	**HDPE Macro2**	**PE Macro2**	**PS Macro2**
T1	Day 0	0	0	0	0	0	0
	Day 140	3.010	0.5953	0.4595	0.2196	0.1820	1.088
T2	Day 0	0	0	0	0	0	0
	Day 140	4.266	0.9285	1.352	0.7454	14.93	1.461
T3	Day 0	0	0	0	0	0	0
	Day 140	1.802	1.392	1.394	1.155	1.068	1.6176
T4	Day 0	0	0	0	0	0	0
	Day 140	2.895	1.075	0.4477	0.7103	0.6447	1.475

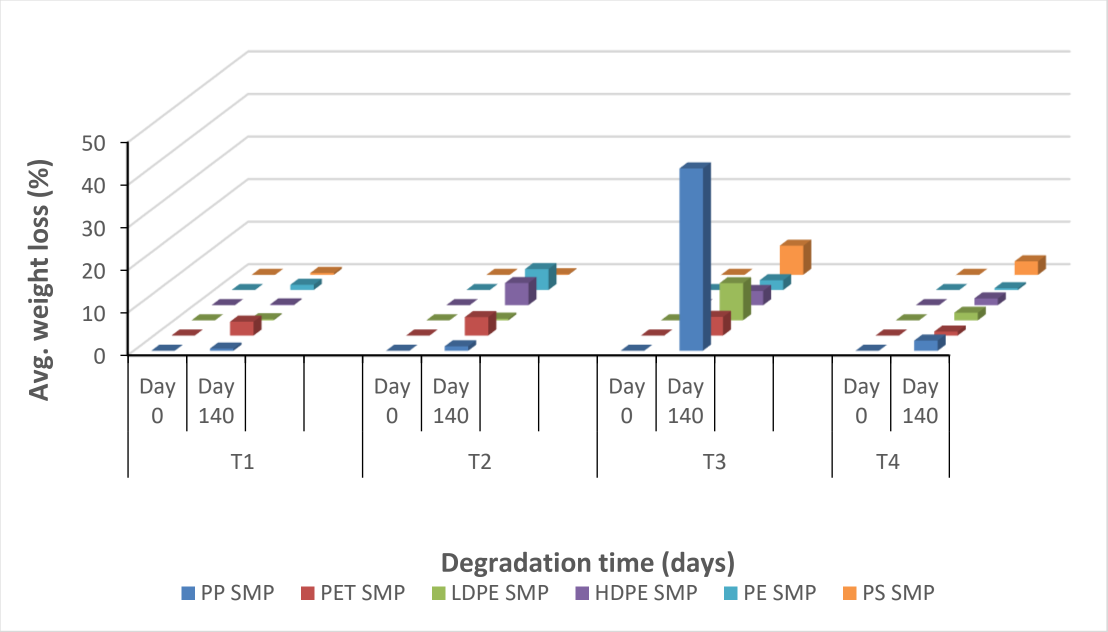


Figure 22. Avg. Weight Loss% Over Degradation Time (Days) of PP, PET, LDPE, HDPE, PE, and PS Small MPs (SMPs) After 140 Days of Exposure to T1, T2, T3, and T4.

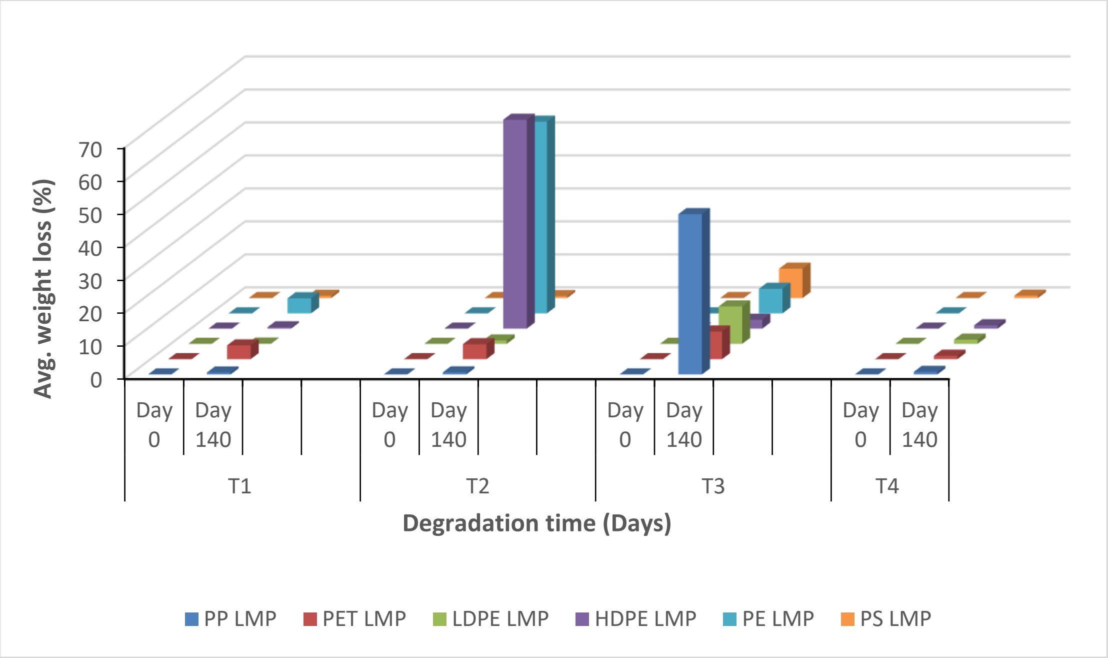


Figure 23. Avg. Weight Loss% Over Degradation Time (Days) of PP, PET, LDPE, HDPE, PE, and PS LMPs After 140 Days of Exposure to T1, T2, T3, and T4.

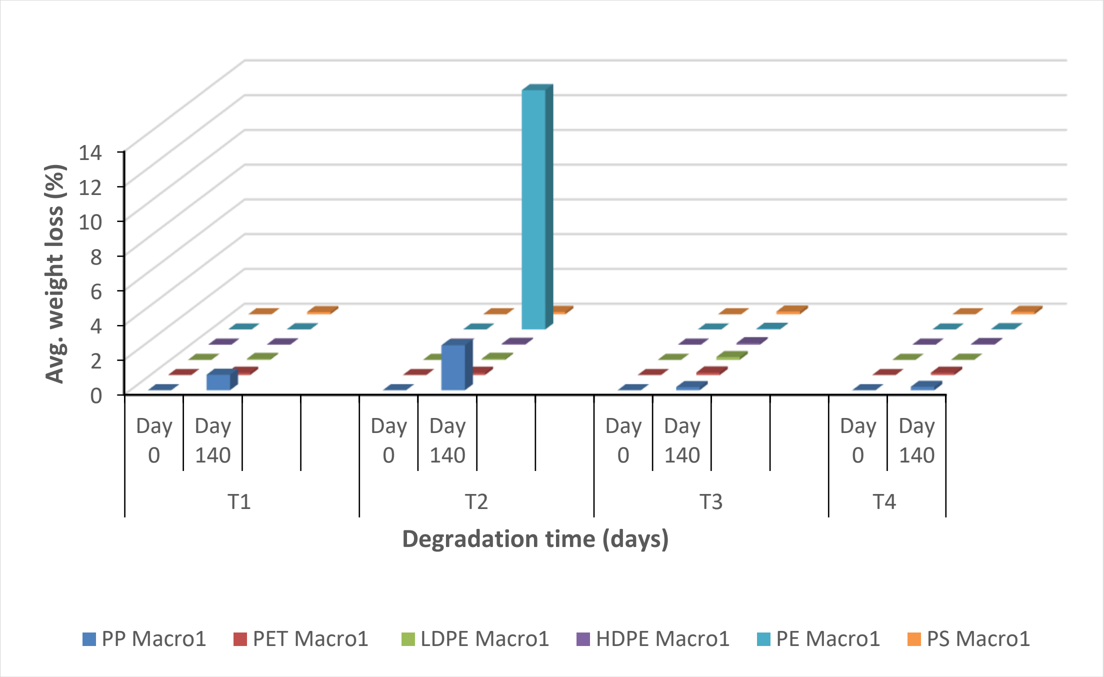


Figure 24. Avg. Weight Loss% Over Degradation Time (Days) of PP, PET, LDPE, HDPE, PE, and PS Macros1 After 140 Days of Exposure to T1, T2, T3, and T4.

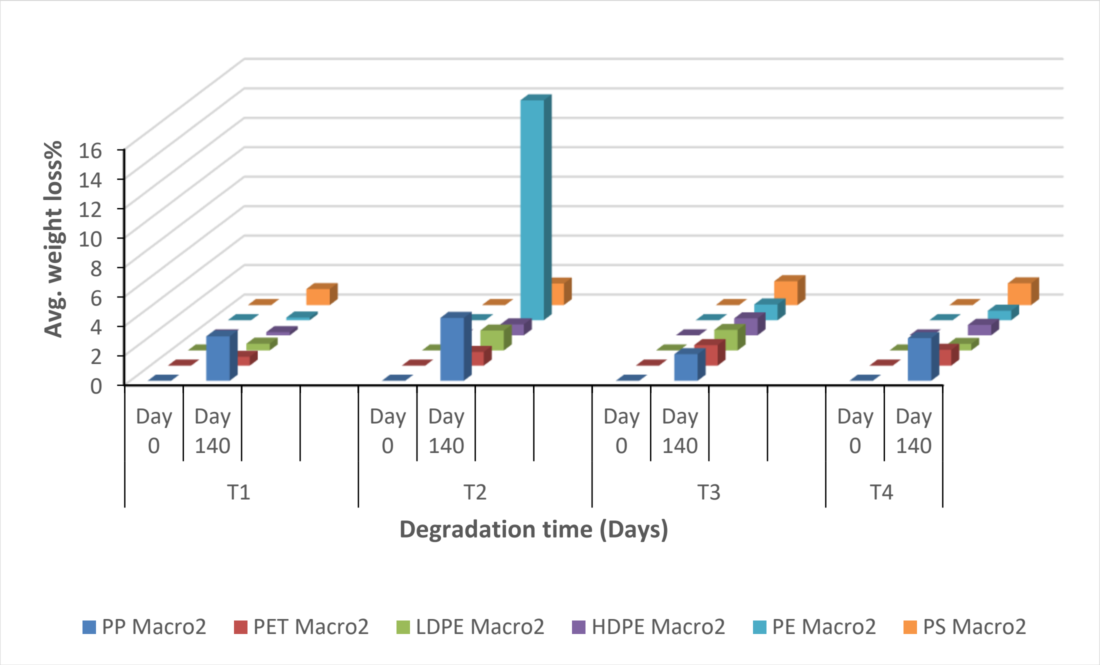


Figure 25. Avg. Weight Loss% Over Degradation Time (Days) of PP, PET, LDPE, HDPE, PE, and PS Macros2 After 140 Days of Exposure to T1, T2, T3, and T4.

According to the average weight loss% results, the smaller the size of the plastic particles, the higher their degradation. For instance, MPs showed a higher average weight loss% than macroplastics for all types of plastics. Remarkably, within the Macro size category, Macros2 showed more weight loss% than Macros1. Likewise, LMPs showed more weight loss% than Macro2. Thus, it showed the highest weight loss% as shown in **Figure** 23 and **Table** 8. Based on the literature, the smaller plastic particles degrade faster than the larger sizes because oxygen will attack them more readily (Chinaglia et al., 2018; Dimassi et al., 2022). It should be mentioned that some SMPs which had the smallest particle size were showing weight loss% less than LMPs, both are in the same size category which is MPs. This could be due to the fact that the 100mL glass reagent bottles used in the experimental set-up of SMPs were covered with temperature-resistant caps to eliminate evaporation due to high temperatures and maintain the same seawater level for additives leachability analysis. This restricted the amount of sunlight that reached the MPs, depending on the angle of the sun as the only mode of entry into the bottles was from the sides of the glass bottles. On the other hand, LMPs and Macros, which were put in the tanks, were covered with a glass lid which allowed sunlight exposure from all sides of the tank. Based on weight loss%, within the MPs size category, the four different treatments affected the various plastic types in a distinctive way, where T2 was the most effective treatment in degrading LMPs of HDPE and PE, since this treatment showed higher weight loss% compared to other treatments. However, T3 was the most effective treatment for most of the plastic types (LDPE, PET, PP, and PS), where a higher weight loss% was calculated. These findings were expected since both treatments (T2 and T3) were the outdoor tanks which were exposed to all different environmental conditions including sunlight and temperature. The reason behind the higher degradation of HDPE and PE in T2 (outdoor sand) over

T3 may be due to their higher flexibility since both of these types used in this experiment were flexible. In addition, the backbone chains of PE are composed of C-C single bonds, which do not undergo hydrolysis easily. Moreover, it resists photo-oxidative degradation because of the lack of UV- visible chromophores. Furthermore, the high content of carbon in HDPE and the straight chain molecules, which are held by intermolecular forces, along with the absence of side branches make the chains highly compacted. In addition to the additives/colorants used in the polymer to enhance its flexibility. Furthermore, the characteristics of sandy soil used in this study (e.g., pH, particle size, microbial species, etc.). All these properties may be the reason behind the higher degradation of flexible plastics (HDPE and PE) after being exposed to onshore conditions. The degradation rate of each plastic type (r_{deg}) was calculated by using this equation:

$$r_{deg} = -\frac{\Delta m}{\Delta t}, \text{ g/d}$$

Degradation rates of various plastics with different sizes after 140 days of exposure to four different treatments are shown in **Table** 11. All plastic types demonstrated a reduction in weight over the 160 days of exposure to different outdoor and indoor conditions. However, the weight loss scale was highly variable based on the polymer type, size, and treatment. For instance, SMP-PE and SMP-HDPE showed a similar high degradation rate of 0.000186 g/d when exposed to T2 as shown in **Table** 11. In addition, SMP-LDPE, SMP-PS, SMP-PET, and SMP-PP showed their highest degradation rates of 0.000311 g/d, 0.000244 g/d, 0.000157 g/d, and 0.00015 g/d, respectively, when exposed to T3. On the other hand, macroplastics showed lower weight loss% and different degradation rates than small plastics. If we suppose that the degradation process happens mainly on the exposed surface of plastic samples. Then the rate of degradation (r_{deg}, g/d) must be proportional to the polymer rate constant and the surface area. Hence, the degradation rate does not only depend on the basic characteristics of the plastics such as the MW, additives, polymer types, and the environmental conditions including temperature and UV light. It will also depend on the extrinsic characteristics (e.g., the shape and size of the plastics). Plastic samples which have similar mass and composition, but the different surface areas can illustrate different degradation rates (Chamas et al., 2020). If we assume that the degradation will occur only at the polymer surface level, then the rate of degradation will be strictly proportional to the surface area (SA).

Table 11. Degradation Rates of Various Plastics with Different Sizes After 140 Days of Exposure to Four Different Treatments.

Treatments	**Degradation rates of SMPs (g/d)**					
	PP	**PET**	**LDPE**	**HDPE**	**PE**	**PS**
T1	1.80x10^{-5}	0.000116	9.57 x10^{-6}	6.68 x10^{-6}	4.43 x10^{-6}	1.55 x10^{-5}
T2	3.75x10^{-5}	0.000155	1.41x10^{-5}	0.000186	0.000186	4.929 x10^{-6}
T3	0.00015	0.000157	0.000311	0.000119	0.0000823	0.000244
T4	8.54x10^{-5}	3.35x10^{-5}	6.51x10^{-5}	5.69 x10^{-5}	1.50 x10^{-5}	0.0001131
	Degradation rates of LMPs (g/d)					
T1	4.45 x10^{-7}	7.86 x10^{-7}	1.24 x10^{-7}	1.55 x10^{-8}	9.96 x10^{-7}	2.05 x10^{-7}
T2	4.35 x10^{-7}	3.91 x10^{-6}	1.68 x10^{-6}	1.80 x10^{-6}	1.99 x10^{-6}	1.91 x10^{-7}
T3	1.07 x10^{-6}	4.40 x10^{-7}	1.86 x10^{-7}	4.89 x10^{-6}	2.41 x10^{-7}	2.22 x10^{-6}
T4	4.72 x10^{-7}	2.14 x10^{-7}	1.71 x10^{-6}	4.34 x10^{-8}	6.95 x10^{-7}	1.90 x10^{-7}
	Degradation rates of Macro2 (g/d)					
T1	4.55 x10^{-6}	7.00 x10^{-7}	2.39 x10^{-6}	6.79 x10^{-7}	1.94 x10^{-7}	1.22 x10^{-6}
T2	7.92 x10^{-7}	5.04 x10^{-6}	6.33 x10^{-6}	1.22 x10^{-7}	1.14 x10^{-6}	1.53 x10^{-6}
T3	1.18 x10^{-7}	1.74 x10^{-7}	1.74 x10^{-7}	3.11 x10^{-6}	1.01 x10^{-6}	2.07 x10^{-6}
T4	1.00 x10^{-5}	1.58 x10^{-7}	2.23 x10^{-6}	3.21 x10^{-8}	1.90 x10^{-6}	1.39 x10^{-6}
	Degradation rates of Macro1 (g/d)					
T1	3.30 x10^{-6}	5.82 x10^{-6}	1.13 x10^{-5}	1.79 x10^{-8}	1.09 x10^{-6}	1.79 x10^{-7}
T2	1.24 x10^{-5}	5.04 x10^{-6}	1.04 x10^{-5}	2.14 x10^{-7}	1.70 x10^{-5}	1.96 x10^{-7}
T3	7.48 x10^{-6}	3.03 x10^{-5}	1.58 x10^{-5}	8.48 x10^{-6}	1.52 x10^{-6}	5.63 x10^{-6}
T4	8.14 x10^{-6}	5.34 x10^{-6}	1.11 x10^{-6}	3.57 x10^{-6}	4.09 x10^{-6}	5.89 x10^{-7}

Weight loss% findings were in alignment with FTIR, and SEM-EDX results, as well as the statistical analysis, where LMP-PE and LMP-HDPE showed a significant difference when exposed to T2, which could be explained by the effectiveness of the characteristics of sandy soil used in this study (e.g., pH, particle size, microbial species, etc.) in degrading these two types of flexible plastics. On the other hand, LMP-PP, LMP-PS, LMP-PET, and LMP-LDPE showed significant differences when exposed to T3. It should be noted that both treatments were exposed to outdoor conditions where high UV-light and temperature play a great role in the degradation of all the different plastic polymers. Once the plastic polymers are exposed to sunlight, UV-light is absorbed by some of these polymers on a variable scale depending on several properties including polymer type, additives, UV-stabilizers, etc.). This UV light excites the photons in the material and creates free radicals. These free radicals will potentially form oxygen hydroperoxides in the presence of oxygen, and these compounds will eventually break the polymer chains. This phenomenon is known as “chain scission”.

It should be also mentioned that even though results showed a reduction in the weight of plastics, the build-up of microalgae on the surface of some plastics, even after being washed several times with deionized water, can affect the weight loss%.

4.4 DSC analysis

DSC thermal analysis was used in this study to measure the change of physical properties in the different plastic samples along with temperature over time. This analysis provides information about how the temperature and heat flow are associated with the plastic material transitions along with the change of temperature over time. This method is one of the most well-known methods of analysing polymers and their composites (Aljabali et al., 2022). DSC analysis was chosen in this research due to the susceptibility of polymers to swings in temperature. When plastic polymers are heated, some of them are likely to melt. In addition, exposing some polymers to a too cold temperature may result in their explosion. Thus, this analytical instrument helps in measuring the performance as well as the degradation of plastic polymers whenever they are exposed to a wide range of temperatures, which includes excessive heat and/or cold. In addition, it analyses the fluctuations in heat flow as the sample changes its state from a solid to a liquid, and it gives information about the product’s durability.

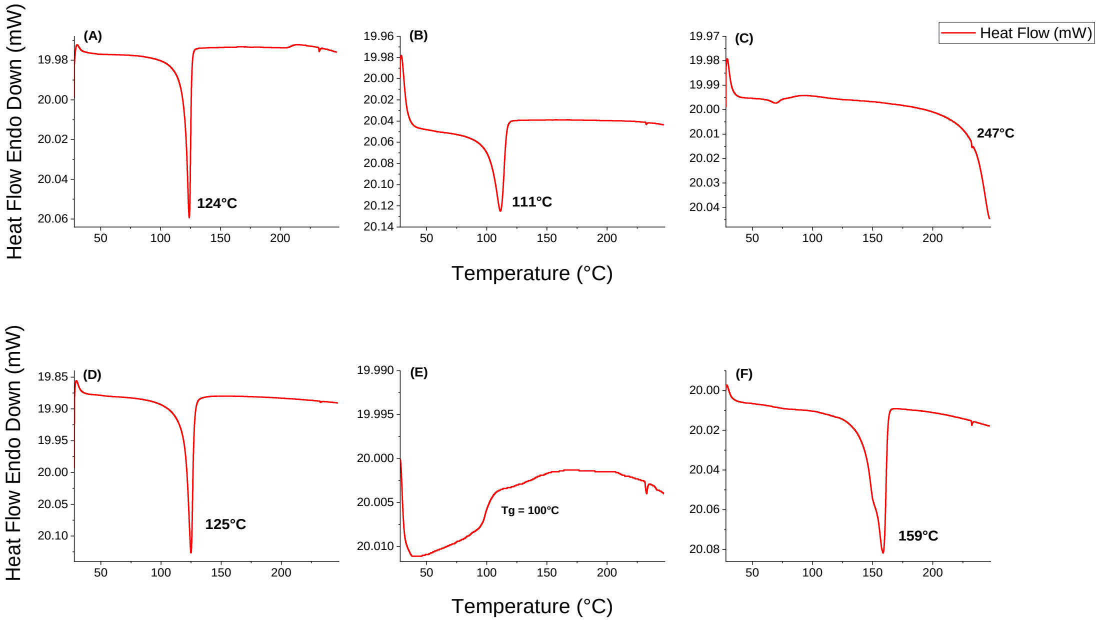


Figure 26. DSC Curves of Endothermic Phase Transition Heat Flow and Temperatures of (A) HDPE (B) LDPE (C) PET (D) PE (E) PS (F) PP Before Exposure, Heating Rate of 10 °C/min under Nitrogen Atmosphere, a Heating Range of 25 °C to 250 °C, Amounts Ranged from 1.162 mg to 2.857 mg.

DSC thermograms of PE, PET, HDPE, LDPE, PS, and PP were shown in **Figure** 26. The solid-to-liquid transitions of all polymers were endothermic events as it was shown as endothermic peaks in DSC curves. These different endothermic peaks are unique for each polymer. Thus, it can be used for the identification of the different plastic polymers, where pure polymers, which are widely accessible in literature, illustrate endothermic peaks according to the measured temperature. DSC curves of almost all plastic samples show two different endothermic peaks. According to the literature, the first peak does not show mass loss%, since it is mainly due to the polymer melting (Cafiero et al., 2015; Majewsky et al., 2016). HDPE, PE, and LDPE show lower melting points with approximate temperature endothermic peaks of 124 °C, 125 °C, and 111°C, and it does not exhibit any overlap with the rest of the tested plastic polymers. On the other hand, Foam PS or expanded polystyrene is an amorphous polymer, where a glass transition temperature (Tg) of around 100 °C was shown in **Figure** 26 (E). Similar values were previously reported by several studies (Pierella et al., 2005; Sastri, 2010). This characteristic temperature shows whenever the material moves from its initial state (glassy state) to a softer material (rubbery state) and afterwards to a melt state. For example, the Tg of HDPE is -100 °C (Greene, 2021). Lower than this temperature, the plastic material will be rigid. On the other hand, more than this temperature, the plastic material will be in a rubbery state. Which is the case for the HDPE used in this project, which was manufactured and commercialised as a flexible garbage bag at room temperature. Other thermoplastic polymers, which are PET and PP showed peaks at higher temperatures, which were 247 °C and 159 °C, respectively. Both polymers are overlaying with each other, especially due to the broad PET peak. Literature reveals that all these common plastics (LDPE, HDPE, PE, PET, PP, and PS) used in this study shows melting peak temperatures which are very close or identical to the experimental values (Batra and Sc, 2014; Greene, 2021). According to the literature, the application of PE commercially is restricted by its low melting point while comparing to other thermoplastics. Commercial grades of PE (e.g., LDPE, and HDPE) usually show a typical melting temperature ranging between 105 °C to 135 °C (Batra and Sc, 2014; Greene, 2021). However, HDPE illustrates higher melting temperatures, which are usually around 130 °C (Camacho and Karlsson, 2001) compared to lower grades of PE due to its higher branching degrees. In addition, it should be noted that phase transition temperatures and melting temperatures can be influenced by the branching degrees of the plastic polymers, the additives, and the size of the particle (Majewsky et al., 2016; Menczel and Prime, 2009). In addition, PET has a very good thermal and chemical resistance due to its high melting temperatures, which start from 240 °C (Greene, 2021; Jog, 1995). This high melting temperature characteristic provides excellent mechanical properties for PET, which can be retained at high temperatures of up to 175 °C (Jog, 1995). Moreover, the melting range of commercial PP usually ranges between 160 °C to 170°C, depending on the crystallinity and atactic (which means the linear polymer, which has asymmetrically substituted C atoms in the repeating unit of the primary chain) polymer material used (Greene, 2021; Maier and Calafut, 1998).

4.5 FTIR analysis

All different plastic types were analysed by using FTIR Spectrum 400 FT-IR, from PerkinElmer, using UATR, eight scans per sample, 4 cm^{-1} resolution. The spectrum range of analysis was 4,000 cm^{-1} to 400 cm^{-1}. The FTIR spectra for all six types of plastics with their different size categories after 12 weeks (84 days) and 20 weeks (140 days) of exposure to the four different treatments are shown in **Figures** 27-32.

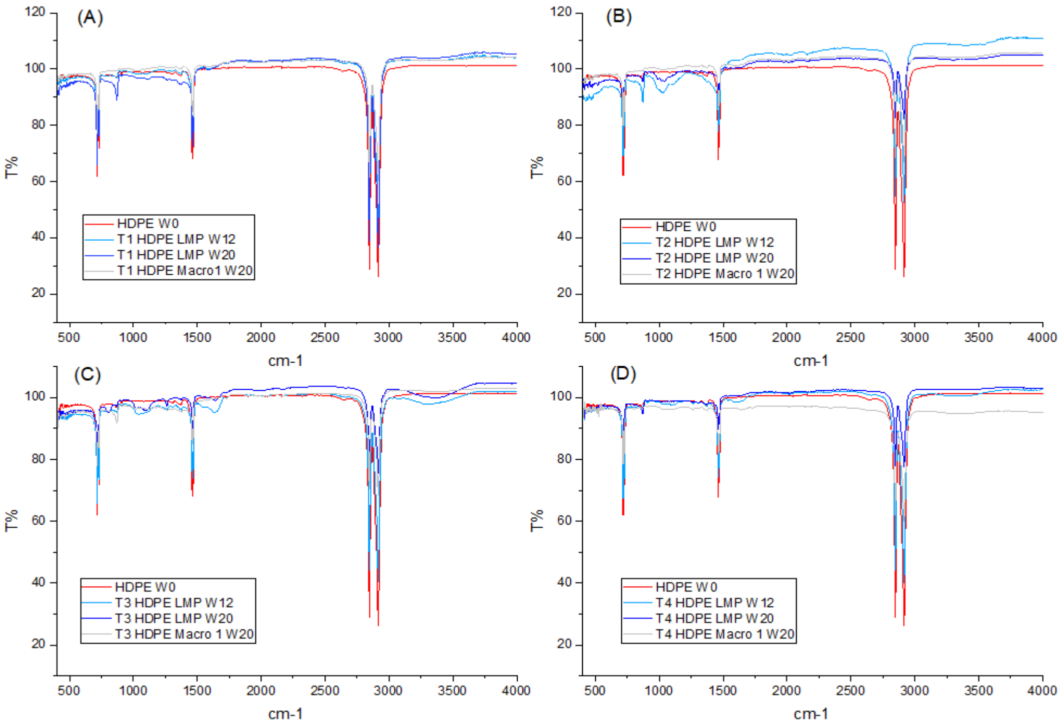


Figure 27. FTIR Spectra of LMP and Macro1 HDPE After 12 Weeks and 20 Weeks of Exposure to T1, T2, T3, and T4.

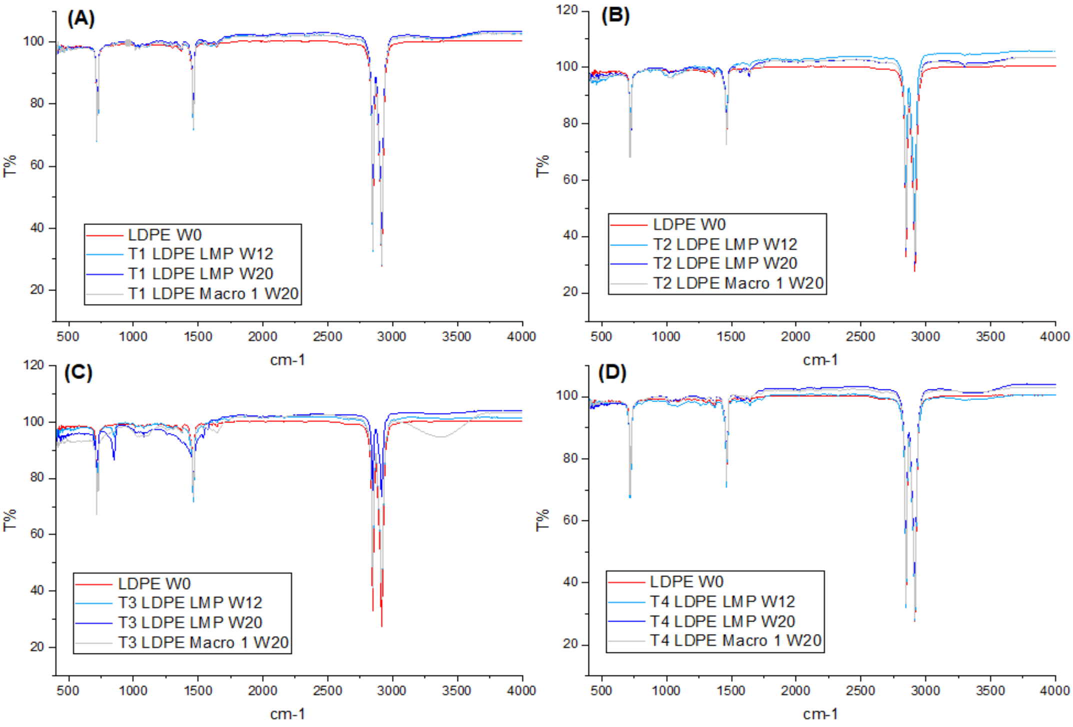


Figure 28. FTIR Spectra of LMP and Macro1 LDPE After 12 Weeks and 20 Weeks of Exposure to T1, T2, T3, and T4.

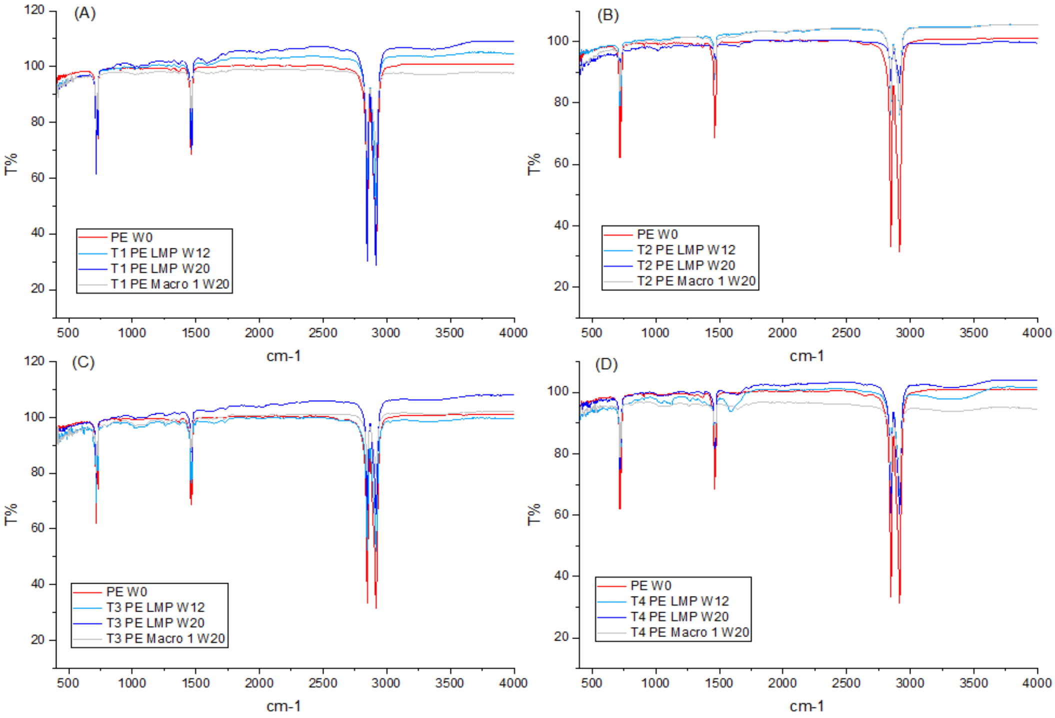


Figure 29. FTIR Spectra of LMP and Macro1 PE After 12 Weeks and 20 Weeks of Exposure to T1, T2, T3, and T4.

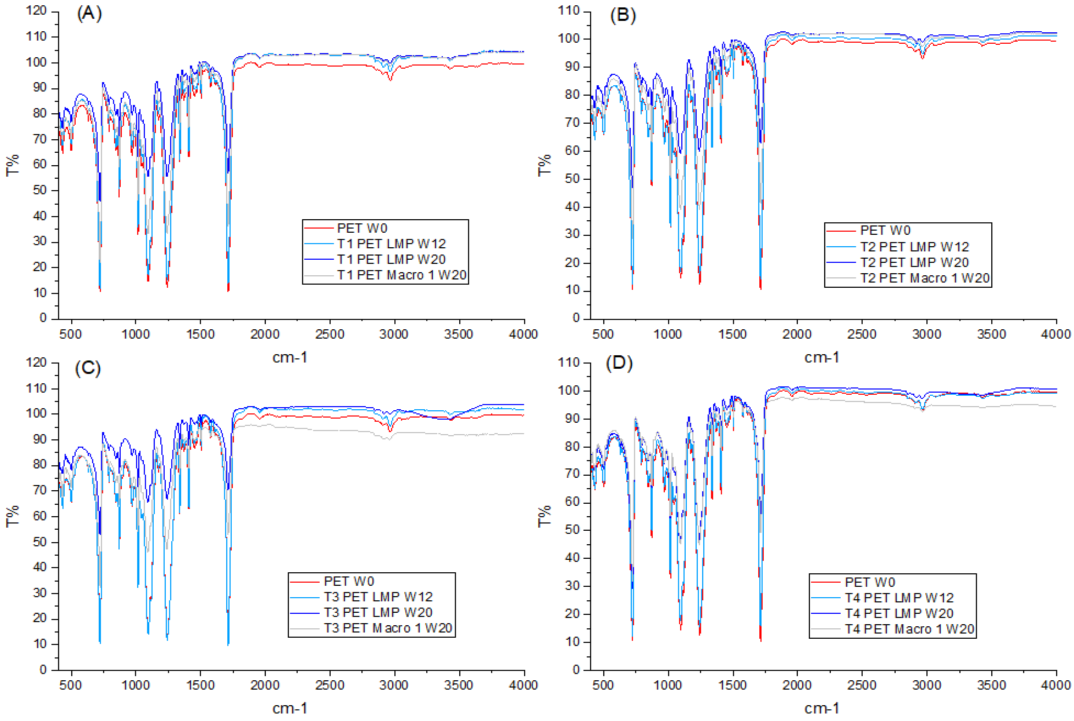


Figure 30. FTIR Spectra of LMP and Macro1 PET After 12 Weeks and 20 Weeks of Exposure to T1, T2, T3, and T4.

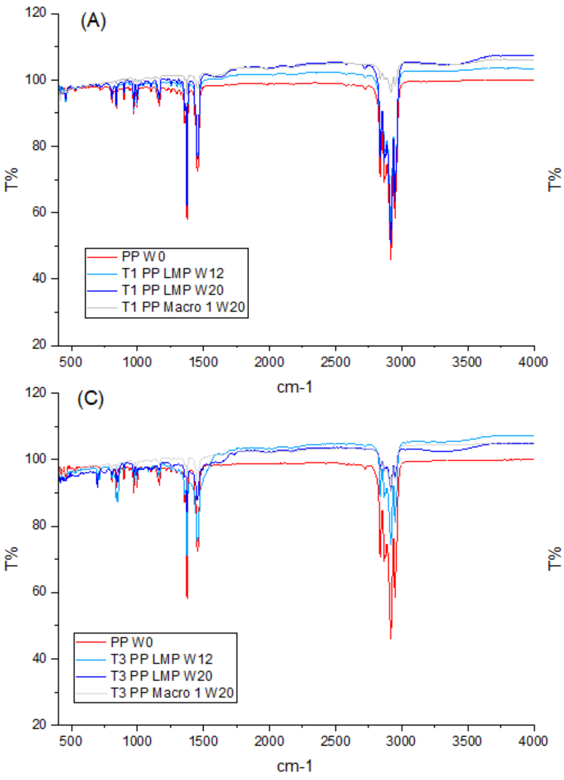


Figure 31. FTIR Spectra of LMP and Macro1 PP After 12 Weeks and 20 Weeks of Exposure to T1, T2, T3, and T4.

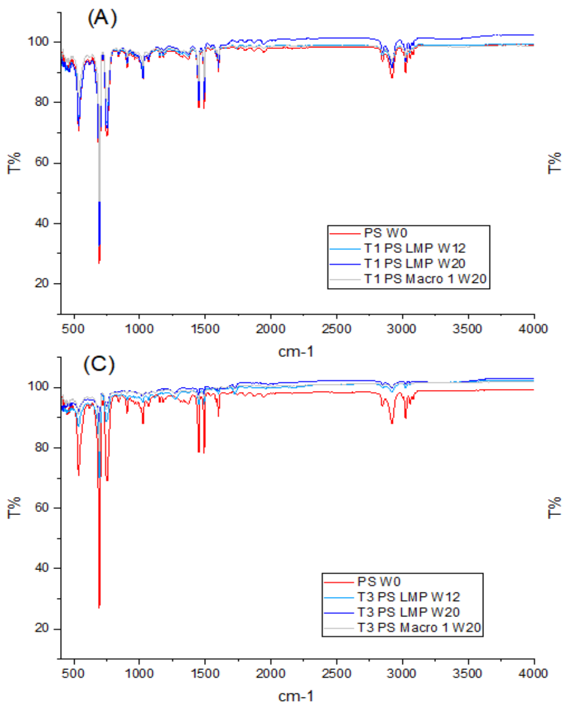


Figure 32. FTIR Spectra of LMP and Macro1 PS After 12 Weeks and 20 Weeks of Exposure to T1, T2, T3, and T4.

FTIR spectra for all different plastics showed great alteration in the characteristics of the transmission bands. The characteristic peaks for each plastic type were detected by FTIR. According to FTIR findings, smaller plastic particles (LMP) in all plastic types showed greater changes in the characteristics of the transmission bands. This change gradually increased over time while being exposed to the different treatments. While comparing FTIR spectra of LMPs, which were exposed to different treatments, T2 was found to be the most effective treatment which showed greater changes in the characteristics of the transmission bands of HDPE-LMP and PE-LMP. Thus, T2 was the most effective at degrading LMP-HDPE and LMP-PE. On the other hand, T3 was effective at degrading LMP-PP, LMP-LDPE, LMP-PET, and LMP-PS, where greater changes in the characteristics of transmission bands were noticed. It is interesting to mention that these treatments did not show the same effect for macro-sized plastics. For instance, T3 was the most effective treatment at degrading for Macro-HDPE instead of T2, this could be due to the fact that larger plastics were observed to be floating on the surface of the SW where they were exposed to direct sunlight. In contrast, the smaller HDPE particles were mostly sinking to the bottom of the tank. Moreover, the adhesion of the flexible LMP-HDPE to other bigger particles, caused them to remain under the larger particles. This shielded them for a while from direct sunlight after which they would again be dispersed due to wave abrasion simulation. This incident can also occur in reality, where plastics can adhere to other particles or be covered by different objects (e.g., other plastics, algae, seaweeds, etc.) in the ocean. Thus, it will not be directly affected by the sunlight factor. Yet, it will be affected by other degradation factors such as salinity, temperature, pH, etc. However, this was not the case for the flexible Macro-PE, where T2 showed the highest changes in the characteristics of the transmission bands of Macro-PE. This is due to the slow degradation of PE in the natural environment. In addition, the backbone chains of PE are composed exclusively of C-C single bonds, which will not undergo hydrolysis easily. Moreover, it resists photo-oxidative degradation because of the lack of UV-visible chromophores. As a result, it showed more degradation while exposed to T2 (outdoor sand), and this was confirmed by the significant changes in the characteristics of transmission bands compared to PE prior to exposure. T3 was also the most effective treatment for degrading LDPE-Macro, PET-Macro, and PS-Macro.

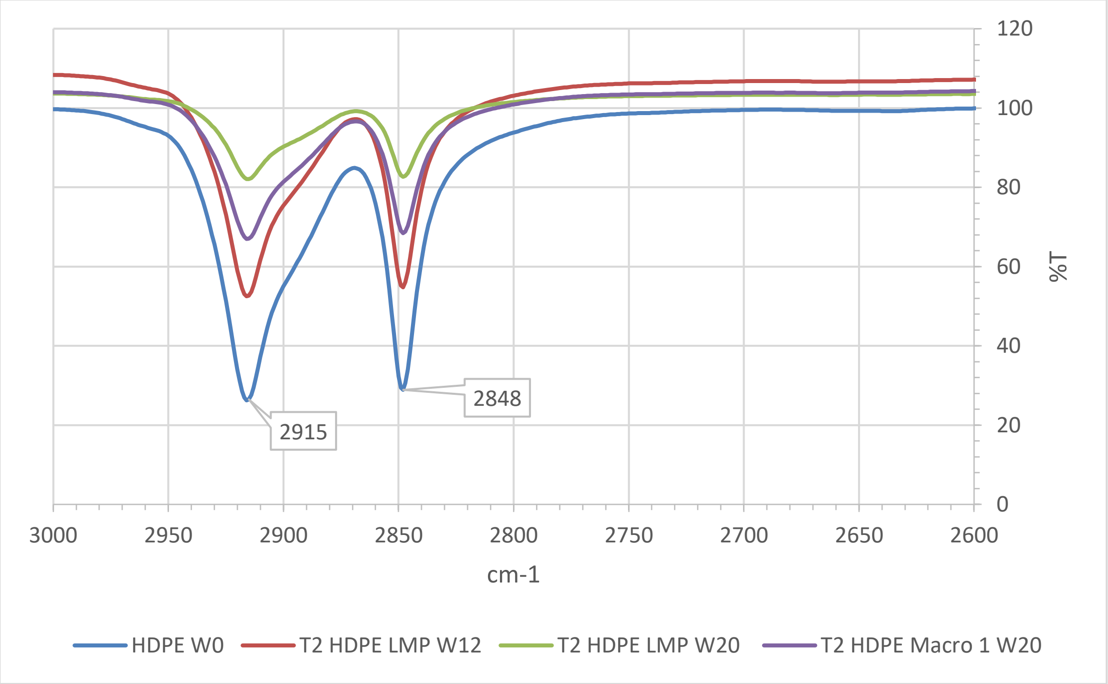


Figure 33. Characteristic Peaks of 2915 cm^{-1} and 2848 cm^{-1}- FTIR Spectra of LMP and Macro1 HDPE After 12 Weeks and 20 Weeks of Exposure to T2.

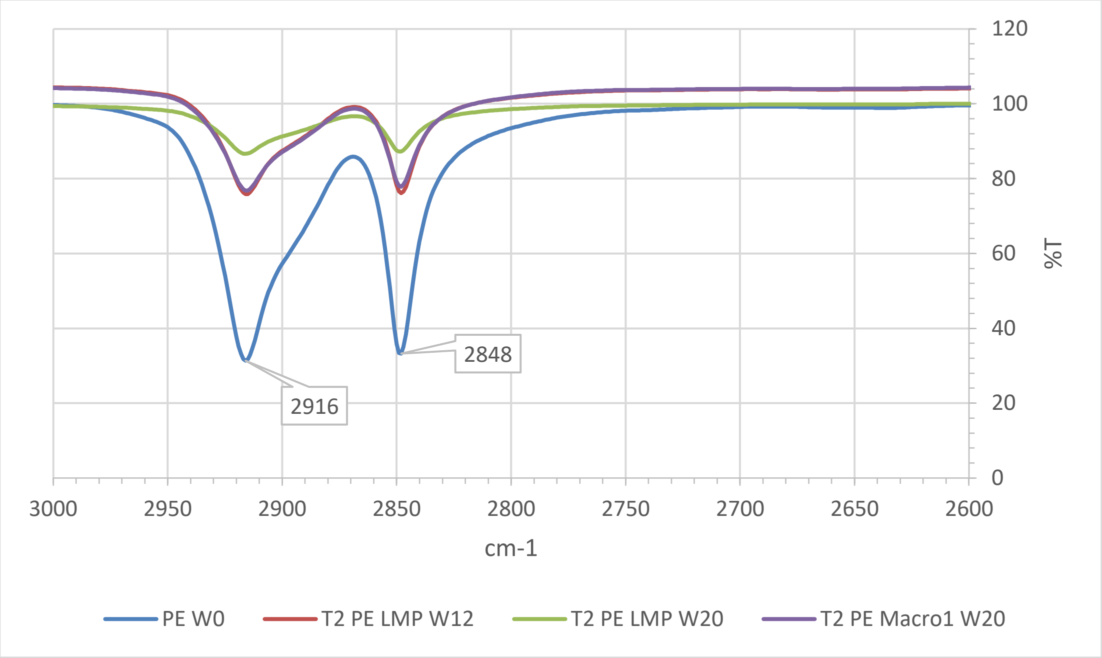


Figure 34. Characteristic Peaks of 2916 cm^{-1} and 2848 cm^{-1}- FTIR Spectra of LMP and Macro1 PE After 12 Weeks and 20 Weeks of Exposure to T2.

The FTIR characteristic peaks of HDPE were 2916 cm^{-1}, 2848 cm^{-1}, 1473 cm^{-1}, 1462 cm^{-1}, 718 cm^{-1}, and 407 cm^{-1}. In addition, the characteristic peaks of PE were 2916 cm^{-1}, 2848 cm^{-1}, 1472 cm^{-1}, 1462 cm^{-1}, 731 cm^{-1}, 718 cm^{-1}, and 410 cm^{-1}. A significant increase in the transmission at 2915 cm^{-1} and 2848 cm^{-1} over time as shown in **Figures** 33 and 34. This gradual increase indicates the increased oxidation of the polymer chains with exposing the samples to solar radiation over time. Similarly, other characteristic peaks for HDPE and PE were found to be higher, with an increase in their degradation over time across all treatments (e.g., 1462 cm^{-1}, 718 cm^{-1} for HDPE, and 1472 cm^{-1} and 731 cm^{-1} for PE). The difference could be detected even at a short duration of 12 weeks (84 days) across all different plastic samples.

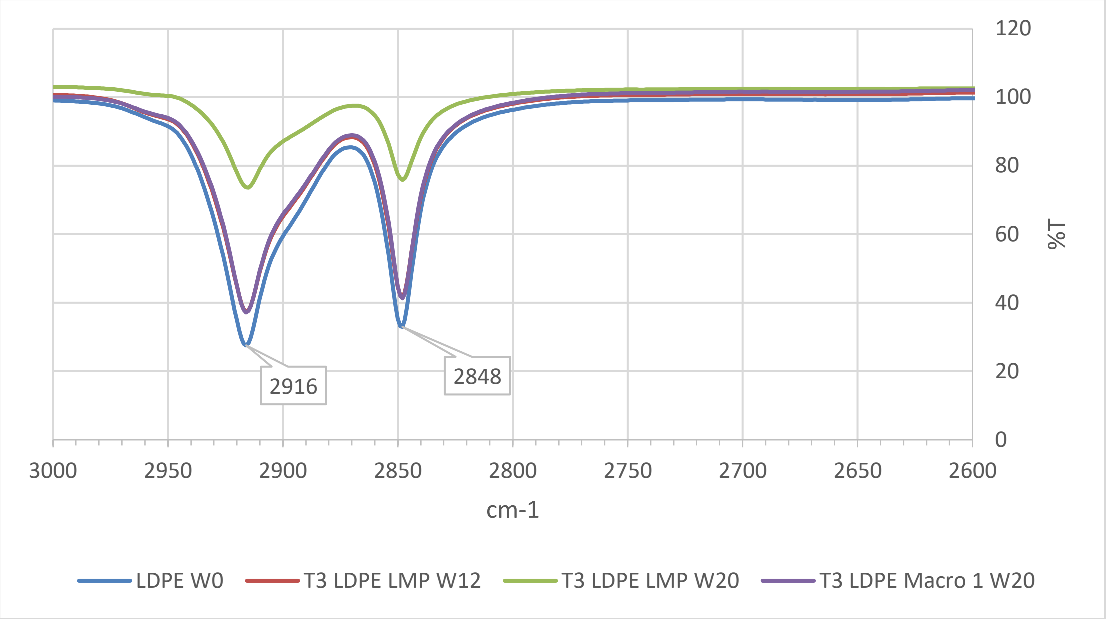


Figure 35. Characteristic Peaks of 2916 cm^{-1} and 2848 cm^{-1}- FTIR Spectra of LMP and Macro1 LDPE After 12 Weeks and 20 Weeks of Exposure to T3.

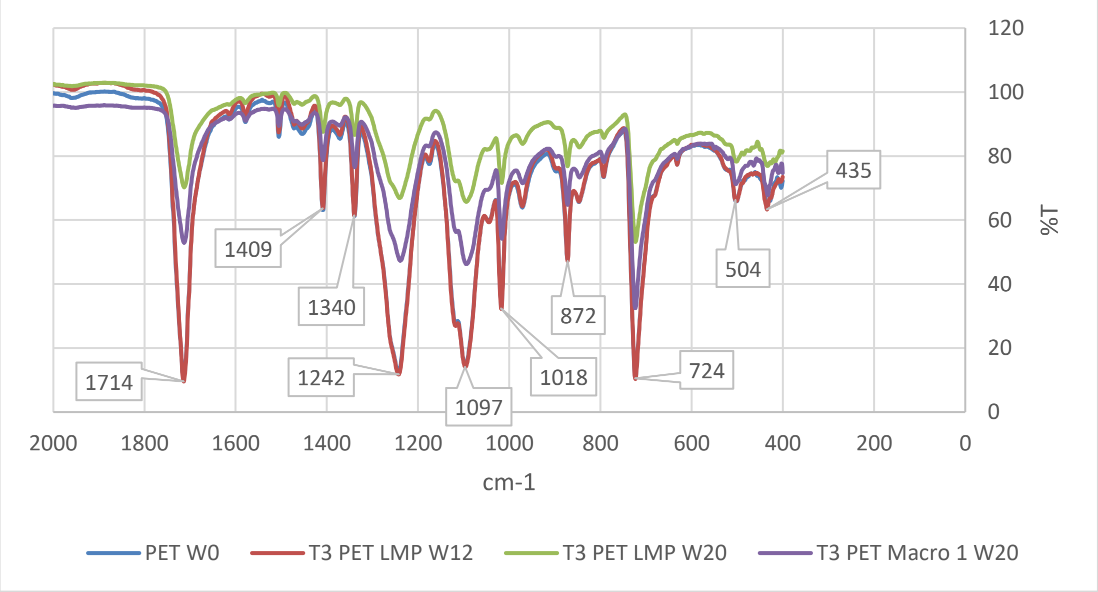


Figure 36. Characteristic Peaks Between 1714 cm^{-1} and 435 cm^{-1}- FTIR Spectra of LMP and Macro1 PET After 12 Weeks and 20 Weeks of Exposure to T3.

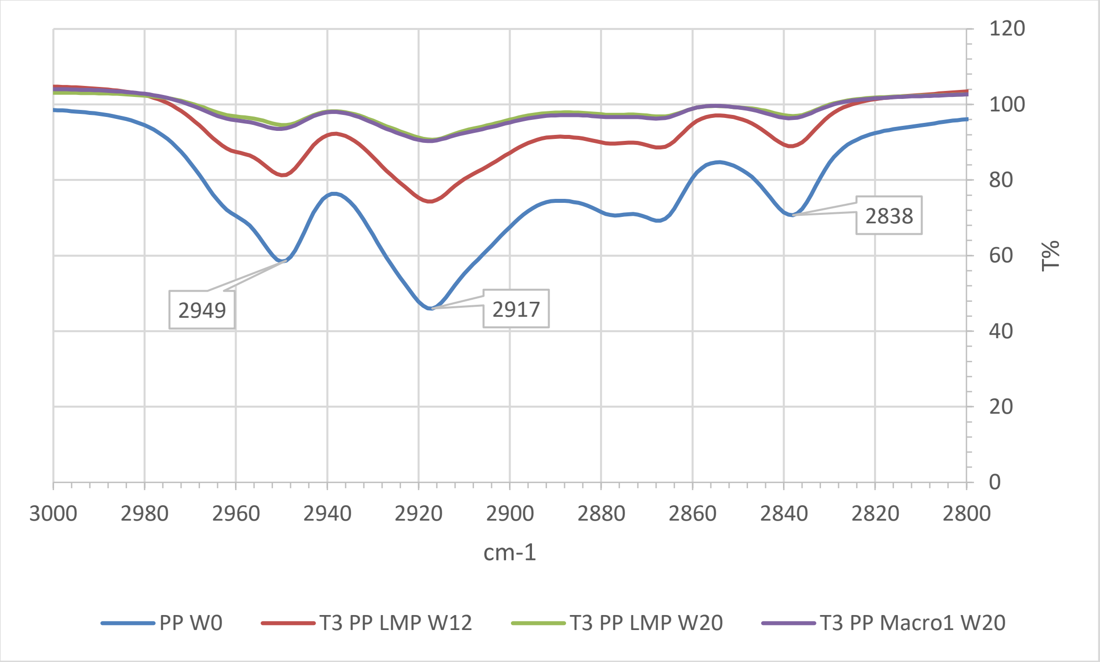


Figure 37. Characteristic Peaks Between 1714 cm^{-1} and 435 cm^{-1}- FTIR Spectra of LMP and Macro1 PP After 12 Weeks and 20 Weeks of Exposure to T3.

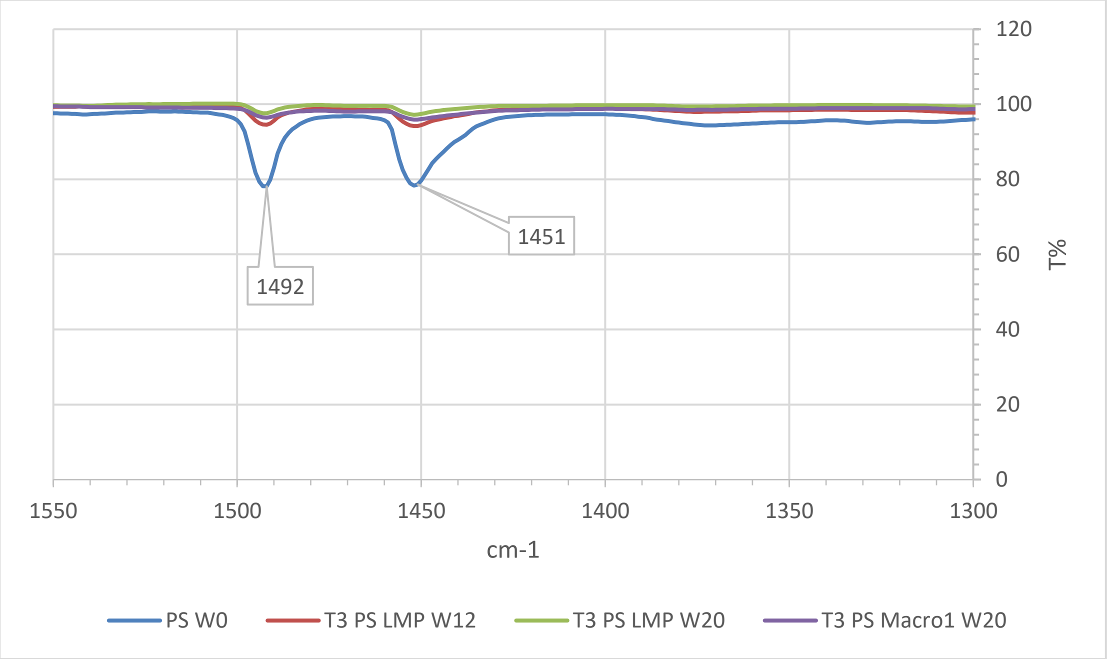


Figure 38. Characteristic Peaks Between 1714 cm^{-1} and 435 cm^{-1}- FTIR Spectra of LMP and Macro1 PS After 12 Weeks and 20 Weeks of Exposure to T3.

Based on the FTIR analysis conducted, the FTIR characteristic peaks of LDPE were 2916 cm^{-1}, 2848 cm^{-1}, 1463 cm^{-1}, 1368 cm^{-1}, 729 cm^{-1}, 719 cm^{-1}, and 418 cm^{-1}. A significant gradual increase in the transmission at 2916 cm^{-1} and 2848 cm^{-1} over time as shown in **Figure** 35. In addition, PET is characterized with several peaks in FTIR spectra which mainly includes 2967 cm^{-1}, 1714 cm^{-1}, 1578 cm^{-1}, 1505 cm^{-1}, 1453 cm^{-1}, 1409 cm^{-1}, 1371 cm^{-1}, 1340 cm^{-1}, 1242 cm^{-1}, 1097 cm^{-1}, 1018 cm^{-1}, 872 cm^{-1},724 cm^{-1}, 504 cm^{-1}, and 435 cm^{-1}. A significant gradual increase in the transmission of peaks between 1714 cm^{-1} and 435 cm^{-1} over time as shown in **Figure** 36. Moreover, The FTIR characteristics of PP were mainly 2949 cm^{-1}, 2917 cm^{-1}, 2867 cm^{-1}, 2838 cm^{-1}, 1456 cm^{-1}, 1376 cm^{-1}, and 1167 cm^{-1}. A significant gradual increase in the transmission at 2949 cm^{-1} and 2917 cm^{-1} and 2838 cm^{-1} over time as shown in **Figure** 37. Furthermore, The FTIR characteristics of PS were mainly 3059 cm^{-1}, 3025 cm^{-1}, 2920 cm^{-1}, 2849 cm^{-1}, 1601 cm^{-1}, 1492 cm^{-1}, and 1451 cm^{-1}, 1371 cm^{-1}, and 695 cm^{-1}. A significant gradual increase in the transmission at 1492 cm^{-1} and 1451 cm^{-1} over time as shown in **Figure** 38. Based on all the transmission data from samples exposed to T3 and T4 (indoor and outdoor seawater), the oxidation process is much more evident in LDPE, PP, PET, and PS samples when left in SW under outdoor conditions over those left indoors under controlled laboratory conditions (T4). In addition, the dissolved oxygen in seawater coupled with sunlight radiation increases the oxidation process through UV-irradiation. Despite all of these degradation-favourable conditions, PE and HDPE showed better degradation while exposed to T2 (outdoor onshore). As previously mentioned, the reason behind this may be due to the backbone chains of PE which are composed of C-C single bonds, which do not undergo hydrolysis easily. Moreover, they resist the photo-oxidative degradation because of the lack of UV- visible chromophores. Furthermore, the high content of carbon in HDPE and the straight chain molecules which are held by intermolecular forces, along with the absence of side branches make the chains highly compacted, in addition to the additives/colorants used in the polymer to enhance its flexibility. All of these properties may be the reason behind the higher degradation of HDPE and PE after being exposed to onshore conditions.

The effect of treatments of each plastic type and its different sizes was in alignment with the statistical analysis (PCA), where FTIR data was used as input data for analysis.

4.6 SEM-EDX analysis

SEM analysis coupled with EDX was performed in this study to better visualize the surface of the different plastic samples by using a high-energy beam of electrons. SEM micrographs for all different types of plastics before degradation and after 140 days of exposure to different treatments (T2 and T3) were generated. Due to the limited number of samples which can be analysed, plastic samples were selected based on weight loss% findings. PE and HDPE showed higher weight loss% after being exposed to T2 while LDPE, PP, PET, and PS showed higher degradation after being exposed to T3. SEM micrographs showed obvious variations in the morphologies of all different plastics, as illustrated in **Figures** 39 and 40, due to the exposure to different environmental conditions (e.g., sunlight, temperature, salinity, pH, and wave abrasion). SEM micrographs before degradation showed clear smooth surfaces for all types of plastics. On the other hand, SEM images of all types of plastics after 140 days of exposure to T2 and T3 developed visible degradation signs (e.g., small holes, small fissures, disintegration, cracks, and grooves). It should be noted that degradation and fragmentation signs were more visible in the LMPs than in Macros. Thus, SEM analysis findings were in alignment with the weight loss% results and FTIR spectra. Several studies have shown that SEM/EDX analysis is effective in studying the degradation and fragmentation of plastics (Fries et al., 2013; Ioakeimidis et al., 2016). In addition, EDX analysis is helpful in providing concentrations of the sample's chemical composition. This combined technique (SEM-EDX) was found to be extremely useful in the detection of MPs and their degradation process because of its micro-scale characteristics as well as its high magnification which reaches up to 500,000x (Imhof et al., 2012; Vianello et al., 2013). Moreover, it provides information on the morphology, composition, and topography of MPs in samples extracted from the environment (Scimeca et al., 2018). EDX results for the different plastic samples before and after degradation are shown in **Figures** 41 and 42.

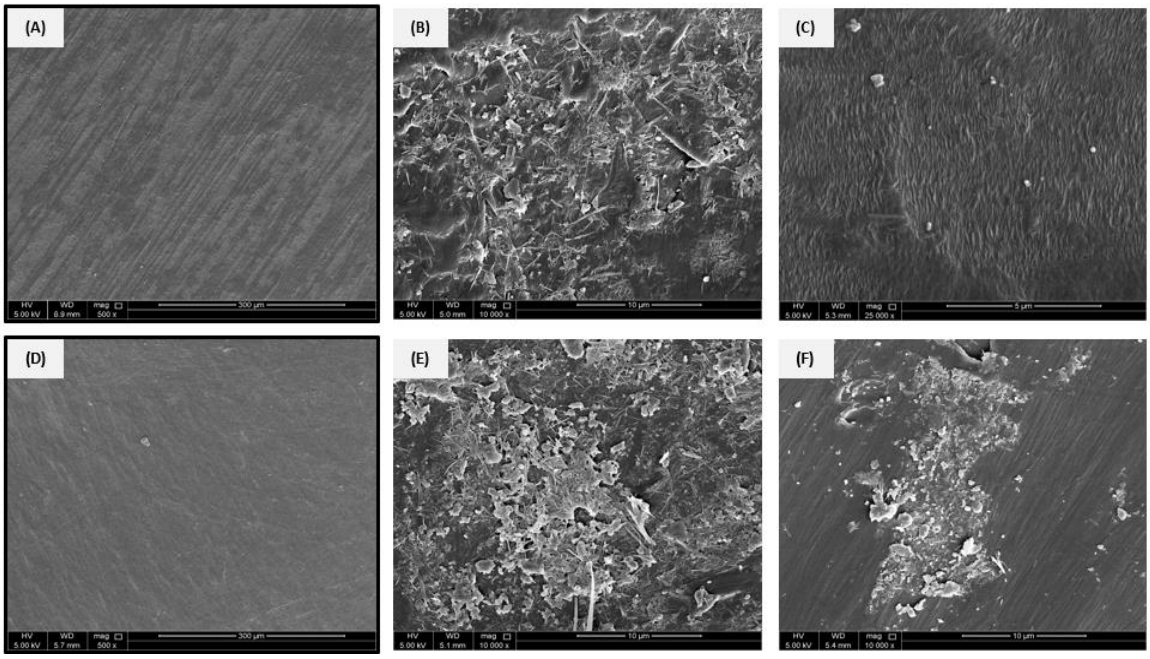


Figure 39. SEM Micrographs of HDPE and PE: (A) HDPE Before Degradation (Day 0), (B) LMP-HDPE After 140 Days of Exposure to T2, (C) Macro1-HDPE After 140 Days of Exposure to T2, (D) PE Before Degradation (Day 0), (E) LMP-PE After 140 Days of Exposure to T2, (F) Macro1- PE After 140 Days of Exposure to T2.

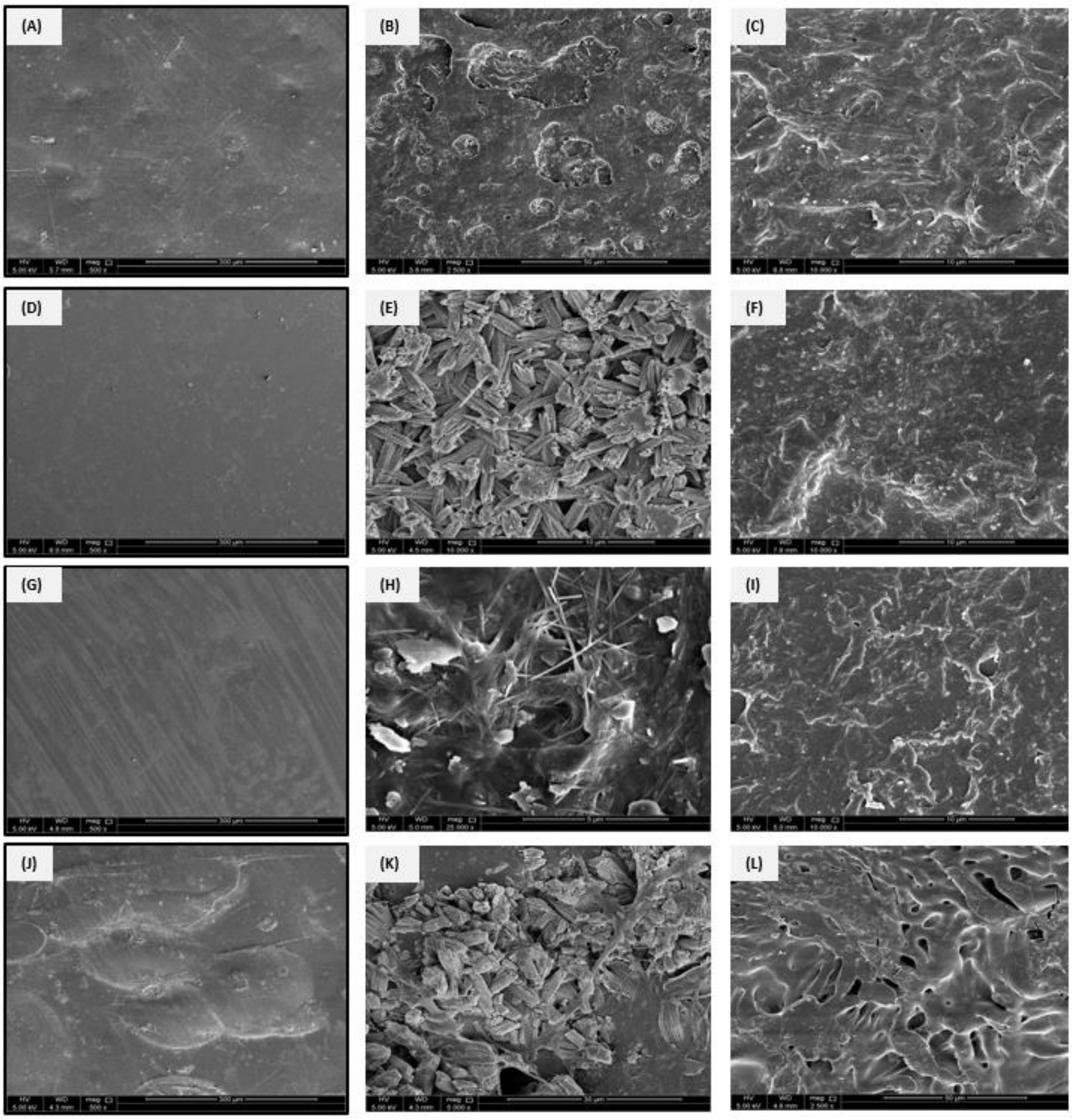
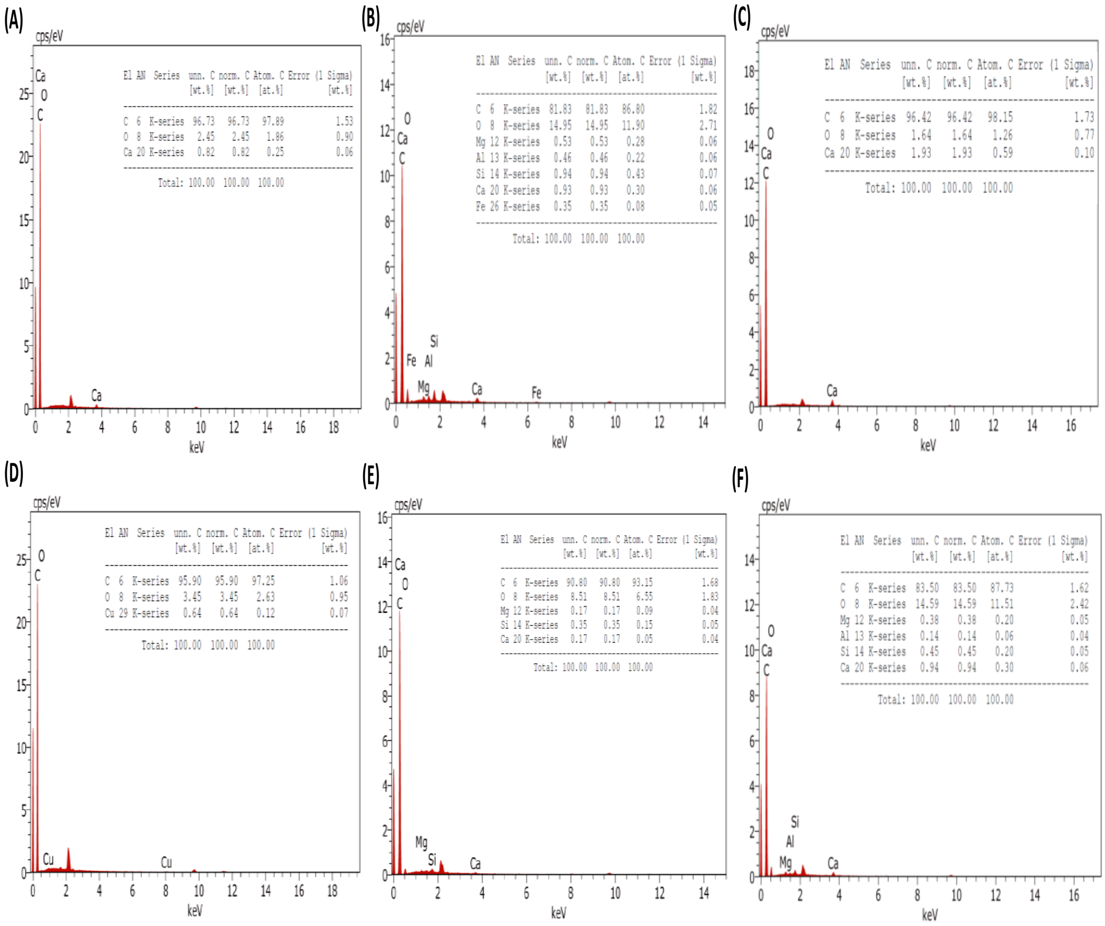


Figure 40. SEM Micrographs of LDPE, PP, PET, and PS: (A) LDPE Before Degradation (Day 0), (B) LMP-LDPE After 140 Days of Exposure to T3, (C) Macro1-LDPE After 140 Days of Exposure to T3, (D) PP Before Degradation (Day 0), (E) LMP-PP After 140 Days of Exposure to T3, (F) Macro1-PP After 140 Days of Exposure to T3, (G) PET Before Degradation (Day 0), (H) LMP-PET After 140 Days of Exposure to T3, (I) Macro1-PET After 140 Days of Exposure to T3, (J) PS Before Degradation (Day 0), (K) LMP-PS After 140 Days of Exposure to T3, (L) Macro1-PS After 140 Days of Exposure to T3.



(A)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
C  6  K-series  96.73   96.73   97.89             1.53
O  8  K-series   2.45    2.45    1.86             0.90
Ca 20 K-series   0.82    0.82    0.25             0.06
-------------------------------------------------------
        Total: 100.00  100.00  100.00
```

(B)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
C  6  K-series  81.83   81.83   86.80             1.82
O  8  K-series  14.95   14.95   11.90             2.71
Mg 12 K-series   0.53    0.53    0.28             0.06
Al 13 K-series   0.46    0.46    0.22             0.06
Si 14 K-series   0.94    0.94    0.43             0.07
Ca 20 K-series   0.93    0.93    0.30             0.06
Fe 26 K-series   0.35    0.35    0.08             0.05
-------------------------------------------------------
        Total: 100.00  100.00  100.00
```

(C)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
C  6  K-series  96.42   96.42   98.15             1.73
O  8  K-series   1.64    1.64    1.26             0.77
Ca 20 K-series   1.93    1.93    0.59             0.10
-------------------------------------------------------
        Total: 100.00  100.00  100.00
```

(D)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
C  6  K-series  95.90   95.90   97.25             1.06
O  8  K-series   3.45    3.45    2.63             0.95
Cu 29 K-series   0.64    0.64    0.12             0.07
-------------------------------------------------------
        Total: 100.00  100.00  100.00
```

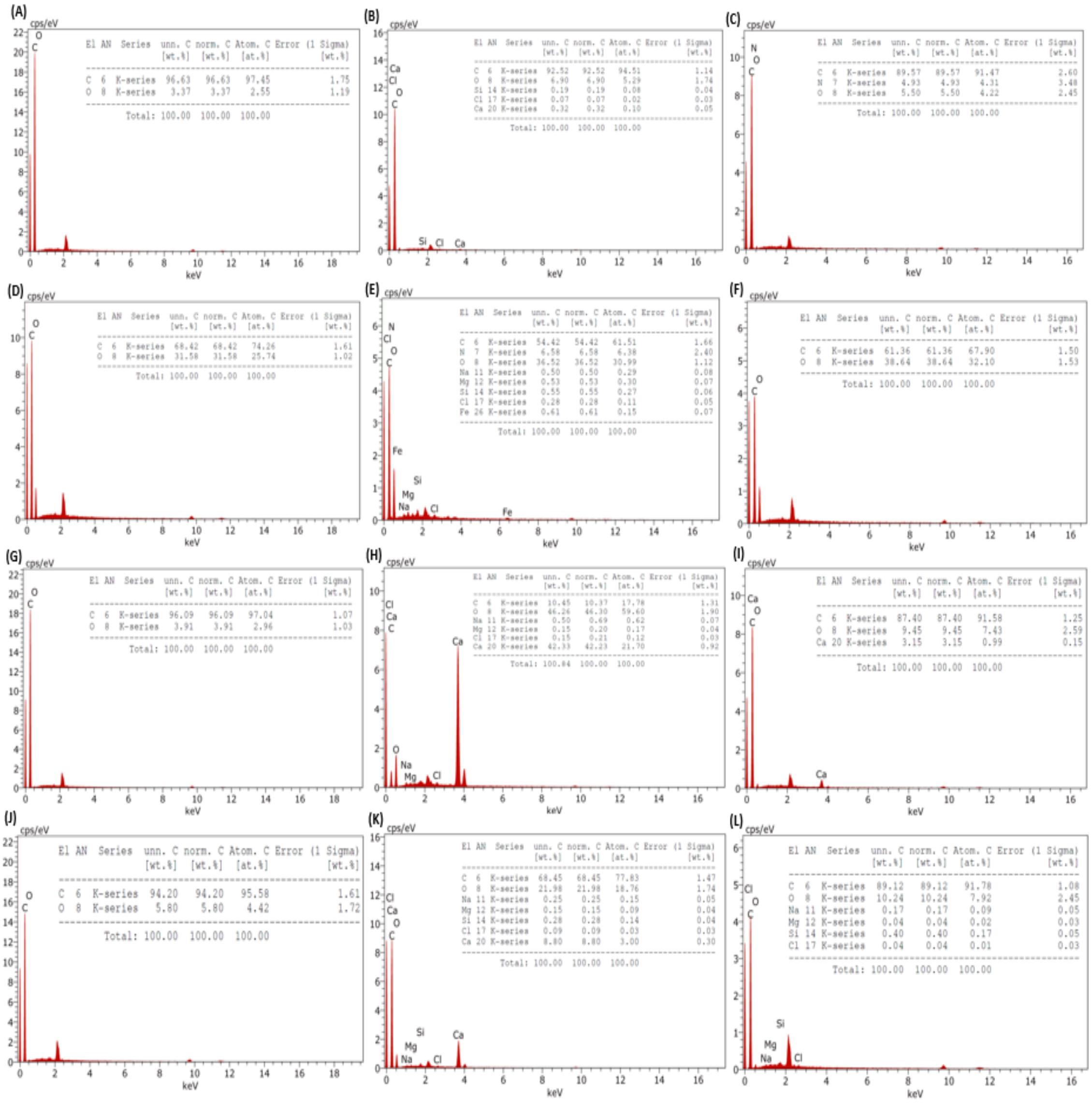
(E)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
C  6  K-series  90.80   90.80   93.15             1.68
O  8  K-series   8.51    8.51    6.55             1.83
Mg 12 K-series   0.17    0.17    0.09             0.04
Si 14 K-series   0.35    0.35    0.15             0.05
Ca 20 K-series   0.17    0.17    0.05             0.04
-------------------------------------------------------
        Total: 100.00  100.00  100.00
```

(F)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
C  6  K-series  83.50   83.50   87.73             1.62
O  8  K-series  14.59   14.59   11.51             2.42
Mg 12 K-series   0.38    0.38    0.20             0.05
Al 13 K-series   0.14    0.14    0.06             0.04
Si 14 K-series   0.45    0.45    0.20             0.05
Ca 20 K-series   0.94    0.94    0.30             0.06
-------------------------------------------------------
        Total: 100.00  100.00  100.00
```

Figure 41. EDX Results for HDPE and PE: (A) EDX HDPE Before Degradation, (B) EDX LMP-HDPE after 140 Days of Exposure to T2, (C) EDX Macro1- HDPE After 140 Days of Exposure to T2, (D) EDX PE Before Exposure, (E) EDX LMP-PE After 140 Days of Exposure to T2, (F) EDX Macro1- PE After 140 Days of Exposure to T2.



(A)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C  6  K-series   96.63   96.63   97.45            1.75
O  8  K-series    3.37    3.37    2.55            1.19
------------------------------------------------------
        Total:  100.00  100.00  100.00
```

(B)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C   6 K-series   92.52   92.52   94.51            1.14
O   8 K-series    6.90    6.90    5.29            1.74
Si 14 K-series    0.19    0.19    0.08            0.04
Cl 17 K-series    0.07    0.07    0.02            0.03
Ca 20 K-series    0.32    0.32    0.10            0.05
------------------------------------------------------
        Total:  100.00  100.00  100.00
```

(C)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C  6  K-series   89.57   89.57   91.47            2.60
N  7  K-series    4.93    4.93    4.31            3.48
O  8  K-series    5.50    5.50    4.22            2.45
------------------------------------------------------
        Total:  100.00  100.00  100.00
```

(D)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C  6  K-series   68.42   68.42   74.26            1.61
O  8  K-series   31.58   31.58   25.74            1.02
------------------------------------------------------
        Total:  100.00  100.00  100.00
```

(E)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C   6 K-series   54.42   54.42   61.51            1.66
N   7 K-series    6.58    6.58    6.38            2.40
O   8 K-series   36.52   36.52   30.99            1.12
Na 11 K-series    0.50    0.50    0.29            0.08
Mg 12 K-series    0.53    0.53    0.30            0.07
Si 14 K-series    0.55    0.55    0.27            0.06
Cl 17 K-series    0.28    0.28    0.11            0.05
Fe 26 K-series    0.61    0.61    0.15            0.07
------------------------------------------------------
        Total:  100.00  100.00  100.00
```

(F)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C  6  K-series   61.36   61.36   67.90            1.50
O  8  K-series   38.64   38.64   32.10            1.53
------------------------------------------------------
        Total:  100.00  100.00  100.00
```

(G)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C  6  K-series   96.09   96.09   97.04            1.07
O  8  K-series    3.91    3.91    2.96            1.03
------------------------------------------------------
        Total:  100.00  100.00  100.00
```

(H)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C   6 K-series   10.45   10.37   17.78            1.31
O   8 K-series   46.26   46.30   59.60            1.90
Na 11 K-series    0.50    0.69    0.62            0.07
Mg 12 K-series    0.15    0.20    0.17            0.04
Cl 17 K-series    0.15    0.21    0.12            0.03
Ca 20 K-series   42.33   42.23   21.70            0.92
------------------------------------------------------
        Total:  100.84  100.00  100.00
```

(I)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C   6 K-series   87.40   87.40   91.58            1.25
O   8 K-series    9.45    9.45    7.43            2.59
Ca 20 K-series    3.15    3.15    0.99            0.15
------------------------------------------------------
        Total:  100.00  100.00  100.00
```

(J)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C  6  K-series   94.20   94.20   95.58            1.61
O  8  K-series    5.80    5.80    4.42            1.72
------------------------------------------------------
        Total:  100.00  100.00  100.00
```

(K)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C   6 K-series   68.45   68.45   77.83            1.47
O   8 K-series   21.98   21.98   18.76            1.74
Na 11 K-series    0.25    0.25    0.15            0.05
Mg 12 K-series    0.15    0.15    0.09            0.04
Si 14 K-series    0.28    0.28    0.14            0.04
Cl 17 K-series    0.09    0.09    0.03            0.03
Ca 20 K-series    8.80    8.80    3.00            0.30
------------------------------------------------------
        Total:  100.00  100.00  100.00
```

(L)

```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
------------------------------------------------------
C   6 K-series   89.12   89.12   91.78            1.08
O   8 K-series   10.24   10.24    7.92            2.45
Na 11 K-series    0.17    0.17    0.09            0.05
Mg 12 K-series    0.04    0.04    0.02            0.03
Si 14 K-series    0.40    0.40    0.17            0.05
Cl 17 K-series    0.04    0.04    0.01            0.03
------------------------------------------------------
        Total:  100.00  100.00  100.00
```

Figure 42. EDX Results for LDPE, PET, PP, and PS: (A) EDX LDPE Before Degradation, (B) EDX LMP-LDPE After 140 Days of Exposure to T3, (C) EDX Macro1- LDPE After 140 Days of Exposure to T3, (D) EDX PET Before Exposure, (E) EDX LMP-PET After 140 Days of Exposure to T3, (F) EDX Macro1- PET After 140 Days of Exposure to T3, (G) EDX PP Before degradation, (H) EDX LMP-PP After 140 Days of Exposure to T3, (I) EDX Macro1-PP After 140 Days of Exposure to T3, (J) EDX PS Before Degradation, (K) EDX LMP-PS After 140 Days of Exposure to T3, and (L) EDX Macro1-PS After 140 Days of Exposure to T3.

Whilst SEM analysis was effective in the identification of plastic degradation signs and changes in the morphologies, EDX analysis helped in the quantification of the elemental composition concentration of the plastic samples prior to and after exposure to different environmental treatments (T2 and T3). Observed results showed that plastics prior to degradation were mainly composed of carbon with more than 95%, except for PET which showed a lower C% of more than 68% as shown in **Figure** 42 (D). Other elements such as Ca and Cu were also present with an overall concentration of less than 1% as displayed in **Figure** 41 (A) and (D). After 140 days of exposure to T2 and T3, other elements including Mg, Al, Si, Ca, Fe, Na, and Cl were present with an overall concentration of less than 5%, except for LMP-PP which showed a relatively high concentration of Ca of more than 40% as illustrated in **Figure** 42 (H). it needs to be mentioned that, regardless to which treatment (T2 or T3) the plastics were exposed to, more elements were found in the smaller plastic particles (LMPs) than in the Macros. This is mainly related to their higher degradation. Based on IC results, elements like Chloride, Sulfate, Sodium, Potassium, Calcium, and Magnesium are expected to be produced from the SW due to the availability of these elements in the SW samples as shown in **Appendix** A. The SW sample was diluted 1000 times, where 0.1 mL of the raw SW sample was mixed with 100 ml of deionized water and used for IC anions and cations analysis by using 850 Professional IC from Metrohm. However, the presence of other elements including Al, Si, and Fe may be due to the chemical additives and colorants which are used in the different plastic types, since silicate or alumina can be used as stabilizers for some polymers (Ranta-Korpi et al., 2014; Schoppe, 2012). In addition, some of the most commonly used plastic additives are inorganic pigments which includes iron oxide (Hahladakis et al., 2018). Moreover, these resulting chemical elements may be present due to the chemical environmental degradation mechanism, where the changes happen at the molecular level such as the oxidation of polymer chains leading to new molecules which are shorter in length (Chamas et al., 2020).

4.7 GC-MS analysis

Despite the fact that phthalates are suspected to be part of the EDCs list, they are still being incorporated in several commonly used house products including cosmetics, plastics, inks, medical devices, and detergents (LaFleur and Schug, 2011). Certain phthalates (e.g., DBP, BBP, and DEHP) are supposed to be endocrine system disruptor since it competes for binding to the estrogen receptor with 17β-estradiol (Ghisari and Bonefeld-Jorgensen, 2009). These harmful substances enter the environment directly from plastic materials production and indirectly through the volatile emissions and leachate from polymers (Kavlock et al., 2002). The reason behind their easy leaching into the environment is the fact that they are not chemically bound in the plastic polymeric structures (Dimassi et al., 2022). Thus, those harmful chemical substances were selected besides BPA which is also as important as phthalates for the inspection of their chemical leaching to the surrounding SW samples used in the investigation of plastic degradation and fragmentation.

Gas chromatograms of all chemical compounds which were isolated from the SW samples before and after being exposed to two different treatments (T3 and T4) are shown in **Figures** 43-45. It is interesting to mention that the identification of DBP, DEHP, and BPA were confirmed by GC/MS analysis after only 140 days of exposure to T3 and T4. In addition, BBP compound was not detected in the SW samples after 140 days of the experiment. It should be also mentioned that raw Qatari SW samples (prior exposure to any treatment) contained DBP and DEHP with concentrations of 89.65 µg/L and 106.2 µg/L, respectively, as shown in **Figure** 43 (A), which can be explained by the presence of degraded plastics in the Qatari environment. These concentrations were subtracted from the sample results to better understand the effect of outdoor and indoor conditions. The concentration of extracted SW leachate of these compounds increased especially after 140 days of exposing plastics to outdoor environmental conditions. Moreover, BPA was detected in the SW sample after 140 days of exposing plastics to outdoor environmental conditions (T3) (e.g., sunlight, pH, salinity, temperature, and wave abrasion) with a concentration of 34 µg/L.

The recovery percentages of all chemical compounds in the SW samples have shown satisfactory recovery% ranging from 89.14% to 103.12%. The average recovery% and the linearity data of the four standards are illustrated in **Table** 12. The average recovery% findings showed high values at low concentrations which validate the appropriate performance of the applied procedure. Taking into consideration the different types of phthalates extraction from the SW, phthalates recovery% findings of this study showed higher values than findings found elsewhere (Paluselli et al., 2018). The authors stated that their optimized conditions showed percentages of 125%, 13%, and 75% for BBP, DEHP, and DBP, respectively (Paluselli et al., 2018). In addition, findings showed excellent correlation coefficients, where $R^2 > 0.99$ for all compounds. This also confirms the linearity and accuracy of the protocol adapted in this study.

Table 12. Linearity Data Between the Spiked Concentrations of the Four Standards and their Measured Average Peak Areas Along with the Recovery% Data.

Compound	Calibration curve- spiked concentrations (µg/L)	R^2	Slope (V/ µg/L)	y-intercept (V)	Spiked concentrat-ion (µg/L) -recovery%	Avg. recovery %
DBP	25, 100, 200, 1000, and 2500	0.9992	3231.7	89143	50, 500, and 2000	102.1, 98.90, and 98.06
BPA	25, 100, 200, 1000, and 2500	0.9998	761.48	19790	50, 500, and 2000	93.30, 92.65, and 95.33
BBP	25, 100, 200, 1000, and 2500	0.9998	2062.3	33801	50, 500, and 2000	90.75, 95.01, and 97.30
DEHP	25, 100, 200, 1000, and 2500	0.9995	3331.6	2618.6	50, 500, and 2000	90.01, 95.81, and 99.74

The concentrations of phthalates and BPA in SW samples before and after exposing different types of plastics to indoor and outdoor environmental conditions for 140 days was calculated by using the following equation:

Concentration (µg/L) = Sample peak area/Response Factor (Ahmed et al.)

Where RF is the peak area of each pure standard compound over the known concentration (ppb or µg/L) of the compound, which is simply the slope of the calibration curve of each chemical compound.

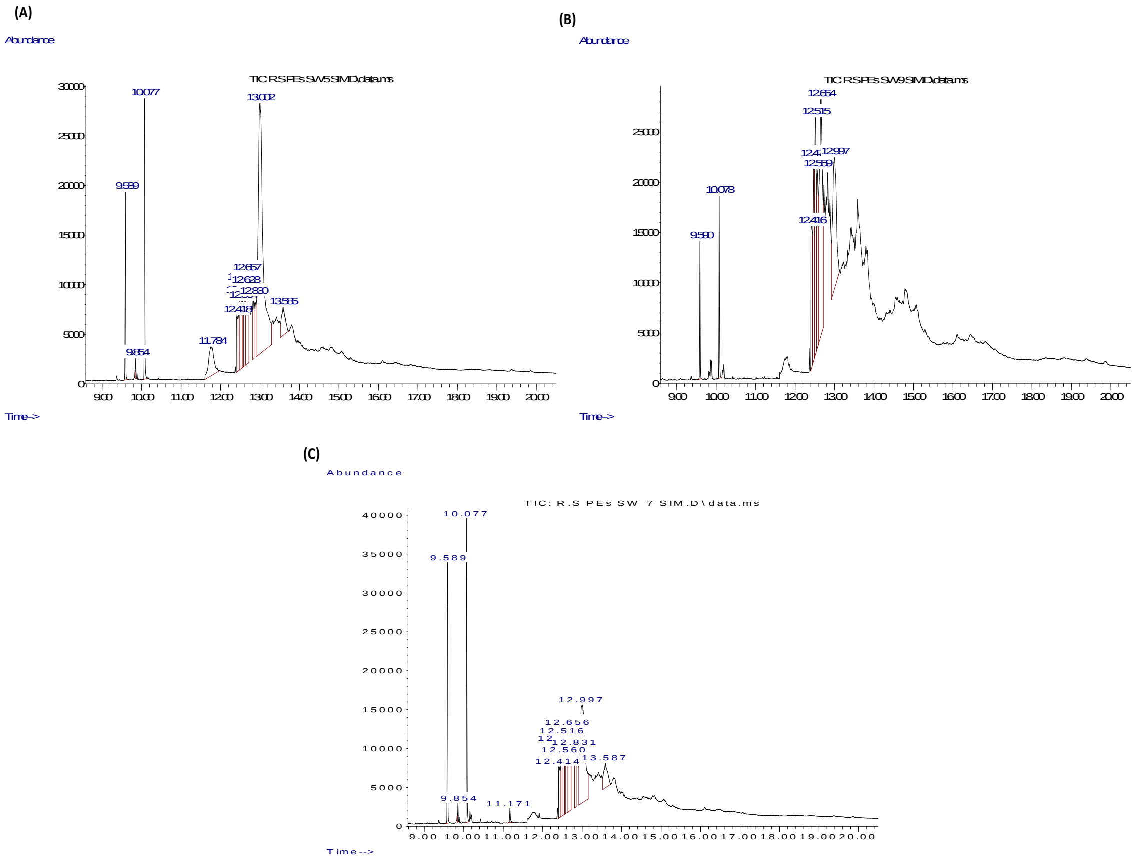


Figure 43. GC-MS Chromatograms of SW in Indoor and Outdoor Experimental Tanks, (A) at Day 0 Before Exposure to T3 and T4, (B) Plastic Additives Leachate at Day 140 After Exposure to T4, (C) Plastics Additives Leachate at Day 140 After Exposure to T3.

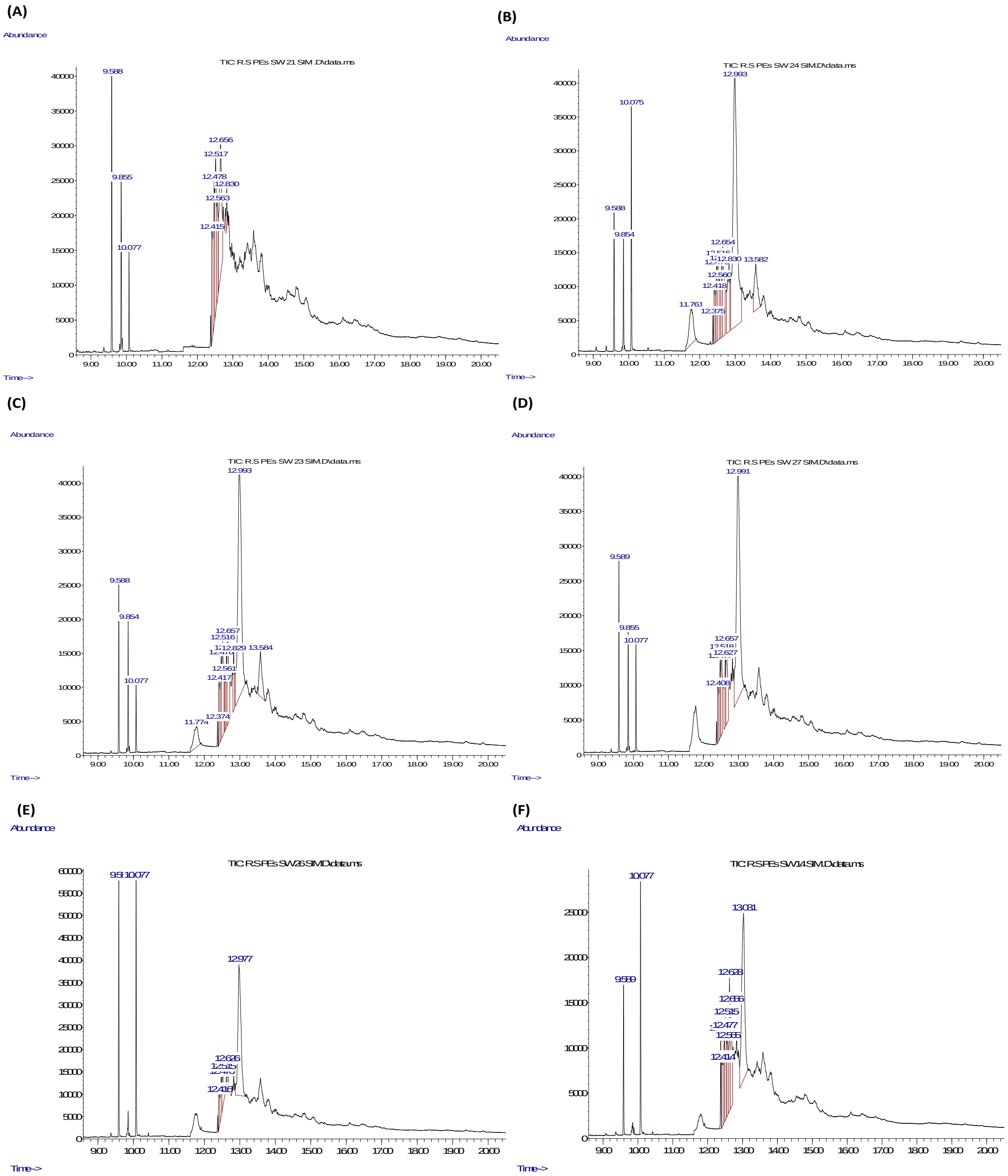


Figure 44. GC Chromatograms of SW, (A) SMP-HDPE Leachate After 140 Days of Exposure to T3, (B) SMP-LDPE Leachate After 140 Days of Exposure to T3, (C) SMP-PE Leachate After 140 Days of Exposure to T3, (D) SMP-PET Leachate After 140 Days of Exposure to T3, (E) SMP-PP Leachate After 140 Days of T3, (F) SMP-PS Leachate After 140 Days of T3.

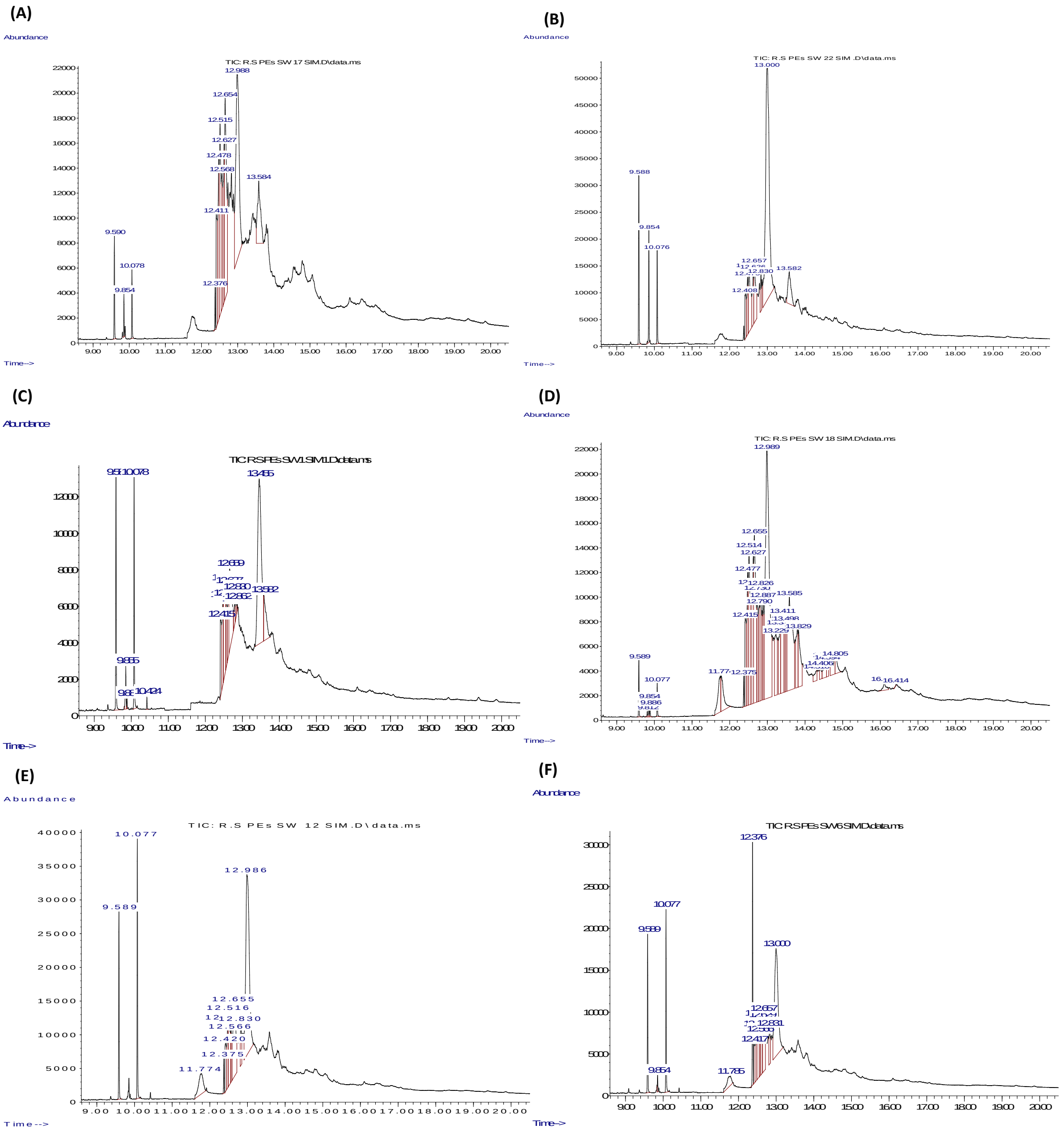


Figure 45. GC Chromatograms of SW, (A) SMP-HDPE Leachate After 140 Days of Exposure to T4, (B) SMP-LDPE Leachate After 140 Days of Exposure to T4, (C) SMP-PE Leachate After 140 Days of Exposure to T4, (D) SMP-PET Leachate After 140 Days of Exposure to T4, (E) SMP-PP Leachate After 140 Days of T4, (F) SMP-PS Leachate After 140 Days of T4.

Effect of outdoor environmental conditions on the total amount of Phthalates and Bisphenol A leached

Results showed that regardless of the indoor conditions (no sunlight and controlled temperature), different plastics leached certain phthalates and BPA into the surrounding seawater. Yet, higher concentrations were mostly detected in SW after exposing plastics to outdoor environmental conditions due to the high temperatures and sunlight intensities. DBP, DEHP, and BPA were detected in SW with higher concentrations of 33 µg/L, 19 µg/L, and 34 µg/L, respectively, after exposing the different plastics to T3. The absence of the other targeted phthalate (BBP) can be explained by the absence of this compound from the selected plastics or to its low release rate to the SW because of its high affinity with the polymeric structure. While DBP, and DEHP, only were identified in the SW sample after exposing the plastics to indoor conditions T4. No DBP concentration was detected from the SW samples after exposing plastics to T4 and T3 except for SMP-PS, SMP-PP, and SMP-PE. This drop in initial concentration which was available in the raw SW could be explained by the adsorption of pollutants and chemicals by MPs. Studies showed that MPs have the ability to absorb pollutants in seawater (Gallo et al., 2018). This indicates that plastics act as a transport medium and a source of harmful chemicals in the seawater environment along with the potential leachability of different additives embedded in them. However, a relatively higher concentration of DEHP was present in the indoor SW sample (313 µg/L). The reason behind this may be the easy leaching of this compound into the environment due to the fact that it is not chemically bound in the plastic polymeric structures. Thus, DEHP embedded in plastics was mainly affected by pH, salinity, and wave abrasion simulation of the SW. Overall, the higher leaching concentrations were measured mostly in the outdoor environmental conditions (T3) due to the exposure to high temperatures and sunlight intensities compared to indoor conditions. This could be explained by the fact that these compounds are susceptible to photodegradation via free radial attack, biodegradation, and to a limited extent hydrolysis. This means that the reason behind the high concentrations in outdoor samples for these three exceptions may be due to the presence of algae in the outdoor tanks which were developed mainly due to the sunlight (biodegradation), in addition to the presence of sunlight (photodegradation), as well as hydrolysis to a lesser extent. However, hydrolysis of these compounds could be excluded from these assumptions since it is also occurring in indoor set-ups. However, higher concentrations of DBP and DEHP were leached out from some indoor SW samples. This shows that wave abrasion promoted the leaching of DEHP and DBP. Since indoor samples were put, periodically, on the shaker platform to mimic the wave abrasion at a speed of 180 rpm for the experimental period. On the other hand, outdoor samples were only mixed manually from time to time. The average total leachate concentration (µg/L) from MPs experiments as well as tank experimental set-ups after 140 days of exposing plastics to T3 and T4 as shown in **Table** 13.

Table 13. Average Total Leachate Concentration (µg/L) from MPs Experiments and Tank Experimental Set-ups After 140 Days of Exposing Plastics to T3 and T4.

Avg. Total leachate concentration (µg/L)		
Compounds	**T4**	**T3**
	Tanks	
DBP	56	33
BPA	**-**	34
DEHP	313	19
	SMP-HDPE	
DBP	-	-
DEHP	75	123
	SMP-LDPE	
DBP	-	-
DEHP	18	105
	SMP-PE	
DBP	41	-
DEHP	-	26
	SMP-PET	
DBP	-	-
DEHP	-	16
	SMP-PP	
DBP	-	5.3
DEHP	95	-
	SMP-PS	
DBP	5	-
DEHP	10	115

Results shows that the total leachate concentrations of identified targeted chemical compounds from T3 SW samples ranged from 5 µg/L to 123 µg/L. Although, BBP was not detected in this study, a previous study showed the presence of this compound along with DBP and DEHP in coastal seawater (Xie et al., 2005). This confirms the presence of these compounds in the SW in different locations worldwide. These different chemical compounds are mainly originating from plastic polymer industries due to their use as plastic additives to increase the durability, flexibility, and transparency. DEHP was the most abundant compound found in all SW samples analysed, followed by DBP, and then BPA. Although larger leaching concentrations were measured in the outdoor environmental conditions (T3) due to the exposure to high temperatures and sunlight intensities compared to indoor conditions, some indoor

SW samples showed relatively higher concentrations such as DEHP and DBP from the tank with concentrations of 313 µg/L and 56 µg/L, DBP in SMP-PE experiment with a concentration of 41 µg/L, DEHP in SMP-PP experiment with a concentration of 95 µg/L, and DBP from SMP-PS with a low concentration of 5 µg/L as shown in **Table** 13.

Based on SMP leaching results after exposing plastics to T3, it can be concluded that PP was the most responsible plastic type for the leaching of DBP due to the detected average concentration of the compound identified in the SW sample which was 5.3 µg/L. On the other hand, HDPE was the most responsible plastic type for the leaching of DEHP with an average concentration of 123 µg/L, followed by PS, LDPE, PE, and PET with concentrations of 115 µg/L, 105 µg/L, 26 µg/L, and 16 µg/L, respectively. These variations in the leaching concentrations are mainly due to the differences in the polymeric structures, backbone chains, melting points, and the effect of colorant types since each of these used plastic types has their own unique color. From the leaching concentration results of DEHP, it can be concluded that higher temperatures and sunlight intensities promoted the leaching of DEHP. These findings were in alignment with a recent study conducted to investigate the effects of pH and temperatures on the leaching of DEHP and DBP (Li and Tang, 2022).

Although BPA was identified in the outdoor SW in the tank experiment, it was not found in the SMPs experiments. This could be explained by the undetectable concentrations of BPA due to the extremely low concentrations which were leached out from each plastic type alone. However, when all plastic types were put in the same tank and exposed to outdoor conditions for 140 days, a leaching concentration of 34 µg/L was detected for BPA.

A recent research study investigated the release of phthalates into the surrounding SW from the degraded plastics (Paluselli et al., 2019). Findings showed that phthalates were released in a range of 71 ng/g to 241 ng/g (Paluselli et al., 2019), where DBP was released from PE with a highest value of 120.1 ± 18.0 ng/g of plastic. In addition, it was found that the exposure to light as well as bacteria raised the total amount of phthalates released from plastics made of polyvinyl chloride by a factor of up to 5. Findings were aligned with the results of the current study where light/sunlight can affect the leachability of phthalates as well as PBA to the surrounding SW.

The identification of DBP, DEHP, and BPA were confirmed by GC/MS analysis after only 140 days of exposure to T3 and T4. Results showed that regardless of the indoor conditions, different plastics leached certain amounts phthalates and BPA to the surrounding seawater. While comparing the maximum permissible levels of phthalates and BPA in the drinking water as shown in **Table** 14, it was found that these concentrations are considered high for such a short period, and it is a high of concern to treat the SW, especially if the SW will be desalinated to be used as drinking water, a whole treatment process needs to be done in order to lower these high concentrations.

Table 14. The Maximum Permissible Levels of Phthalates (DEHP, and DBP) and BPA in Drinking Water Regulated by the European Union and China (Dueñas-Moreno et al., 2022).

Compounds	Maximum permissible levels in drinking water (µg/L)
DBP	3
BPA	2.5
DEHP	8

4.8 Statistical analysis

In this project, a multivariate statistical method was performed, where the PCA and cluster analysis were applied using FTIR spectra as input data. The effect of treatment, size, and time on all different plastic types was studied. Firstly, PCA was performed to study the effect of all four treatments at a specific time (e.g., week 20 was chosen for this analysis since it was the last experimental week where results showed the highest potential degradation). In addition, this analysis was performed on the smaller size sub-category (LMP) for this study due to its higher degradation (weight loss%) and a higher percentage of variance. Subsequently, the effect of time and size on a specific treatment was studied by performing PCA for the most effective treatment for each plastic type. The most effective treatment for each plastic type was chosen based on the highest variance percentage, and correlation matrix values. Finally, a combination of effects was performed by mainly combining the effect of outdoor treatments (T2 and T3) on various plastic types with 2 different sizes (LMPs and Macros).

4.8.1 Effect of treatment on plastic types at a specific time

The effect of different treatments on the various plastic types was investigated at a specific time (week 20 or day 140) by using PCA. The FTIR results of all different types of LMPs after 140 days of exposure to four different treatments (T1, T2, T3, and T4) were analysed via PCA, as shown in **Figure.** 46.

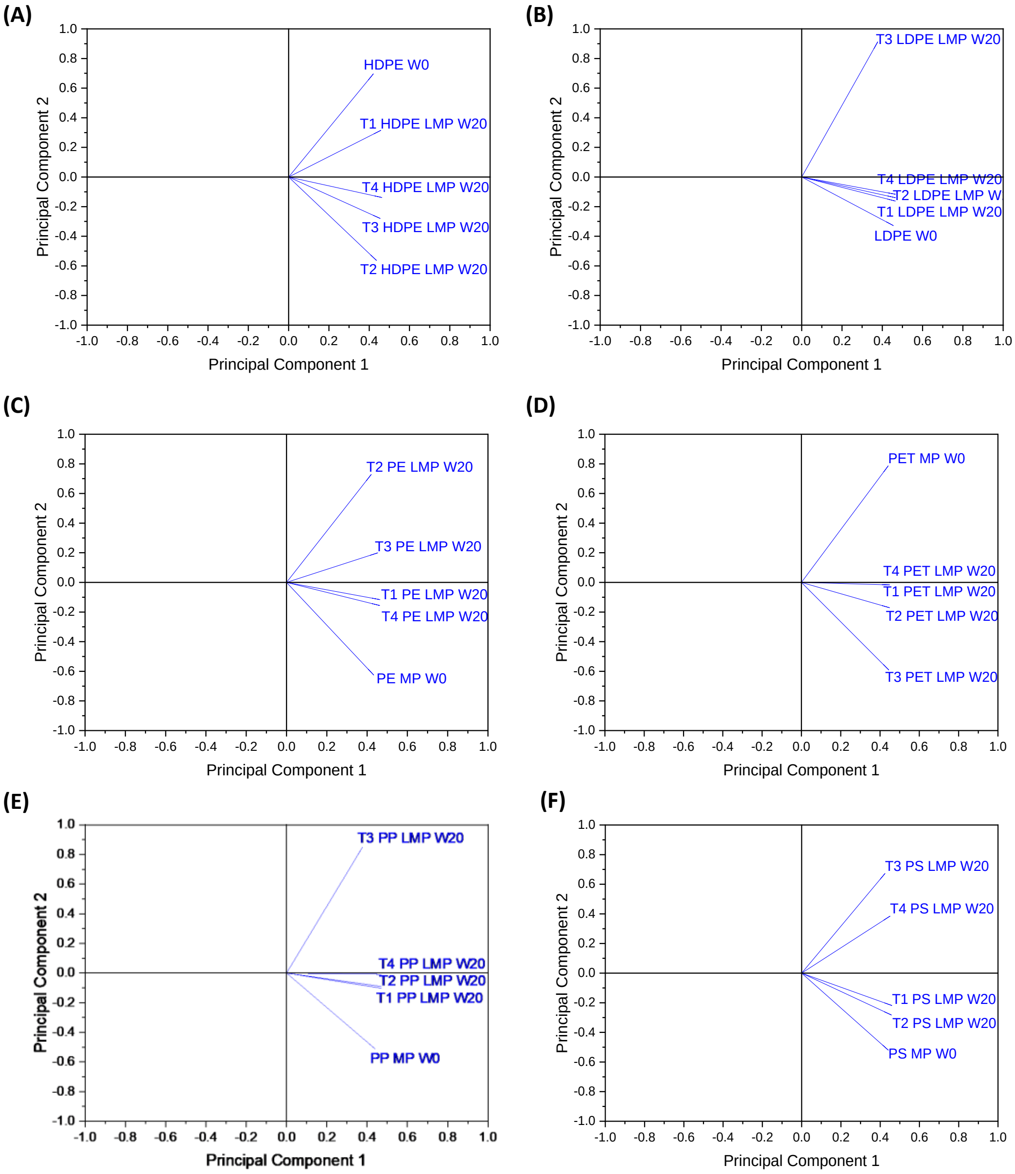


Figure 46. PCA: Effect of Four Treatments on Different Plastic Types at a Specific Time (week 20/day 140): Loading Plots of (A) HDPE-LMP, (B) LDPE-LMP, (C) PE-LMP, (D) PET-LMP, (E) PP-LMP, (F) PS-LMP.

LMPs were selected in this analysis due to their higher degradation (weight loss%), SEM-EDX analysis, as well as their larger shifts in the transmission peaks of FTIR spectra. The correlation matrix data which demonstrates the effect of treatments for different types of LMPs are shown in **Tables** 15-20.

Table 15. Correlation Matrix- Effect of Treatment on HDPE LMP.

	HDPE W0	T1 HDPE LMP W20	T2 HDPE LMP W20	T3 HDPE LMP W20	T4 HDPE LMP W20
HDPE W0	1	0.9599	0.6807	0.78589	0.84902
T1 HDPE LMP W20	0.9599	1	0.83502	0.91867	0.94042
T2 HDPE LMP W20	0.6807	0.83502	1	0.95224	0.95423
T3 HDPE LMP W20	0.78589	0.91867	0.95224	1	0.95342
T4 HDPE LMP W20	0.84902	0.94042	0.95423	0.95342	1

Table 16. Correlation Matrix- Effect of Treatment on LDPE LMP.

	LDPE W0	T1 LDPE LMP W20	T2 LDPE LMP W20	T3 LDPE LMP W20	T4 LDPE LMP W20
LDPE W0	1	0.98918	0.98685	0.66207	0.98279
T1 LDPE LMP W20	0.98918	1	0.99914	0.74016	0.99891
T2 LDPE LMP W20	0.98685	0.99914	1	0.74973	0.99887
T3 LDPE LMP W20	0.66207	0.74016	0.74973	1	0.75872
T4 LDPE LMP W20	0.98279	0.99891	0.99887	0.75872	1

Table 17. Correlation Matrix- Effect of Treatment on PE LMP.

	PE MP W0	T1 PE LMP W20	T2 PE LMP W20	T3 PE LMP W20	T4 PE LMP W20
PE MP W0	1	0.94601	0.71422	0.84633	0.95012
T1 PE LMP W20	0.94601	1	0.86935	0.96859	0.99578
T2 PE LMP W20	0.71422	0.86935	1	0.89631	0.85983
T3 PE LMP W20	0.84633	0.96859	0.89631	1	0.95608
T4 PE LMP W20	0.95012	0.99578	0.85983	0.95608	1

Table 18. Correlation Matrix- Effect of Treatment on PET LMP.

	PET MP W0	T1 PET LMP W20	T2 PET LMP W20	T3 PET LMP W20	T4 PET LMP W20
PET MP W0	1	0.98178	0.9719	0.94827	0.97954
T1 PET LMP W20	0.98178	1	0.99725	0.98819	0.99601
T2 PET LMP W20	0.9719	0.99725	1	0.98979	0.99706
T3 PET LMP W20	0.94827	0.98819	0.98979	1	0.98662
T4 PET LMP W20	0.97954	0.99601	0.99706	0.98662	1

Table 19. Correlation Matrix- Effect of Treatment on PP LMP.

	PP MP W0	T1 PP LMP W20	T2 PP LMP W20	T3 PP LMP W20	T4 PP LMP W20
PP MP W0	1	0.95098	0.94728	0.52532	0.92773
T1 PP LMP W20	0.95098	1	0.99481	0.74981	0.99587
T2 PP LMP W20	0.94728	0.99481	1	0.75471	0.99587
T3 PP LMP W20	0.52532	0.74981	0.75471	1	0.79135
T4 PP LMP W20	0.92773	0.99587	0.99587	0.79135	1

Table 20. Correlation Matrix- Effect of Treatment on PS LMP.

	PS MP W0	T1 PS LMP W20	T2 PS LMP W20	T3 PS LMP W20	T4 PS LMP W2
PS MP W0	1	0.98089	0.98644	0.74704	0.85193
T1 PS LMP W20	0.98089	1	0.99606	0.85664	0.92703
T2 PS LMP W20	0.98644	0.99606	1	0.83395	0.91666
T3 PS LMP W20	0.74704	0.85664	0.83395	1	0.97292
T4 PS LMP W20	0.85193	0.92703	0.91666	0.97292	1

The PCA diagram in **Figure** 46 (A) shows a 98.73% cumulative variation within the FTIR spectra of the six different plastic types through the principal components (PC1 and PC2). From **Figure** 46 (A), it is evident that HDPE before exposure (HDPE W0) and HDPE LMP after 140 days of exposure to T1 (T1 HDPE LMP W20) did not show a great difference as they are lying close to each other on the loading plot of PCA diagram, which can also be noted from their correlation values as T1 HDPE LMP W20 showed a value of 0.9599 which is close to 1 as illustrated in **Table** 15. Thus, there is a huge significant difference between the FTIR of HDPE prior to degradation and after being exposed to T1 for 140 days. This can also be noted in their weight loss% results. Thus, the PCA helps in categorizing the effect of treatments on different plastic types into groups or "clusters" and the plastics which fall into the same cluster are similar to each other than ones in different clusters. The different clusters of the PCA loading plot are shown in **Figure** 46. The FTIR data was arranged mostly in the positive values of PC1, however it was displayed in the positive as well as the negative scale of the PC2 based variance% of the data. The PCA diagrams in **Figure** 46 (B, C, D, E, and F) show cumulative percentage variations of 99.84%, 98.36%, 99.78%, 99.71%, and 99.65%, respectively, within the FTIR spectra of the six different plastic types through the principal components (PC1 and PC2). This means that these variance percentages were preserved when modeling the PCA loading plots with the first 2 principal components.

PCA findings revealed that the treatment which showed the highest significant difference for LMP-HDPE and LMP-PE was T2, with correlation values of 0.6807, and 0.71422, respectively, while comparing the effect of the treatment with their similar plastic-type prior to exposure at Day0/W0 (as a reference), as shown in **Tables** 15 and 17. On the other hand, T3 showed the highest significant difference for LMP-LDPE, LMP-PET, LMP-PP, and LMP-PS, with correlation values of 0.66207, 0.94827, 0.52532, 0.74704, respectively, while comparing the effect of treatments with their similar plastic-type prior to exposure at Day 0/W 0, as shown in **Tables** 16, 18, 19, and 20.

Using PCA, the different plastic types were correlated with the four treatments used in this study by using FTIR as input data. Based on the correlation results, outdoor treatments (T2 and T3) showed a higher significant difference than other treatments for all different plastic types mainly due to high temperatures, and sunlight intensities along with pH, salinity, and wave abrasion which were present in the indoor conditions as well.

The effect of four treatments on different macro-sized plastic types at a specific time (week 20/day 140) was also performed using PCA as shown in **Appendix** B. **Figure** 51 to ensure the alignment of weight loss%, FTIR, and SEM-EDX results with the statistical analysis.

4.8.2 Effect of time on outdoor treatments (T2 and T3) for different plastic types

The effect of time on outdoor treatments (T2 and T3) for the different plastic types was investigated by using PCA. The FTIR results of all different types of LMPs after 12 weeks/84 days and 20 weeks/140 days of exposure to two different treatments (T2 and T3) were analysed using PCA, as shown in **Figure** 47.

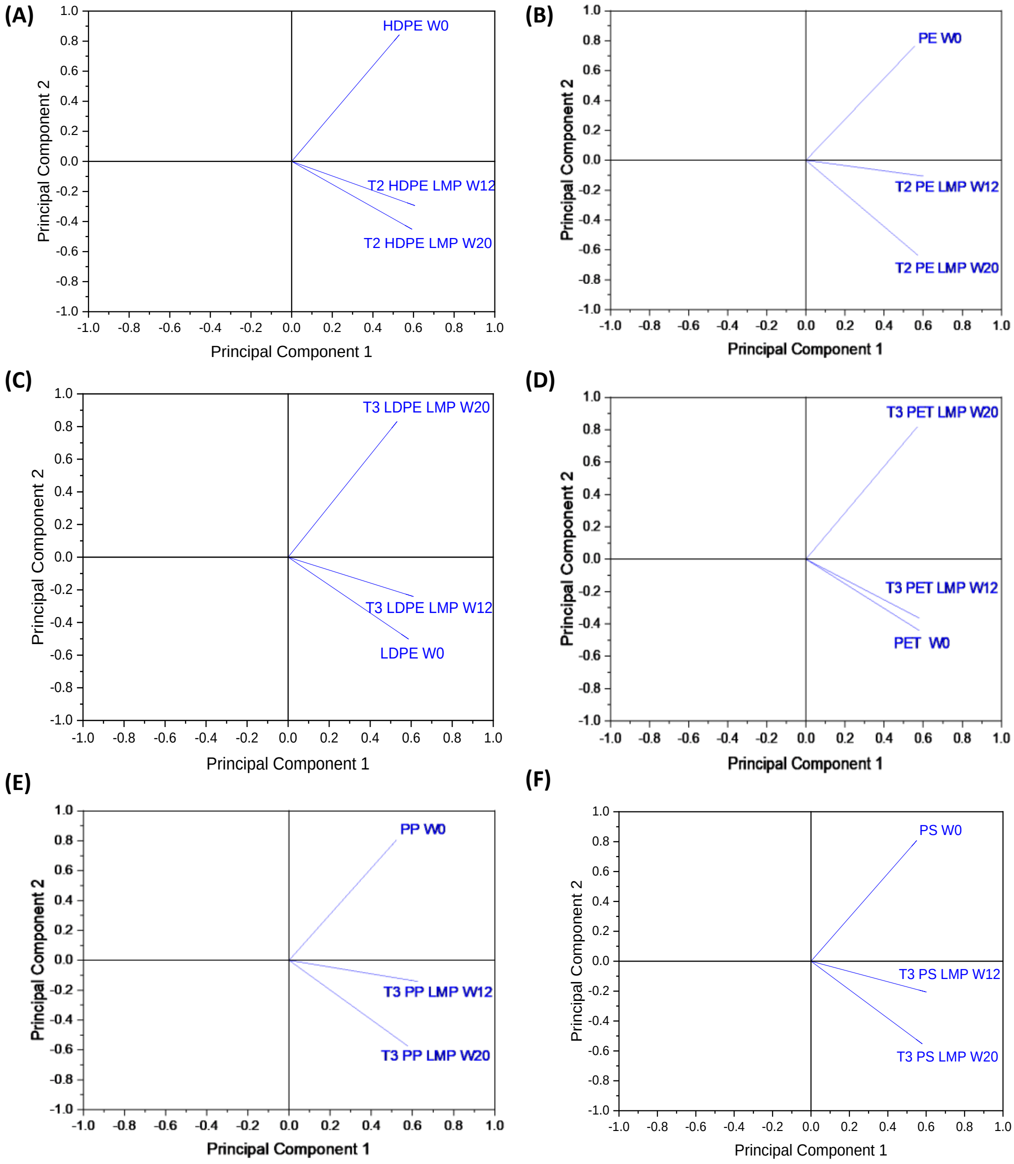


Figure 47. PCA: Effect of Time on Outdoor Treatments (T2 and T3) for Different Plastic Types: Loading Plots of (A) Effect of Time on T2- HDPE-LMP, (B) Effect of Time on T2- PE-LMP, (C) Effect of Time on T3 – LDPE-LMP, (D) Effect of Time on T3- PET-LMP, (E) Effect of Time on T3- PP-LMP, and (F) Effect of Time on T3- PS-LMP.

Table 21. Correlation Matrix- Effect of Time on Specific Treatment (T2) HDPE LMP.

	HDPE W0	T2 HDPE LMP W12	T2 HDPE LMP W20
HDPE W0	1	0.74801	0.6807
T2 HDPE LMP W12	0.74801	1	0.98619
T2 HDPE LMP W20	0.6807	0.98619	1

Table 22. Correlation Matrix- Effect of Time on Specific Treatment (T2) PE LMP.

	PE W0	T2 PE LMP W12	T2 PE LMP W20
PE W0	1	0.85089	0.71422
T2 PE LMP W12	0.85089	1	0.90766
T2 PE LMP W20	0.71422	0.90766	1

Table 23. Correlation Matrix- Effect of Time on Specific Treatment (T3) LDPE LMP.

	LDPE W0	T3 LDPE LMP W12	T3 LDPE LMP W20
LDPE W0	1	0.9846	0.66207
T3 LDPE LMP W12	0.9846	1	0.77512
T3 LDPE LMP W20	0.66207	0.77512	1

Table 24. Correlation Matrix- Effect of Time on Specific Treatment (T3) PET LMP.

	PET W0	T3 PET LMP W12	T3 PET LMP W20
PET W0	1	0.99962	0.94827
T3 PET LMP W12	0.99962	1	0.95426
T3 PET LMP W20	0.94827	0.95426	1

Table 25. Correlation Matrix- Effect of Time on Specific Treatment (T3) PP LMP.

	PP W0	T3 PP LMP W12	T3 PP LMP W20
PP W0	1	0.7516	0.52532
T3 PP LMP W12	0.7516	1	0.92905
T3 PP LMP W20	0.52532	0.92905	1

Table 26. Correlation Matrix- Effect of Time on Specific Treatment (T3) PS LMP.

	PS W0	T3 PS LMP W12	T3 PS LMP W20
PS W0	1	0.85029	0.74704
T3 PS LMP W12	0.85029	1	0.96912
T3 PS LMP W20	0.74704	0.96912	1

The effect of time on outdoor treatments (T2 and T3) for different plastic types was analysed using PCA. T2 and T3 were selected based on the highest difference, and correlation values for each plastic type. PCA diagrams in **Figure** 47 (A-F) show cumulative percentage variations of 99.70%, 98.04%, 99.93%, 99.99%, 99.19%, and 99.51%, respectively, within the FTIR spectra of the six different plastic types through the principal components (PC1 and PC2). This means that these variance percentages were preserved when modeling the PCA loading plots with the first 2 principal components.

PCA analysis for LMP-HDPE and LMP-PE was performed by studying the effect of time on T2 since this treatment showed the highest significant difference. On the other hand, T3 was chosen to perform PCA analysis of other types (LMP-LDPE, LMP-PP, LMP-PS, and LMP-PET) for the same reason. The PCA diagrams in **Figure** 47 shows that week 20 showed the highest significant difference in all plastic types (LMP-HDPE, LMP-PE, LMP-LDPE, LMP-PET, LMP-PP, LMP-PS) with correlation values of 0.6807, 0.71422, 0.66207, 0.94827, 0.52532, and 0.74704 as shown in **Tables** 21-26. In addition, PCA diagrams for LMP-HDPE, LMP-PE, LMP-PE, LMP-PP, and LMP-PS showed that week12 and week20 were categorized in the same cluster, which means there is no significant difference in the FTIR spectra between these 2 sampling periods as shown in **Figure** 47 (A, B, E, and F). Although there is no significant difference between these plastic types after 12 weeks and 20 weeks of exposure to T2 and T3, the FTIR spectra results show shifts and/or differences in the characteristics of transmission bands. On the other hand, PCA diagrams for LMP-LDPE, and LMP-PET showed that week 12 and week 20 were categorized in different clusters, where week12 was close to the reference week (week 0) as shown in **Figure** 47 (C, and D). The reasons behind the different behaviour of the different plastics when exposed to T2 and T3, are mainly the polymeric structures, branching, additives, and colorants used in each type of plastic. All of these aforementioned reasons affect the plastic degradation and fragmentation processes.

4.8.3 Effect of particle size on outdoor treatments (T2 and T3) for different plastic types

The effect of particle size on outdoor treatments (T2 and T3) for the different plastic types was also investigated using PCA. The FTIR results of all different types of LMPs and Macros1 after 20 weeks/140 days of exposure to two different treatments (T2 and T3) were analysed using PCA, as shown in **Figure** 48. Macro1 size was selected to be the representative size for the macroplastics category due to the limitation of the number of samples to be tested/analysed as well as LMPs, which also were representing the MP category.

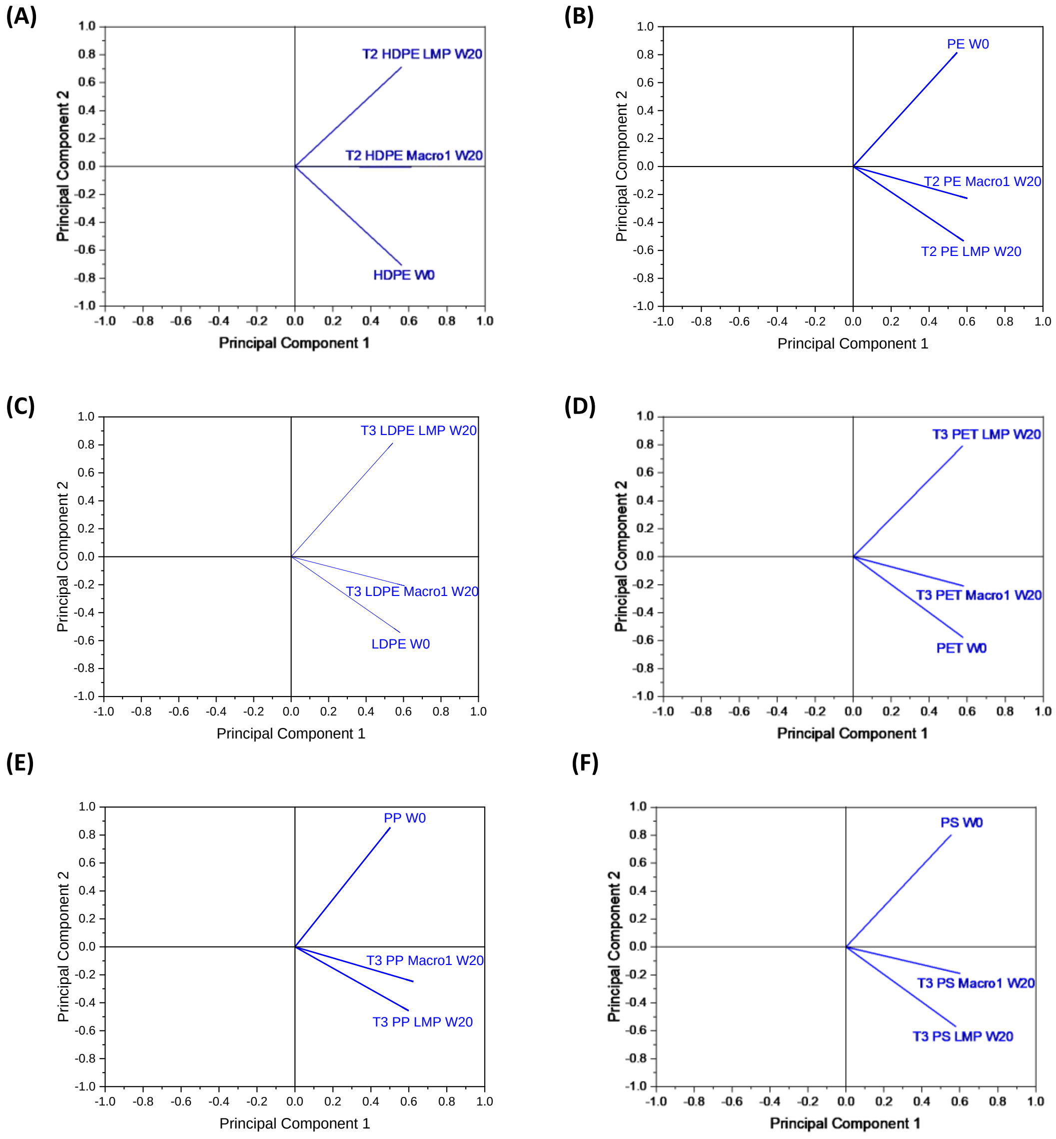


Figure 48. PCA: Effect of Particle Size on Outdoor Treatments (T2 and T3) for Different Plastic Types: Loading Plots of (A) Effect of Size on T2 – HDPE, (B) Effect of Size on T2 – PE, (C) Effect of Size on T3 – LDPE, (D) Effect of Size on T3 – PET, (E) Effect of Size on T3 – PP, (F) Effect of Size on T3 – PS.

Table 27. Correlation Matrix- Effect of Size on T2- HDPE.

	HDPE W0	T2 HDPE LMP W20	T2 HDPE Macro1 W20
HDPE W0	1	0.6807	0.91492
T2 HDPE LMP W20	0.6807	1	0.91235
T2 HDPE Macro1 W20	0.91492	0.91235	1

Table 28. Correlation Matrix- Effect of Size on T2- PE.

	PE W0	T2 PE LMP W20	T2 PE Macro1 W20
PE W0	1	0.71422	0.80787
T2 PE LMP W20	0.71422	1	0.9419
T2 PE Macro1 W20	0.80787	0.9419	1

Table 29. Correlation Matrix- Effect of Size on T3- LDPE.

	LDPE W0	T3 LDPE LMP W20	T3 LDPE Macro1 W20
LDPE W0	1	0.66207	0.91722
T3 LDPE LMP W20	0.66207	1	0.77568
T3 LDPE Macro1 W20	0.91722	0.77568	1

Table 30. Correlation Matrix- Effect of Size on T3- PET.

	PET W0	T3 PET LMP W20	T3 PET Macro1 W20
PET W0	1	0.94827	0.97821
T3 PET LMP W20	0.94827	1	0.96326
T3 PET Macro1 W20	0.97821	0.96326	1

Table 31. Correlation Matrix- Effect of Size on T3- PP.

	PP W0	T3 PP LMP W20	T3 PP Macro1 W20
PP W0	1	0.52532	0.64197
T3 PP LMP W20	0.52532	1	0.94535
T3 PP Macro1 W20	0.64197	0.94535	1

Table 32. Correlation Matrix- Effect of Size on T3- PS.

	PS W0	T3 PS LMP W20	T3 PS Macro1 W20
PS W0	1	0.74704	0.85372
T3 PS LMP W20	0.74704	1	0.95769
T3 PS Macro1 W20	0.85372	0.95769	1

Again, T2 and T3 were selected based on the significant difference, and correlation values for each plastic type. PCA diagrams in **Figure** 48 (A-F) show cumulative percentage variations of 99.86%, 98.49%, 97.81%, 99.35%, 98.56%, and 99.20%, respectively, within the FTIR spectra of the six different plastic types through the principal components (PC1 and PC2). This means that these variance percentages were preserved when modeling the PCA loading plots with the first 2 principal components.

PCA analysis of LMP-HDPE and LMP-PE was performed by studying the effect of time on T2 since this treatment showed the highest significant difference. On the other hand, T3 was chosen to perform PCA analysis on other types (LMP-LDPE, LMP-PP, LMP-PS, and LMP-PET) for the same reason. The PCA diagrams in **Figure** 48 show that plastics with smaller sizes (LMPs) showed the highest significant difference among all plastic types (LMP-HDPE, LMP-PE, LMP-LDPE, LMP-PET, LMP-PP, LMP-PS) with correlation values of 0.6807, 0.71422, 0.66207, 0.94827, 0.52532, and 0.74704 as shown in **Tables** 27-32. In addition, PCA diagrams for all different types of plastics except HDPE showed that LMPs and Macros were categorized in the same cluster, which means there is no significant difference in the FTIR spectra between these 2 sizes as shown in **Figure** 48 (B, C, D, E, and F). Although, there is no significant difference between these different sizes after 20 weeks of exposure to T2 and T3, the FTIR spectra results show shifts and/or differences in the characteristics of transmission bands. On the other hand, PCA diagrams for HDPE show that Macro size plastics were categorized in different clusters (in between 2 clusters) as shown in **Figure** 48 (A). This confirms that the smaller the plastic pieces, the higher their degradation due to the relatively greater surface area compared to their volume.

4.8.4 Combination of effects – Effect of outdoor treatments (T2 and T3) on various plastic types with 2 different sizes (LMPs and Macros)

A combination of effects was carried out by studying the effect of outdoor treatments (T2 and T3) on the various plastic types with 2 different sizes (LMPs and Macros) using PCA as shown in **Figure** 49. This analysis was helpful in investigating which plastic type showed the most significant difference after being exposed to 140 days/ 20 weeks of T2 or T3. Thus, to conclude the plastic type that showed higher degradation for both T2 and T3 based on the FTIR results.

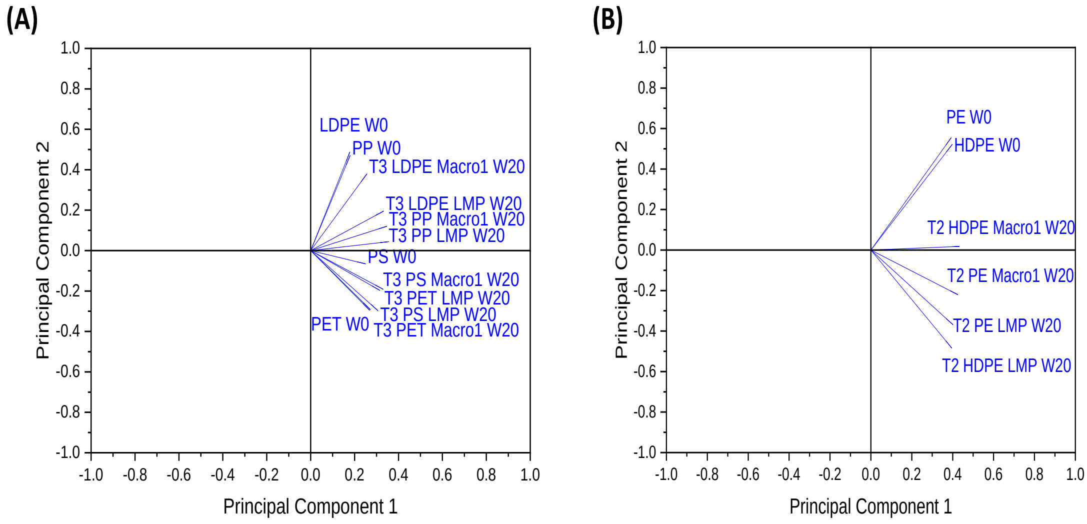


Figure 49. PCA: Effect of Outdoor Treatments (T2 and T3) on Various Plastic Types with 2 Different Sizes (LMPs and Macros) (A) Effect of Treatment T3 on LMPs and Macros of LDPE, PP, PS, and PET (B) Effect of Treatment T2 on LMPs and Macros of HDPE and PE.

Table 33. Correlation Matrix- Effect of Treatment T3 on LMPs and Macros of LDPE, PP, PS, and PET.

	LDPE W0	PET W0	PP W0	PS W0	T3 LDPE Macro1 W20	T3 PET Macro1 W20	T3 PP Macro1 W20	T3 PS Macro1 W20	T3 PET LMP W20	T3 LDPE LMP W20	T3 PP LMP W20	T3 PS LMP W20
LDPE W0	1	0.04543	0.7941	0.19317	0.91722	0.06894	0.49504	0.06266	0.05098	0.66207	0.37956	0.09356
PET W0	0.04543	1	0.02913	0.27061	0.22373	0.97821	0.49208	0.5325	0.94827	0.47207	0.55079	0.58657
PP W0	0.7941	0.02913	1	0.18616	0.71603	0.02297	0.64197	0.08398	0.01643	0.59245	0.52532	0.1036
PS W0	0.19317	0.27061	0.18616	1	0.33666	0.29984	0.51939	0.85372	0.39811	0.44588	0.56048	0.74704
T3 LDPE Macro1 W20	0.91722	0.22373	0.71603	0.33666	1	0.26259	0.63303	0.29536	0.31319	0.77568	0.5935	0.37544
T3 PET Macro1 W20	0.06894	0.97821	0.02297	0.29984	0.26259	1	0.48528	0.54515	0.96326	0.46286	0.53875	0.60726
T3 PP Macro1 W20	0.49504	0.49208	0.64197	0.51939	0.63303	0.48528	1	0.71826	0.59702	0.85218	0.94535	0.76844
T3 PS Macro1 W20	0.06266	0.5325	0.08398	0.85372	0.29536	0.54515	0.71826	1	0.6863	0.60254	0.77368	0.95769
T3 PET LMP W20	0.05098	0.94827	0.01643	0.39811	0.31319	0.96326	0.59702	0.6863	1	0.54303	0.67255	0.76742
T3 LDPE LMP W20	0.66207	0.47207	0.59245	0.44588	0.77568	0.46286	0.85218	0.60254	0.54303	1	0.87558	0.62352
T3 PP LMP W20	0.37956	0.55079	0.52532	0.56048	0.5935	0.53875	0.94535	0.77368	0.67255	0.87558	1	0.82637
T3 PS LMP W20	0.09356	0.58657	0.1036	0.74704	0.37544	0.60726	0.76844	0.95769	0.76742	0.62352	0.82637	1

Table 34. Correlation Matrix- Effect of Treatment T2 on LMPs and Macros of HDPE and PE.

	HDPE W0	PE W0	T2 HDPE Macro1 W20	T2 PE Macro1 W20	T2 HDPE LMP W20	T2 PE LMP W20
HDPE W0	1	0.99772	0.91492	0.82108	0.6807	0.72678
PE W0	0.99772	1	0.90092	0.80787	0.65471	0.71422
T2 HDPE Macro1 W20	0.91492	0.90092	1	0.96868	0.91235	0.89419
T2 PE Macro1 W20	0.82108	0.80787	0.96868	1	0.94921	0.9419
T2 HDPE LMP W20	0.6807	0.65471	0.91235	0.94921	1	0.90403
T2 PE LMP W20	0.72678	0.71422	0.89419	0.9419	0.90403	1

PCA diagrams in **Figure** 49 (A and B) show cumulative percentage variations of 80.02%, and 97.87%, respectively, within the FTIR spectra of the six different plastic types through the principal components (PC1 and PC2). This means that these variance percentages were preserved when modeling the PCA loading plots with the first 2 principal components.

Once again, PCA analysis of HDPE and PE was performed by studying the effect of time on T2 since this treatment showed the most significant difference. On the other hand, T3 was chosen to perform PCA analysis on other types (LDPE, PP, PS, and PET) for the same reason. Findings show that LMP-PP has the most significant difference when compared with its reference with a correlation value of 0.52532, followed by LMP-LDPE, LMP- PS, and LMP-PET with correlation values of 0.66207, 0.74704, and 0.94827, respectively, as shown in **Table** 33. Thus, based on the PCA diagram in **Figure** 49 (A), LMP-PP can degrade faster than other types of plastics after

20 weeks of exposure to T3, followed by LMP-LDPE, LMP- PS, and LMP-PET. On the other hand, macroplastics showed a different behavior while exposed to the same treatment (T3), where PP showed the most significant difference while compared with its reference with a correlation value of 0.64197, followed by PS, LDPE, and PET with correlation values of 0.85372, 0.91722, and 0.97821, respectively as shown in **Table** 33. Therefore, Macro1-PP can degrade faster than other plastic types after 20 weeks of exposure to T3, followed by Macro1- PS, Macro1-LDPE, and Macro1-PET. This confirms that particle size can affect the degradation and fragmentation processes. The different degradation behavior of macroplastics and MPs while exposed to the same treatment (T3) may be explained by the different polymeric structures, additives, and colorants used in each plastic. In addition, some plastics were afloat, while other plastics sank to the bottom of the tank, this could restrict the amount of sunlight that could have potentially reached some plastics which sank to the bottom (e.g., PET). Moreover, smaller samples have the tendency to roll on the water surface. This continuous rotation of the small samples will prevent biofilm growth on the surface of the small pieces, while edge erosion seemed more likely to happen (Dimassi et al., 2022). Thus, these motion variations will undoubtedly affect the degradation and fragmentation of plastics. It must be mentioned that different plastics behave differently when exposed to temperature as mentioned in previous sections (DSC analysis). For instance, PET is one of the most common thermoplastics with a high melting point of 247 °C. The thermostability of PET explains why results showed the lowest degradation tendencies of both sizes when exposed to T3.

Moreover, results showed that LMP-HDPE has the most significant difference when compared to its reference with a correlation value of 0.6807, followed by LMP-PE with a correlation value of 0.71422, as shown in **Table** 34. Therefore, based on the

PCA diagram in **Figure** 43 (B), LMP-HDPE can degrade faster than LMP-PE. On the other hand, macroplastics showed a different behavior while exposed to the same treatment (T2), where PE showed the most significant difference while compared with its reference with a correlation value of 0.80787, followed by HDPE with a correlation value of 0.91492, as shown in **Table** 34. Hence, Macro-PE can degrade faster than Macro-HDPE after 20 weeks of exposure to T2. Once again, all these findings are in alignment with each other, and it confirms that particle size can and does affect the degradation and fragmentation processes, where the smaller the plastic pieces, the higher their degradation due to the relatively greater surface area compared to their volume. Furthermore, the different degradation behavior of macroplastics and MPs while exposed to the same treatment (T2) may be explained by the different polymeric structures, additives, and colorants used in each plastic. Both plastics (HDPE and PE) were flexible. However, PE was a transparent plastic which indicates that there is no colorant added. On the other hand, HDPE was a black garbage bag where colorants were added. Some of the compounds in plastics such as colorants/dyes and additives affect the degradation of plastics due to their ability to breakdown the polymer chemistry, leading to weakening the original characteristics. The colorant effect was evidently shown in the macroplastics investigations rather than in MPs. The reason behind that may be the slow degradation of PE in the natural environment due to its exclusive backbone chains of C-C single bonds which do not undergo hydrolysis easily as well as its resistance to photooxidative degradation.

CHAPTER 5: CONCLUSIONS AND FUTURE RECOMMENDATIONS-PERSPECTIVES

In order to address the degradation and fragmentation problem of macroplastics and MPs in the marine environment, a simple and reproducible method was used to examine the natural degradation of different plastic types and to pinpoint the complications caused by the presence of several additives (e.g., DBP, DEHP, BPA, BBP) embedded in plastics. Results confirmed that the degradation of plastics under marine conditions depends on several environmental conditions including oxygen availability, luminance, temperature, and plastic polymer's properties (e.g., MW, and additives presence). Weight loss% findings showed significant variations between the different types of plastics, the four treatments used within the same plastic-type, as well as the different size categories. In addition, SEM micrographs showed obvious variations in the morphologies of all different plastics, especially those exposed to outdoor conditions (T2 and T3). Moreover, FTIR results showed that samples were gradually altered chemically under outdoor conditions (T2 and T3) over time. All findings were in alignment with each other, where microplastics degraded faster than macroplastics. It was confirmed that the degradation and fragmentation of plastics differ based on size, and polymer type. Furthermore, HPDE and PE degraded faster under onshore conditions (T2), while other types showed higher degradation under marine conditions (T3). SW samples were characterised by using GC-MS to investigate the presence of four different plastic additives which are BBP, DBP, DEHP, and BPA. Leachability experiments showed that DBP, DEHP, and BPA were detected in the seawater samples while BBP was absent. It was found that wave abrasion promoted the leaching of DEHP and DBP while high temperatures and light intensities promoted the leaching of DEHP.

FTIR, SEM-EDX, weight loss, and degradation rate calculations were in line with PCA analysis, which showed that LMP-PP can degrade faster than other types of plastics after 20 weeks of exposure to T3, followed by LMP-LDPE, LMP- PS, and LMP-PET. On the other hand, macro-plastics exhibited different behavior while exposed to the same treatment (T3), where PP showed the most significant difference when compared to its reference followed by PS, LDPE, and PET. Therefore, Macro1-PP can degrade faster than other plastic types after 20 weeks of exposure to T3, followed by Macro1- PS, Macro1-LDPE, and Macro1-PET. This also confirms that particle size can affect the degradation and fragmentation processes.

While it is widely accepted that plastics can take extremely long to degrade. The onset process of degradation starts almost instantaneously, especially under extreme environmental conditions such as Qatar as was seen in the study. Not only does the degradation process start early, but in fact, as was observed, the degradation is quite significant even for a short period of time. The leachate of these chemical additives that were generated during the 5-month period for quite a small number of plastics means that the plastics in the ocean gyres in large quantities, probably generate a much higher quantity of these additives. While these concentrations may not cause an immediate risk considering the dilution due to the volume of the ocean, their persistent nature could mean that over time, due to biomagnification and bioaccumulation, they could eventually make their way up the food chain until it eventually reaches humans. As such, research needs to be conducted to find alternative substances which are less harmful and eco-friendly to replace the current chemical additives.

While estimating the degradation rates of plastics, as well as the occurrence of phthalates and bisphenols in the seawater environment, is highly important, very limited studies are investigating these crucial issues. As such, further studies are needed to investigate the degradation and fragmentation of other plastic types (e.g., PVC) and the leachability of their degradation by-products.

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APPENDIX A: ION CHROMATOGRAPHY (IC) ANALYSIS

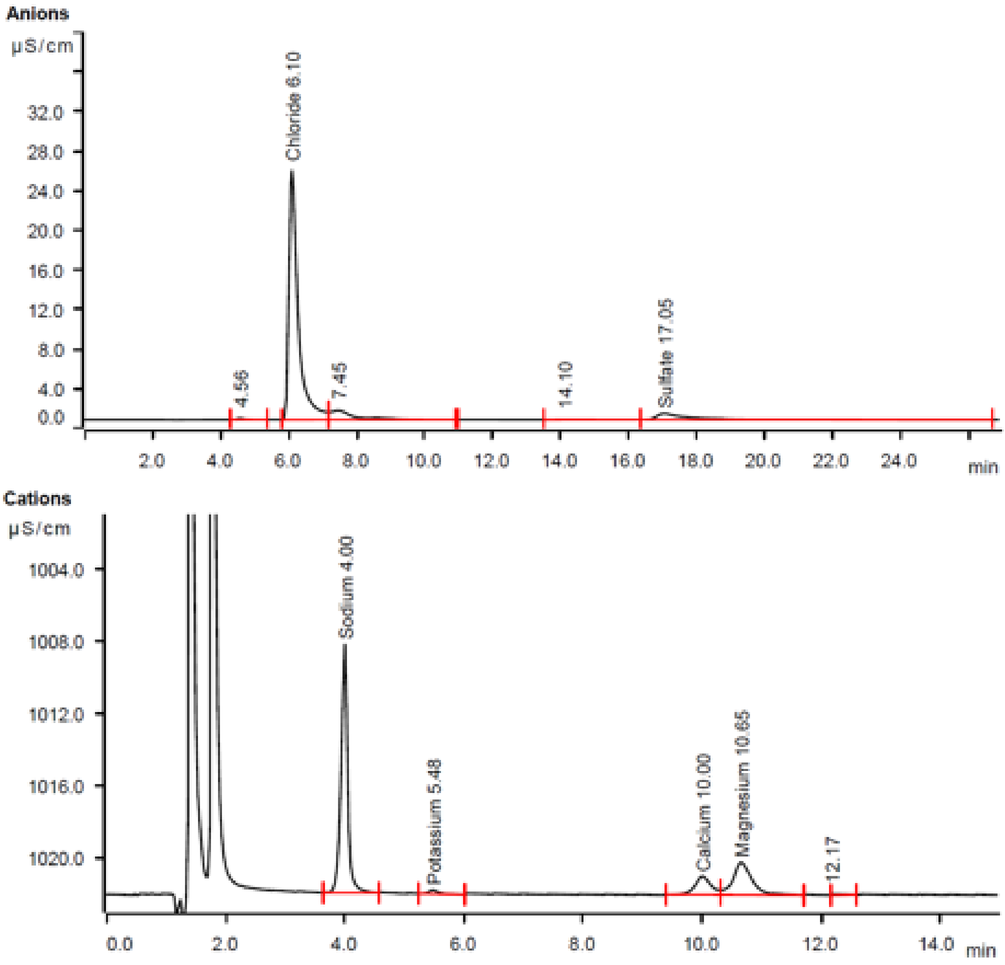

Figure 50. IC results for SW prior experiment

APPENDIX B: PRINCIPAL COMPONENT ANALYSIS (PCA)

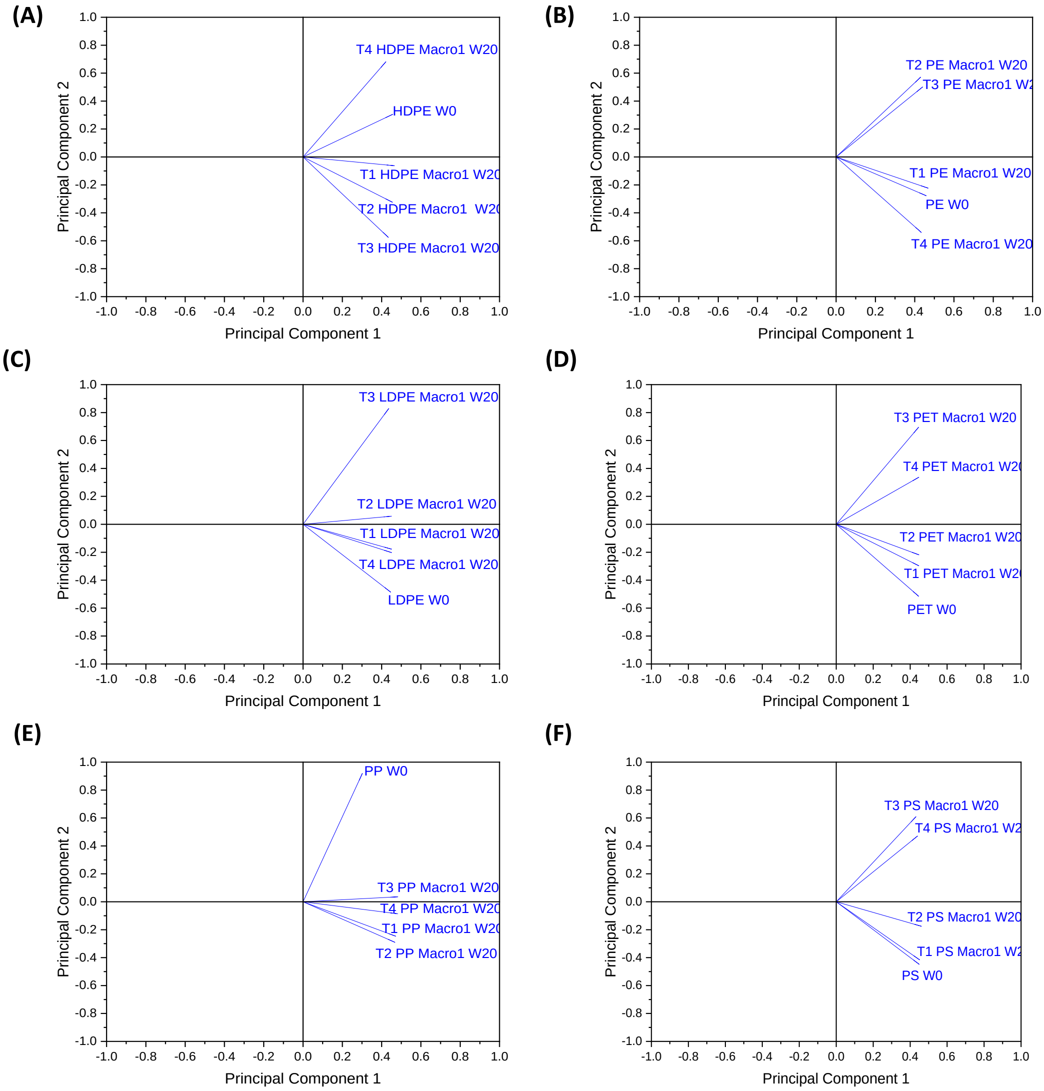

Figure 51. PCA: Effect of four treatments on different plastic types at a specific time (week 20/day 140): loading plots of (A) HDPE-Macro1, (B) PE-Macro1, (C) LDPE-Macro1, (D) PET-Macro1, (E) PP-Macro1, (F) PS-Macro1.