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Degradation assessment of high-density polyethylene (HDPE) debris after long exposure to marine conditions

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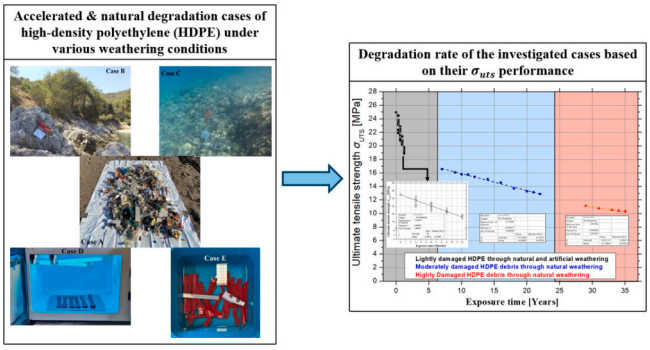
HIGHLIGHTS

- HDPE degradation was investigated in natural and accelerated weathering conditions.
- Correlation between natural and accelerated degradation methods was explored.
- FTIR and SEM revealed key chemical and microstructural changes during degradation.
- Tensile testing indicated a linear σ_{UTS} decrease over exposure time.
- A model was proposed for predicting σ_{UTS} for long-term HDPE degradation rates.

GRAPHICAL ABSTRACT



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ABSTRACT

The degradation of high-density polyethylene (HDPE) in marine environments was investigated under various weathering conditions. HDPE debris were collected from coastal areas near Korinthos, Greece which had been exposed to marine conditions for durations ranging from a few months to several decades; they were analysed alongside with laboratory-manufactured HDPE specimens subjected to controlled weathering exposure. Four (4) different cases were investigated, including exposure to different conditions, namely to (a) natural atmospheric and (b) sea weathering conditions, (c) accelerated ultraviolet (UV) radiation, and finally (d) submersion to artificial seawater for up to twelve (12) months. The degradation assessment was proposed based on performed tensile mechanical tests, while the chemical/microstructural changes were assessed through Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM). FTIR spectroscopy indicated the emergence of carbonyl groups, with peaks appearing between 1740 cm^{-1} and 1645 cm^{-1}, which are crucial indicators of photo-oxidative degradation. Key findings revealed that HDPE specimens experienced significant (8 %) ultimate tensile strength (σ_{UTS}) only after 3 months of atmospheric exposure, while this decrease can reach up to 60 % over the period of 35 years exposure. A strong correlation was observed between the σ_{UTS} decrease between

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the (a) natural environment and (b) accelerated UV weathering exposure. It is noticed that 1½ month of accelerated UV exposure corresponded to similar ultimate tensile strength decrease for 6 months of natural atmospheric degradation. A linear correlation is proposed to assess the long-term materials' tensile properties degradation in marine environments.

1. Introduction

Plastic debris pollution has emerged as one of the most pressing environmental issues of our time, particularly in marine and coastal environments, affecting biodiversity and habitat quality (Ladewig et al., 2024; Tekman et al., 2022). Wildlife can become entangled in larger plastic items, leading to injury, restricted movement, or death (Afonso and Fidelis, 2023). Additionally, many marine species mistake plastic particles for food, ingesting them, which can cause blockages in their digestive systems, malnutrition, or poisoning from the chemicals that leach from plastics (Ramon-Gomez et al., 2024). Microplastics can also accumulate in the food chain, affecting organisms at different trophic levels, from plankton to large predators (Malinowski et al., 2023; Saikumar et al., 2024). The ingestion and entanglement of plastic debris threaten endangered species, disrupt marine ecosystems, and reduce overall habitat quality. In 2022, global plastic production reached 400 million tonnes (Pathak et al., 2023), with single-use plastics making up to 40 % of this amount (Fletcher et al., 2023), contributing substantially to plastic waste and pollution.

Among the several hundred thousand tons of plastics that are discarded into the marine environment every year (Khoo et al., 2021), HDPE stands out due to its extensive use in applications such as packaging, containers, and piping, and its persistence in the environment (Ainali et al., 2021). In response to growing plastic pollution, several voluntary and regulatory initiatives have been implemented globally. The European Union's Single-Use Plastics (SUP) Directive [EU 2019/904] outlines specific measures to reduce the impact of certain plastic products on the environment, including bans on selected items and targets for waste reduction. The EU Circular Economy Action Plan, a key part of the European Green Deal, emphasizes reducing waste, increasing recycling, and transitioning toward a sustainable economy. It includes strategies to design waste out of the economy, thus significantly reducing plastic pollution (Syberg et al., 2021). Additionally, the United Nations' Sustainable Development Goals (SDGs), particularly SDG 12 (Responsible Consumption and Production) and SDG 14 (Life Below Water), align closely with these efforts (Arora and Mishra, 2023). These goals call for global action to manage plastic waste, protect marine biodiversity, and foster sustainable economic growth through responsible production practices. Voluntary initiatives such as The Global Plastics Pact, which brings together businesses, governments, and non-governmental organizations, further demonstrate the global commitment to reducing plastic waste and fostering a circular economy (Horton, 2022).

HDPE is one of the most used plastics (polymer) due to its increased physical properties, such as high chemical resistance, durability, and due to its low manufacturing cost. In fact, polyethylenes (high- and low-density) are the most used synthetic polymers and account for 65 % of the polymer waste in Europe (Sudhakar et al., 2007). Nevertheless, its extensive usage has led to significant environmental concerns, particularly in marine ecosystems. In the scope of valorising marine litter, it is extremely important to identify the nature and quantify the extent of degradation of such polymers under exposure to marine environment. When the HDPE is being illegally rejected into the marine environment (Usman et al., 2022), it is simultaneously subjected to several degradation processes (i.e., photo-oxidation, hydrolysis, etc.), resulting in potential ecological and human health risks. The polymers are considered to be resistant to degradation due to their chemical inertness, nevertheless their prolonged exposure to the environment, i.e. for several decades, has a profound impact on the mechanical properties of the materials (Chamas et al., 2020).

In marine environments, HDPE degradation occurs through a combination of physical, chemical, and biological processes that possibly interact with each other over the whole exposure time. Physical factors such as ultraviolet (UV) radiation, wave action, and mechanical stress cause the fragmentation of HDPE into smaller particles, known as microplastics (Barnes et al., 2009). These microplastics then undergo further chemical changes due to exposure to UV light, a process called photo-oxidation, where UV radiation breaks down polymer bonds (Sivan, 2011). Once initiated, the degradation continues via thermo-oxidative reactions, which are temperature-dependent and can persist even without further UV exposure. Additionally, mechanical forces from waves and biological activity, such as microbial colonization, contribute to further breaking down the material and altering its structural and chemical properties (Singh and Sharma, 2008). These combined processes drive the gradual degradation of HDPE in marine environments, influencing its persistence and environmental impact.

Chemical degradation of HDPE in marine conditions is primarily driven by factors such as temperature, salinity, and PH. Exposure to seawater and its constituents, including ions and reactive oxygen species, can lead to the hydrolytic cleavage of polymer chains, causing a reduction in molecular weight and mechanical strength of HDPE (Mitroka et al., 2013). Moreover, marine organisms, including bacteria, fungi, and algae, release extracellular enzymes capable of degrading HDPE by initiating the breakdown of its polymer structure.

The biological degradation of HDPE involves the colonization of microorganisms on the plastic surface, leading to the formation of biofilms (Di Napoli et al., 2023). These biofilms facilitate the adhesion and growth of organisms, resulting in the production of enzymes and other metabolites that contribute to HDPE degradation. Furthermore, some marine organisms have been found to possess the ability to metabolize HDPE as a carbon source, further accelerating its degradation process.

To study further the degradation mechanisms occurring on HDPE in a marine environment, the research of (Ronkay et al., 2021) developed an artificial accelerated weathering procedure for HDPE bottle caps, simulating the marine environment. The procedure consisted of 2520 h of weathering cycles, moving the sample between a salt spray and a Xenon-chamber. It was indicated that this amount of weathering time corresponds to approximately 3 to 4 years on the sea surface. Through Scanning Electron Microscopy (SEM) it was observed that HDPE caps of bottles were damaged but not enough render it inoperable or cracked.

Furthermore, the study of Cai et al. (2018) investigated HDPE properties after exposure to UV A 340 lamp and submerged to artificial sea water for 3 months, using Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy and SEM analysis. The analysis revealed several cracks and flakes, which are all common degradation patterns during the chemical weathering of plastics. FTIR scan showed only one set of new absorption peaks, which appeared roughly at 1712 cm^{-1}, indicating that carbonyl groups (C═O, ~1700 cm^{-1}) were developed. Since the experiment was conducted in three different environments, it was clear that oxygen's presence and UV irradiation played a vital role in the initiation of the photo-oxidative degradation of polymers.

In addition, to investigate further on the mechanical performance of degraded HDPE, the study by (Koriem et al., 2021) explored the effects of artificial weathering and UV stabilizers on HDPE, demonstrating that non-stabilized HDPE exhibited a significant reduction in mechanical performance after only 300 h of exposure, with a loss of nearly 98 % of toughness. In contrast, the introduction of UV stabilizers such as hindered amine light stabilizers prolonged the mechanical stability of HDPE

up to 1300 h of exposure, with a 40 to 50 % reduction in tensile strength by the end of the test period. (Stapleton et al., 2023) investigated the effect of UV exposure on HDPE and for different water matrices, including saline conditions. They found out that UV exposure led to significant surface cracking and noticed a 30 % decrease in ultimate tensile strength after 28 days of exposure to UV in saltwater, with severe surface deterioration observed under SEM. Additionally, a long-term study (Kim et al., 2022) extended these investigations by conducting a four (4) years outdoor weathering study, finding out that HDPE showed a reduction in fracture strain from 897 % to 175 %, with a 355 MJ/m^2 UV dose only to be required to achieve a 50 % reduction in fracture strain. This long-term outdoor exposure study aligned well with laboratory-based accelerated weathering results, confirming that UV exposure and surface degradation are key factors in the mechanical deterioration of HDPE. Together, these studies consistently point out the significant mechanical degradation of HDPE under prolonged UV exposure, though stabilizers can delay the onset of damage.

Finally, in a previous study of the authors (Lourmpas et al., 2023), it was shown that the mechanical properties of HDPE specimens following exposure to atmospheric and sea weathering conditions might alter with varying exposure time. Utilizing ultraviolet spectrophotometry and tensile testing methods, the investigation concluded on the weathering effects on HDPE over an eight-month (8) period. Key findings revealed a notable decline in the ultimate tensile strength of HDPE, with atmospheric exposure leading to an approximate 10 % reduction, while marine exposure resulted in a 6 % decrease. Furthermore, a significant reduction in the elastic modulus (Young's modulus) was observed, registering a 23 % and 21 % decrease for atmospheric and marine exposure, respectively. The comprehensive analysis extended to other mechanical properties such as strain at maximum stress and yield stress offset, underscoring the pervasive impact of environmental weathering on HDPE's structural integrity. Leveraging these empirical insights, a linear decrease rate equation was proposed for predicting the residual mechanical properties of HDPE post-exposure. The findings of this investigation may provide a basis upon which the present study can expand and experiment with the degradation rate of HDPE polymers on a larger scale.

Overall, HDPE degradation in marine environments is a complex process driven by multiple factors, including UV radiation, salinity, and mechanical stresses induced. The present investigation will attempt to correlate the accelerated weathering tests with the real-world environmental tests regarding the mechanical properties' degradation, by proposing novel correlations to predict the long-term degradation behaviour. Additionally, the present investigation will provide key and novel insights into the mechanical and chemical HDPE degradation patterns by bridging laboratory-based accelerated degradation methods with natural environmental exposure.

2. Materials and methods

2.1. Experimental plan

Fig. 1 shows the main cases of the present investigation, i.e., controllable exposure to natural conditions (Cases B and C for natural atmospheric and natural sea conditions, respectively), accelerated ultraviolet (UV) degradation (Case D) and plastic debris degradation through artificial seawater (Case E) exposure. After the respective treatments and processes, all investigated cases converge at the final steps, where they are subject to a final analysis to characterize the structural integrity of the specimens by investigating their mechanical, chemical and surfaces properties, and finally the physical correlation of the degradation rate between natural and accelerated exposure methods. The specific cases for investigation were selected to represent a wide range of real-world environmental conditions that HDPE is exposed to, ensuring a comprehensive understanding for the degradation mechanisms. Natural atmospheric and sea weathering conditions (Cases B and C, respectively) were chosen to reflect typical marine conditions, where HDPE waste is often retrieved from coastal areas. These cases simulate prolonged exposure to UV radiation, fluctuating temperatures, and mechanical stress from wave action. To complement these, accelerated UV degradation (Case D) was employed to replicate the effects of long-term sun exposure only in a shorter timeframe, allowing for predictions of HDPE performance under natural conditions. Finally, artificial seawater exposure (Case E) was implemented to isolate the impact of seawater salinity and chemical composition on HDPE degradation, without the confounding degradation effects from UV radiation. The selected combination of natural and controlled conditions allows the investigation of HDPE degradation from both, short-term and long-term perspective, simulating various coastal environments of HDPE debris.

2.2. Case A: collection and sorting of plastic debris from coastal areas

To gather sufficient quantities of marine plastic waste and debris, the assistance of various contributors was necessary, including voluntary efforts from ordinary citizens and the involvement of Non-Governmental Organizations (NGOs). "OZON" NGO contributed to this cause, since the members of this organization conducts regularly (almost every month) relevant activities along coastal areas, focusing on the coastline of Korinthos, Greece. In collaboration with members of our laboratory team, the desired type of marine plastic waste was collected (Fig. 2).

Special emphasis was given to the identification of HDPE debris, as according to numerous studies, they belong to or are among the most commonly found types of plastics in oceans and coastlines (O'Connor et al., 2016; Romera-Castillo et al., 2018). Knowing the desired type of plastic made the sorting process easier, as plastics bearing identification

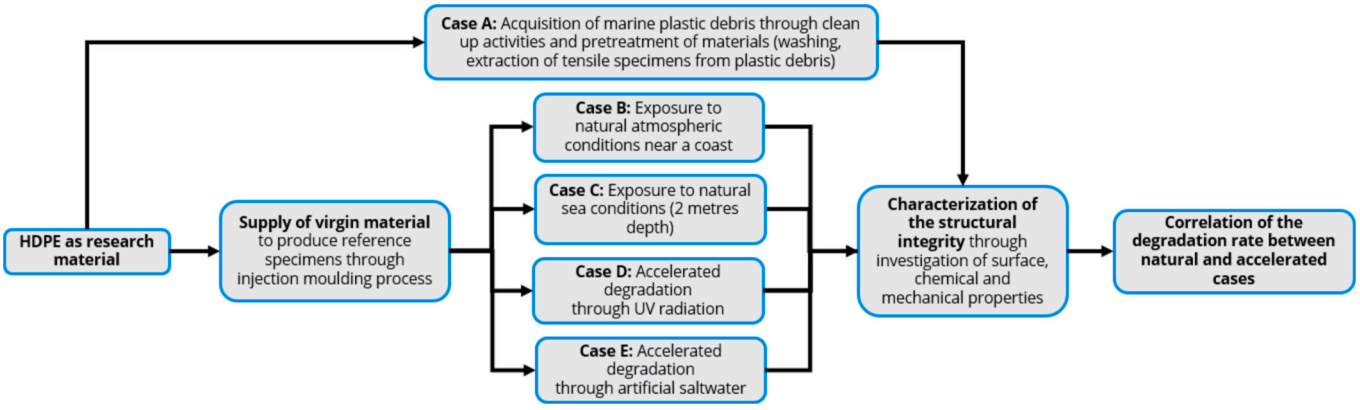


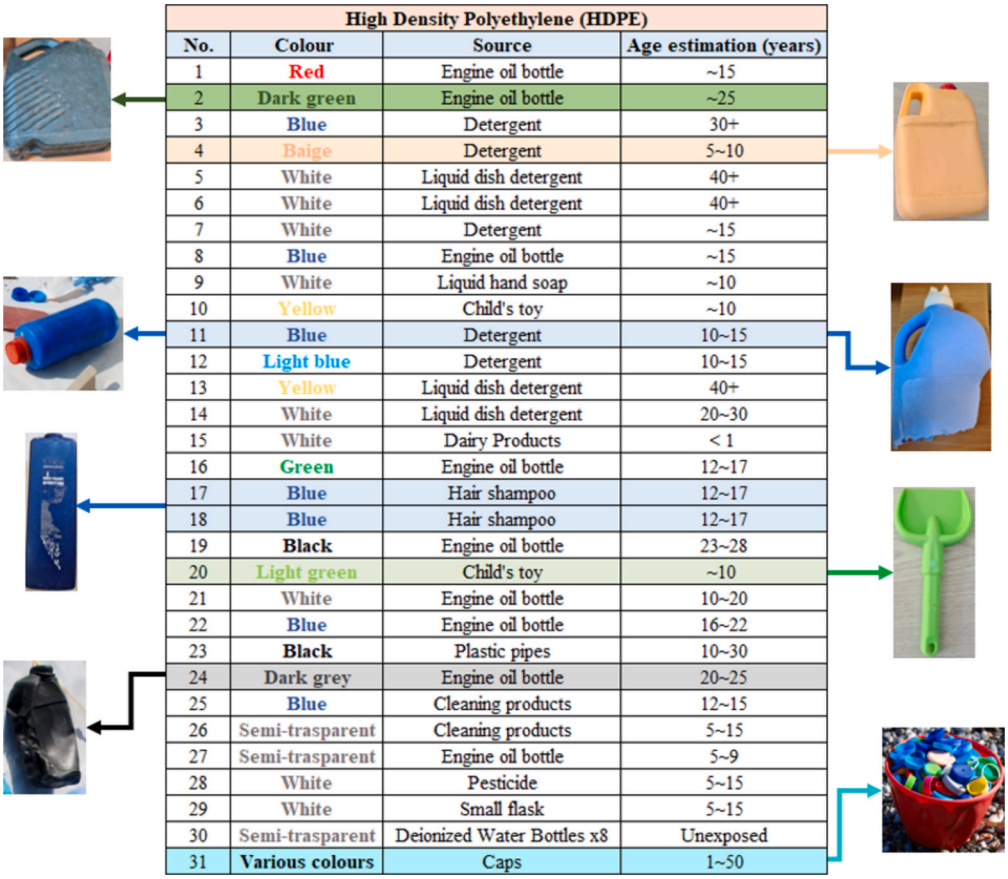
Fig. 1. Experimental procedure flow chart of the present investigation.

Fig. 2. Marine plastic waste collection process on the coast of Korinthos.

marks (Fig. 2) were chosen. Finally, the coast-collected HDPE debris were listed according to their colour, origin source (e.g., soap containers, pots, pallets, etc.), and an estimated weathering exposure age based on their manufacturing date combined with their external structural integrity state at the collection site (Fig. 3). Following, tensile specimens were cut from the plastic waste (debris) material according to the specifications for geometrical dimensions of American Society for Testing Materials (ASTM D638) standard, as shown in Fig. 4.

2.3. Mould design and raw materials

For the production of reference HDPE material, the construction of a mould was deemed necessary. Steel mould was preferred as the construction material due to the specific numbers of specimens that were going to be produced. The parametric design system Creo-Parametric was used for the mould design, utilizing the Part and Assembly platform, as shown in Fig. 5. For the specifications of the specimen produced by the mould, geometric dimensions for tensile test specimens were selected according to ASTM D638 (ASTM International, 2017). Once the mould was designed in the program, the Computer-Aided Design (CAD) file was transferred to a Computer Numerical Control (CNC) operating computer, where the movements and commands followed by the CNC machine were programmed for the mould creation. These commands determined the cutting, milling, and the method of material removal from the original volume of the mould material. Finally, to forge reference samples from virgin material, 50 kg of virgin HDPE were obtained. Through the injection moulding process conducted in industrial facilities, which utilized the new constructed mould, several dozen tensile test specimens were produced according to ASTM D638 (ASTM International, 2017).



High Density Polyethylene (HDPE)			
No.	Colour	Source	Age estimation (years)
1	Red	Engine oil bottle	~15
2	Dark green	Engine oil bottle	~25
3	Blue	Detergent	30+
4	Baige	Detergent	5~10
5	White	Liquid dish detergent	40+
6	White	Liquid dish detergent	40+
7	White	Detergent	~15
8	Blue	Engine oil bottle	~15
9	White	Liquid hand soap	~10
10	Yellow	Child's toy	~10
11	Blue	Detergent	10~15
12	Light blue	Detergent	10~15
13	Yellow	Liquid dish detergent	40+
14	White	Liquid dish detergent	20~30
15	White	Dairy Products	< 1
16	Green	Engine oil bottle	12~17
17	Blue	Hair shampoo	12~17
18	Blue	Hair shampoo	12~17
19	Black	Engine oil bottle	23~28
20	Light green	Child's toy	~10
21	White	Engine oil bottle	10~20
22	Blue	Engine oil bottle	16~22
23	Black	Plastic pipes	10~30
24	Dark grey	Engine oil bottle	20~25
25	Blue	Cleaning products	12~15
26	Semi-trasparent	Cleaning products	5~15
27	Semi-trasparent	Engine oil bottle	5~9
28	White	Pesticide	5~15
29	White	Small flask	5~15
30	Semi-trasparent	Deionized Water Bottles x8	Unexposed
31	Various colours	Caps	1~50

Fig. 3. Comprehensive inventory of all HDPE debris collected, categorized by colour, source (e.g., soap containers, industrial pallets etc.), an initial estimation of age based on weathering conditions, accompanied by illustrative examples of the specific HDPE debris items referenced in the inventory.

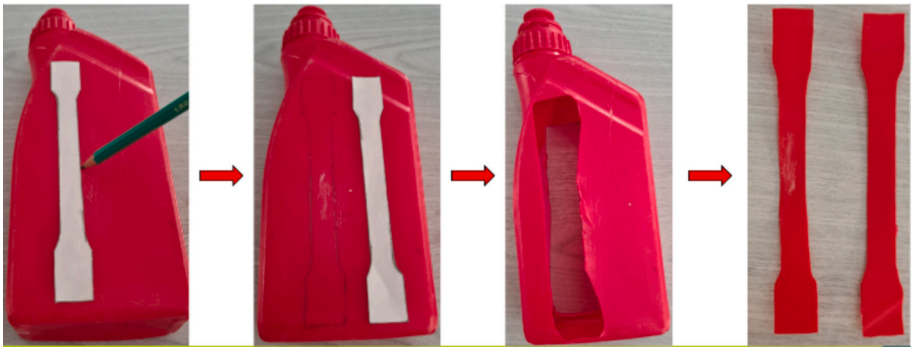


Fig. 4. Method of cutting out tensile test specimens from plastic waste.

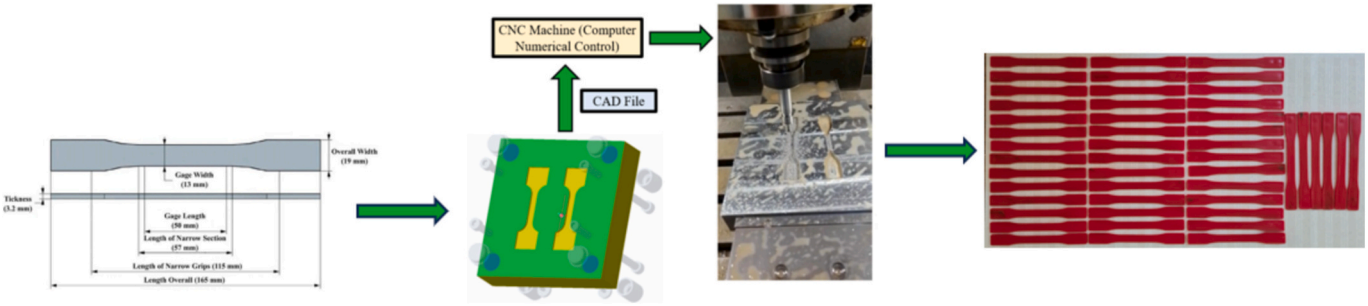


Fig. 5. Flow diagram, depicting how the mould design (based on geometric dimensions according to ASTM D638) was transferred as information to the CNC, which executed the commands for processing the mould and ultimately the tensile specimens were produced utilizing virgin HDPE.

2.4. Natural, artificial, and accelerated weathering cases

Weathering techniques are essential to understand the degradation processes of high-density polyethylene (HDPE) when exposed to various environmental conditions. The present article investigates four (4) different distinct weathering methodologies applied to HDPE specimens, highlighting their exposure to natural atmospheric and sea conditions, accelerated degradation through UV radiation, and controlled artificial saltwater exposure. Each technique provides different insights into the polymer's resilience and degradation mechanisms, contributing to the broader understanding of material performance in different environments.

Firstly, to investigate the effects of coastal conditions on HDPE, seventy-two (72) red-coloured specimens were exposed to a remote

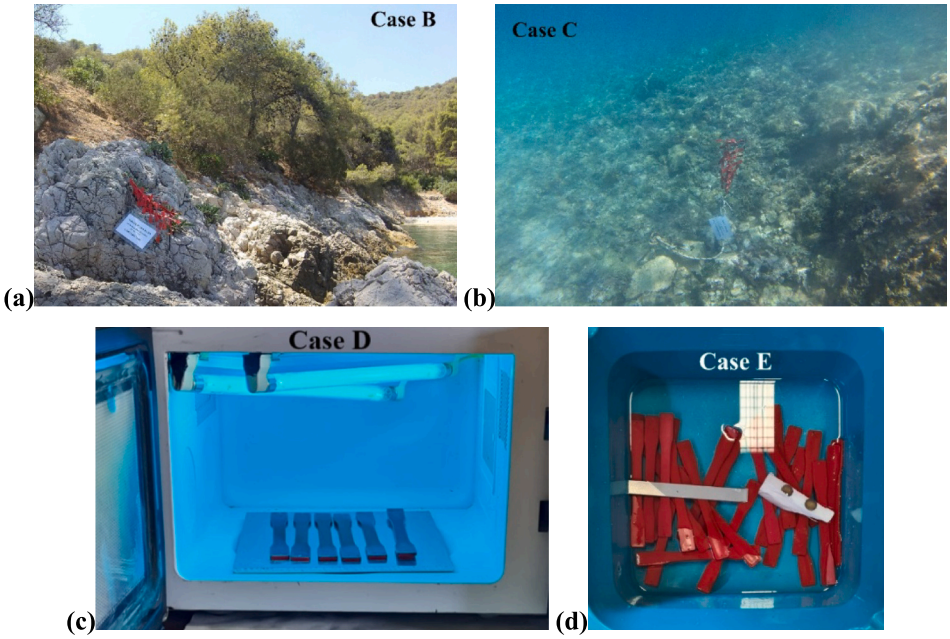


Fig. 6. Image showing the positioning of the HDPE specimens exposed to (a) Case B - natural atmospheric conditions near a coast, (b) Case C - natural marine conditions, submerged into 2 m depth, (c) Case C - accelerated degradation through two UVA 340 nm lamps adjusted on homemade UV chamber and, (d) Case D - submerged into a bucket filled with artificial seawater, covered with UV protection.

coastal area of Korinthos (Fig. 6a and b) for twelve (12) months, from mid-May to late-April of the next year. The specimens were divided into two groups. The first group was subjected to atmospheric conditions (Case B), while the second group was submerged to a depth of 2 m, experiencing the sea's wave action (Case C). Specimens were collected at intervals of 3, 6, 9, and 12 months, and their properties were analysed to determine the degradation rate of HDPE in these conditions.

The goal of the accelerated degradation process through UV chamber (Case D), is to examine the degradation of HDPE, when exposed UV radiation using accelerated weathering techniques for at least 2.5 months. At least 25 specimens were placed overall in a homemade chamber, where two UVA 340 nm lamps were adjusted, as depicted in Fig. 6c. To ensure that all specimens will receive similar UV treatment in the same positioning, several specimens were placed later. The weathering period was divided into 15, 30, 45, 60 and 75 days from which test specimens were collected and the photo-oxidation effects on the mechanical properties of the specimens were examined through tensile tests to determine the degradation rate of this polymer type during the whole process.

To explore the effects of saltwater exposure on the HDPE degradation, a controlled laboratory experiment was designed adhering strictly to the specifications outlined in ASTM D1141 (ASTM International, 2021) for simulating seawater exposure condition (Case E). This solution was intended to mimic the ionic composition of natural seawater, providing a consistent and controlled environment for the experiments, without the influence of UV radiation. A total of twenty-four (24) HDPE specimens were submerged in a large, covered bucket filled with the prepared artificial seawater and a few addition weights, to prevent the specimens from rising to the surface (Fig. 6d). The bucket was specifically designed to shield the specimens from any UV radiation, ensuring that any observed material changes were solely due to saltwater exposure. The specimens were maintained in this setup for a duration of twelve (12) months to assess the cumulative effects of the saltwater environment. The experimental timeline was segmented into four (4) different intervals: specimens were collected at 3, 6, 9, and 12 months, respectively. At each interval, specimens were removed from the saltwater environment, cleaned and subsequently subjected to mechanical testing. The aim of examining and comparing these diverse weathering techniques, was to effectively characterize the degradation behaviours of HDPE under various environmental conditions, which will provide valuable insights into the material's durability and performance.

2.5. Fourier transform infrared spectroscopy

Multiple coastal plastic debris were analysed using FTIR spectroscopy (Shimadzu QATR-10) equipped with an attenuated total reflectance (ATR) diamond crystal attachment, in order to be compared with the reference (unexposed) specimens. Furthermore, three (3) weathered HDPE specimens from each four (4) different weathering times (3–6–9–12 months) were also selected and analysed by FTIR spectroscopy. Ranges of the spectra were set from 4000 to 400 cm^{-1}, and the collection time was 16 s for each measurement. Two different points of each sample were examined. Among the emerged spectra, the most representative resulting spectra were selected and compared with their reference spectra without post-processing or transformation after each experimental cycle. The techniques employed for obtaining infrared spectra for qualitative analysis were according to ASTM E1252 (ASTM International, 2021).

2.6. Microscopy analysis

SEM analysis of HDPE samples involved coating the specimens with a thin layer of gold using the Q150T ES coater. The applied current was 20 mA while the duration of 200 s sputtering, resulted in a film of ~7 nm in thickness. This step was essential to enhance the conductivity of the polymer samples, which are inherently non-conductive, thereby preventing charging under the electron beam. The SEM used for this analysis was the JSM-6390LV by JEOL, known for its high-resolution imaging capabilities and versatility in low vacuum conditions, while the methods utilized for its operation, were according to ASTM E2809 (ASTM International, 2022). The SEM provided detailed surface morphology of the HDPE samples, revealing microstructural features and any surface defects or impurities with exceptional clarity.

2.7. Mechanical tests

Tensile testing is a common method used to evaluate the mechanical properties of plastic materials in order to prepare the manufactured reference specimens, 1000 grit mesh sandpaper was used to polish the side surfaces of the specimens according to ASTM D638 specification (ASTM International, 2017). Before the test samples were mounted onto the tensile testing machine, their geometrical dimensions were verified to ensure the reliability of the experiment.

The tensile tests were conducted using the VTS tensile testing machine equipped with a 10 kN load cell. The crosshead speed of the testing machine was set at 8 mm/min for HDPE, in accordance with ASTM D638 recommendations (ASTM International, 2017). Additionally, an extensometer Epsilon (model 3542) with an initial gauge length of 50 mm ± 25 mm maximum extension was attached to the tensile specimen. Throughout all the tensile tests, a data logger was used to store the load and displacement values onto a computer. As a comparative measure, reference specimens were also utilized, to examine any potential performance deterioration on the mechanical properties of the debris and the recycled specimens. The mechanical force, crosshead displacement and the extension of the gauge length of the specimen was recorded during the mechanical tests and the modulus of elasticity (E), and the ultimate tensile strength (σ_{UTS}) were post-calculated per different sample.

3. Results

3.1. Virgin HDPE material

This section contains the available results performed on the virgin HDPE specimens that were produced for the needs of the present investigation and represents the baseline of the present investigation. To verify the reproducibility of the results, at least twenty (20) reference HDPE specimens were mechanically tested, from which the most representative results, closest to the average value of the examined mechanical properties, were used in Fig. 7. The mean σ_{UTS} obtained from all the reference HDPE specimens was 25 MPa with a standard deviation of approximate 0.5 MPa. In addition, the mean Young's modulus value obtained from these specimens was 641 MPa with a standard deviation of 63 MPa.

3.2. Case A: classification of plastic debris

For the classification of the collected plastic debris, an initial separation was conducted through visual inspection for any apparent damages, correlated with the indicated manufacturing date (Fig. 8). This action assisted in keeping a record of all collected plastic waste and the initial estimation of their degradation time.

Since not all HDPE debris were suitable in size or condition for tensile testing, only a few dozen specimens were examined to enhance the reliability of the results. The selection of the plastic debris specimens was based on factors such as the condition and thickness of the debris specimen, as in some cases, these criteria affected the results in an undesirable manner. Consequently, ten (10) HDPE debris specimens were selected to be further examined.

HDPE is characterized by its linear molecular structure, featuring significantly fewer branching than LDPE (Zhang et al., 2024). This structural difference leads to variations in density between HDPE and

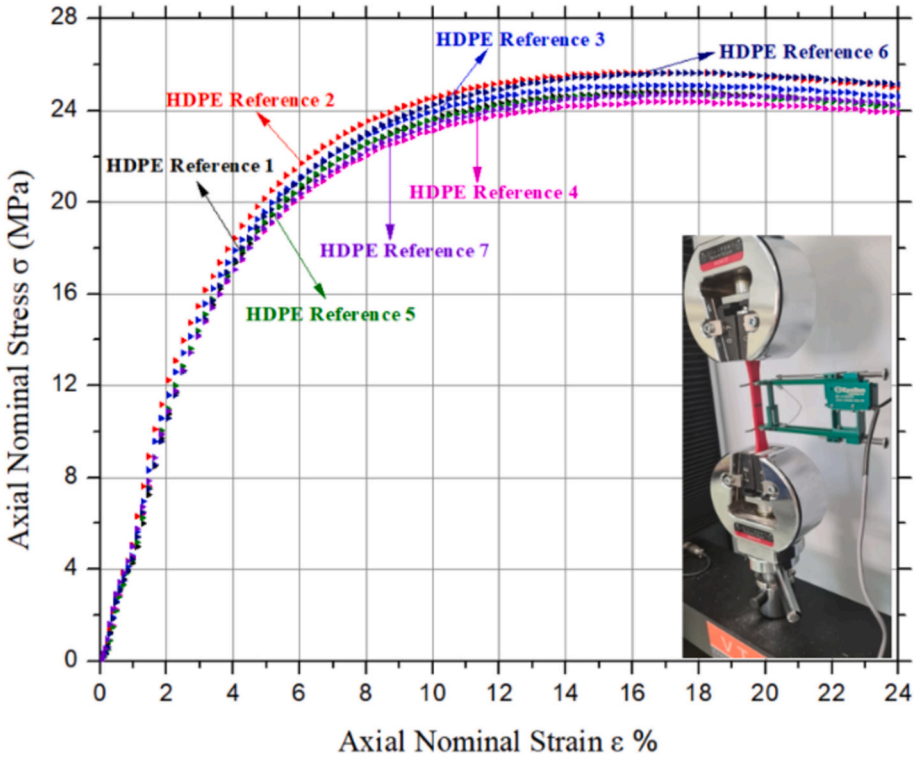


Fig. 7. Typical tensile stress-strain curves of HDPE reference specimens (no exposure) and the representative placing of the specimen on the grips of the VTS tensile testing machine equipped with a 10 kN load cell, along with the attached extensometer.

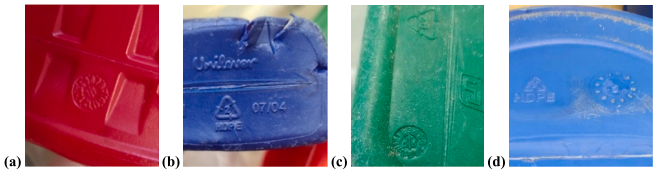


Fig. 8. Representative four (4) examples of coastal plastic debris showing their exact manufacturing date more than 20 years ago.

LDPE, with HDPE densities lying between 0.94 and 0.97 g/cm^3 and LDPE densities ranging from 0.90 to 0.94 g/cm^3 (Fernández-González et al., 2021). The lower density of HDPE facilitates its distinction from marine debris through flotation methods using NaCl. Additionally, unique patterns in its FTIR spectra make this type of plastic readily distinguishable.

In Fig. 9, the IR spectra of unexposed HDPE specimen, is compared with HDPE debris collected and with samples that were exposed for 3, 9 and 12 months. The absorption bands observed from 3000 cm^{-1} to 2800 cm^{-1} correspond to the stretching vibrations of O—H, while the distinct, sharper peaks located at 1470 cm^{-1} and 728 cm^{-1} are identified with the stretching of C═O and the vibrations of C—H, respectively (Singh et al., 2020). These peaks are characteristic absorption bands for this specific type of polymer and are related to the original bonds in the HDPE backbone (Bonifazi et al., 2018).

Nevertheless, new peaks can be distinguished in the absorption bands at 1740 to 1645 cm^{-1}and 1024 cm^{-1}, which appeared only to the samples subjected to natural weathering conditions (UV and seawater exposure) and broaden the longer the weathering conditions take place. Ketones, carboxylic acids, and carbon-carbon double bonds are the three major functional groups that appear during PE photo-degradation, being the formation of carbonyl and vinyl groups a direct indication of main chain scission (Nechifor, 2016). Starting with the peak at 1024 cm^{-1}, it is indicative of C—O oxygen group formations (Silverstein et al., 2005).

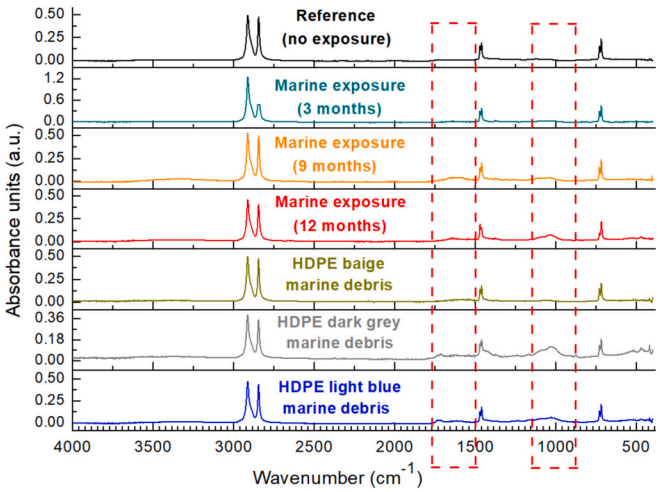


Fig. 9. FTIR spectra of three types of HDPE samples, virgin (unexposed), controlled marine exposure for specific UV irradiation times (i.e., 3 months, 10 months, and 12 months) and HDPE marine debris.

The pronounced oxygen presence on the surface, could be the result of various factors. Air consists of roughly 20 % oxygen, equating to 209.4 mg/L (Ghanadi and Padhye, 2024). In contrast, surface water's dissolved oxygen content ranges between 5 and 11.5 mg-O2/L (Ghanadi and Padhye, 2024). For materials immersed in seawater, oxygen can be introduced through dissolved oxygen along with processes like oxygen diffusion, oxidation, and microbial degradation. Specifically, microbial action can trigger chemical transformations within the polymer. Moreover, prolonged interaction with seawater and the physical agitation from sediment can make it more prone to oxidation.

A lower intensity peak at 1645 cm^{-1}, which is indicative of vinyl groups (Silverstein et al., 2005), further evidence of enhanced

degradation. Peaks occurring in the range of 1700 to 1740 cm^{-1} are associated with the emergence of carbonyl groups, a crucial indicator for assessing the photo-oxidative degradation of plastics (Grause et al., 2020). This emphasis is largely due to the greater stability of carbonyl groups compared to other oxygen-containing functional groups.

According to our findings, it can be summed up that in outdoor environments with access to air, HDPE predominantly undergoes degradation via photo-oxidative processes (photo-degradation in an oxygen-rich setting). This degradation begins as UV light breaks the C—H bonds in the polymer's structure, leading to the creation of free radicals (Yousif and Haddad, 2013). Factors like structural anomalies, impurities, added substances, and the by-products of weathering, including carbonyl and hydroperoxide groups, ketones, and various unsaturated C═C bonds (typically, a vinyl group in HDPE), foster the formation of areas prone to such degradation. The process of photo-oxidative degradation often starts with the rapid production of hydroperoxides, followed by the gradual accumulation of carbonyl groups over longer periods (Rabek, 2012). The escalation of carbonyl group presence throughout the photo-degradation timeline is indicative of the extent of chain scissions within the HDPE framework (Rabek, 2012). As the formation of carbonyl products, detectable by IR peaks ranging from 1650 to 1850 cm^{-1} increases, there is a noticeable decrease in the intensity of the hydroperoxide C—O bands, which have IR peaks between 1000 and 1100 cm^{-1} (Celina et al., 2021). The findings of the FTIR analyses in the present investigation, also comes in agreement with the observations performed by Ghanadi and Padhye (2024).

The SEM analysis provided detailed insights into the surface morphology of HDPE specimens subjected to various weathering

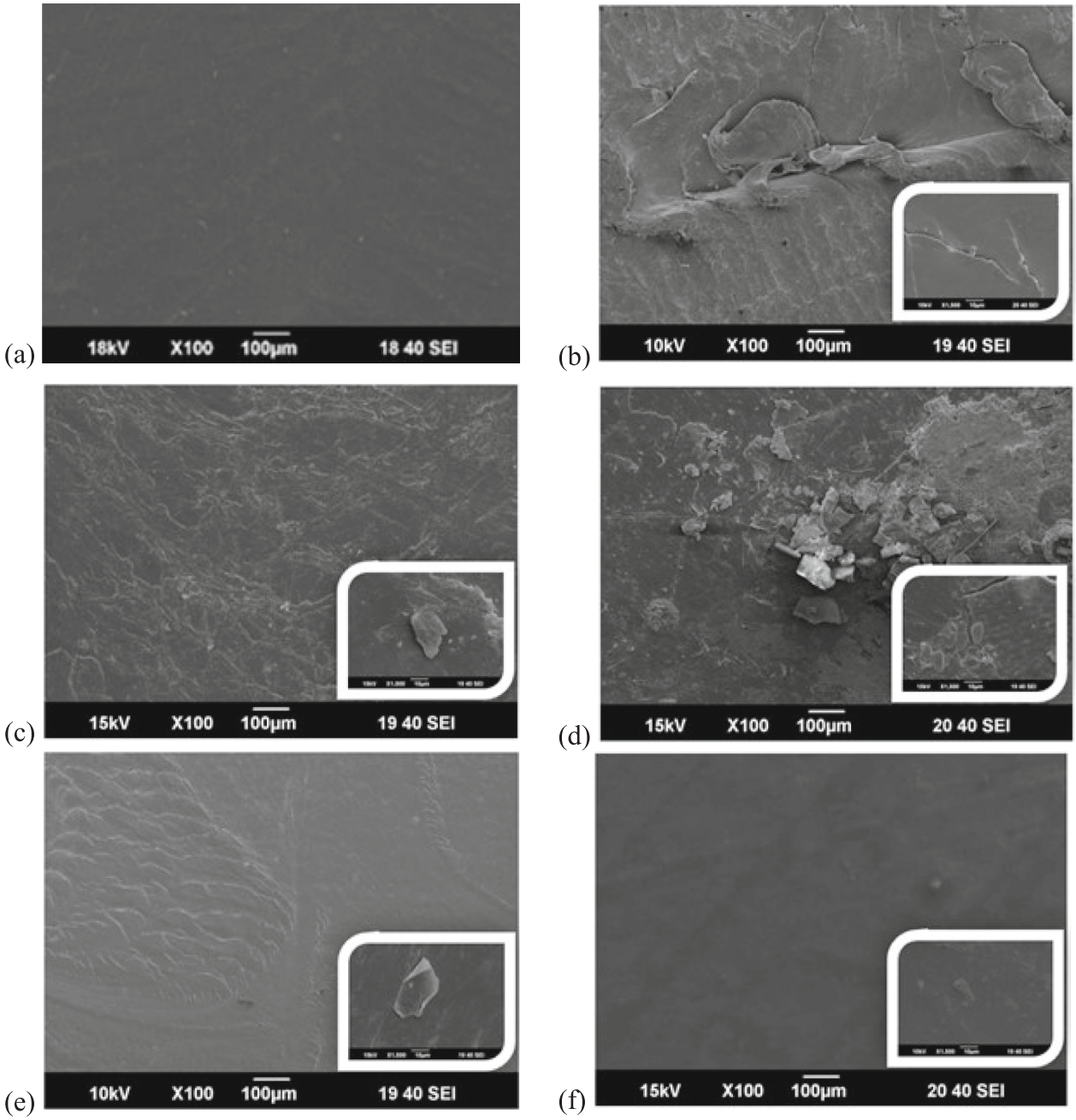


Fig. 10. Scanning electron microscopy images of the following samples: (a) reference unexposed sample, (b) HDPE debris after almost four (4) decades of exposure to coastal conditions, (c) sample exposed to natural atmospheric weathering for 12 months, (d) sample exposed to natural sea weathering for 12 months, (e) sample exposed to accelerated UV degradation for 2.5 months and (f) sample exposed to submersion to artificial seawater for 12 months.

conditions and HDPE debris collected from marine environments. The reference (unexposed) HDPE specimens exhibited smooth and homogeneous surfaces (Fig. 10a), indicating the pristine condition of the material before exposure to any weathering processes. In contrast, the HDPE debris (Fig. 10b) collected from coastal areas, which had been exposed to marine conditions for decades, demonstrated significantly rough and uneven surfaces. The long-term exposure led to pronounced surface deterioration, characterized by extensive flaking, cracks, holes and fractures. These morphological changes are indicative of severe degradation processes, including photo-degradation, hydrolytic degradation, and mechanical abrasion from wave action (Shirvanimoghaddam et al., 2024).

From the data collected after the tensile mechanical tests, values of the ultimate tensile strength σ_{UTS} and Young's modulus E were calculated per each specimen. Typical axial nominal stress – strain curves of different coastal plastic debris can be found in Fig. 11, where the HDPE debris were individually classified into three (3) different categories regarding the decrease of the maximum stress value of the respective curve.

The effects of wear/damage are easily distinguishable, especially for plastic debris that have been exposed to the marine environment for an extensive period of time. The initiation of photooxidation in HDPE debris is attributed to the extraction of hydrogen atoms from free radicals, which emerge from the breakdown of chromophoric impurities, including the hydroperoxides generated during this process (Ibrahim, 2024). As can be seen in Fig. 11, the categorization of HDPE debris concluded into three (3) different damage groups. This separation was arbitrary, and the criterion was the ultimate tensile strength σ_{UTS} and Young's modulus value of the degraded plastic debris. Consequently, the σ_{UTS} and Young's modulus values that were relatively similar were grouped, resulting in light, moderate and high damage categories. Nevertheless, Young's modulus values barely deteriorate between the moderate and the highly damaged groups, while σ_{UTS} is continuously decreasing over exposure time.

To understand this phenomenon, first it should be noted that Young's modulus is a measure of the stiffness of a solid material and defines the relationship between stress (force per unit area) and strain (proportional deformation) in the elastic (reversible) deformation region (Hertzberg et al., 2020). The relatively constant value of Young's modulus, even with degradation, suggests that the stiffness of HDPE is preserved, despite the changes observed in tensile strength and ductility. This outcome may imply that the mechanisms of degradation are predominantly affecting other mechanical properties, like mechanical strength and tensile ductility, rather than mechanical stiffness. Specifically, degradation processes such as chain scission, often driven by UV radiation, primarily weaken the material's ultimate tensile strength by reducing molecular weight, without significantly impacting the material's ability to resist deformation in the elastic region (Allen and Edge, 1992).

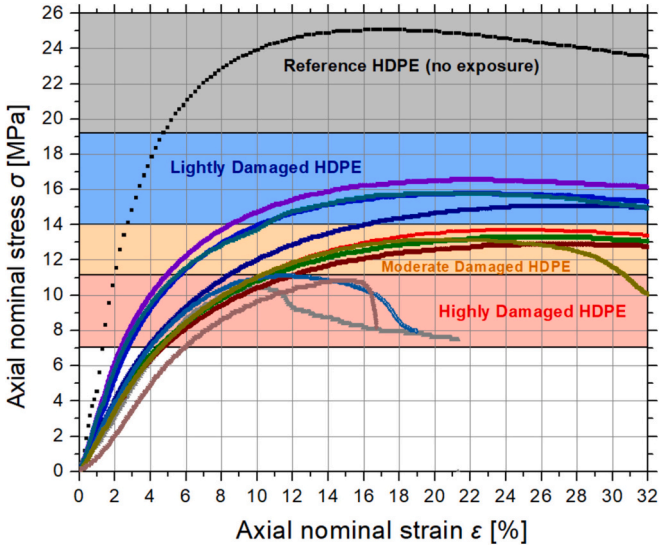


Fig. 11. Typical tensile stress-strain curves comparing HDPE reference specimens with various damage levels of HDPE debris.

This observation may be linked to HDPE's semi-crystalline structure, where the crystalline regions provide some resilience against the degradation occurring primarily in the amorphous regions. The crystalline domains, being more tightly packed and ordered, are likely less susceptible to the surface-level degradative effects that UV radiation induces, such as chain scission in the amorphous phases (Wypych, 2020). Studies have shown that the crystalline regions of polymers like HDPE are typically more resistant to environmental stressors, as they offer structural stability, helping maintain the material's stiffness even as other mechanical properties deteriorate (Wang et al., 2023; Yousif and Haddad, 2013).

Another critical factor influencing this behaviour is the presence of additives used in HDPE manufacturing. Additives such as UV stabilizers and antioxidants are commonly employed to delay degradation processes, preserving mechanical properties such as strength and elasticity (Gijsman, 2017). However, the specific formulations of these additives vary between products and can have a wide range of effects. UV stabilizers may protect the material from early degradation but eventually degrade themselves, leading to a delayed but inevitable deterioration of mechanical properties, especially under extended environmental exposure. Similarly, plasticizers improve flexibility but could lower tensile strength, while reinforcing fillers like glass or carbon fibers may enhance stiffness but at the expense of increased brittleness over time (Bartczak and Galeski, 2014).

Thus, the complex interaction between degradation mechanisms and additive performance needs to be considered to fully explain the observed preservation of mechanical stiffness in HDPE. As environmental factors such as UV radiation and mechanical stress gradually break down the polymer structure, the role of additives in maintaining mechanical integrity becomes increasingly critical. However, their performance under long-term environmental exposure, especially in marine conditions, remains unpredictable and could vary significantly depending on the formulation and the manufacturing process. As a result, σ_{UTS} was chosen as the most reliable factor, to categorize the HDPE debris into damage groups and then, to calculate the percentage (%) reduction of the mechanical property under study. Consequently, the average σ_{UTS} of each category was normalized and it was derived that, for the light tier damage of HDPE debris with mean σ_{UTS} of 15.82 MPa and a standard deviation (STD) of 0.61 MPa, the σ_{UTS} was reduced by 37 %. In addition, for the moderate tier damage of HDPE debris with mean σ_{UTS} of 13.27 MPa and a STD of 0.34 MPa, the σ_{UTS} was reduced by 47 %. Finally, for the high tier damage of HDPE debris with mean σ_{UTS} of 10.57 MPa and a STD of 0.30 MPa, the σ_{UTS} was reduced by 57.70 %.

Based on the calculated mechanical properties, it is evident that significant damage occurred in the microstructure of these HDPE debris. Given the polymeric structure of HDPE, the results indicate the initiation of polymer chain scission occurring within the microstructure of this type of polymer, causing a decrease in molecular weight and deterioration of the examined mechanical properties. A literature review by Zhang et al. (2021) supports these findings by analysing how photo-degradation affects the polymeric structure and tensile properties of HDPE. Even though HDPE is capable to resist photo-degradation due to its chromophore-free structure, manufacturing imperfections or exposure to environmental conditions can introduce impurities acting as chromophores (Zhang et al., 2021). It is also known, that within HDPE carbonyl groups can become chromophores, leading to chain scission through Norrish Type I and II reactions, forming radicals, end-vinyl, and ketone groups (Karlsson and Albertsson, 2002). These radicals may further react with oxygen, creating peroxyl radicals that transform into

peroxide, which then breaks down into macro-alkoxy and hydroxyl radicals. This process catalyses reactions that generate aldehydes, ketones, carboxylic acids, esters, and alcohols, leading to polymer chain scission and cross-linking, which is proved to be a factor for the deterioration of this polymer's mechanical properties (Torikai et al., 1986).

3.3. Cases B & C: exposure to coastal conditions

Based on the representative nominal axial stress-strain curves presented in Fig. 12, it is evident that substantial impairment has also occurred on the tensile properties of the HDPE specimens exposed to natural atmospheric and sea weathering conditions. The damage in the mechanical properties can be observed even within the first three (3) months and a consistent and steady decrease is demonstrated throughout the subsequent months. Taking into account the average values of each exposure time, regarding the two exposure environments, in total almost 21 % σ_{UTS} decrease was noticed for specimens exposed to natural atmospheric weathering conditions and approximate 19 % σ_{UTS} decrease for specimens exposed to natural sea weathering conditions, respectively, over a period of twelve (12) months. As it was stated in the tensile results from HDPE debris, since HDPE is a linear polymer (Kim et al., 2022), since it is composed of long chains of ethylene monomers that are linked together through covalent bonds in a linear, unbranched structure, the results indicate the initiation of chain-breaking activity happening inside the microstructure of the HDPE specimen, which causes a decrease in molecular weight and deterioration of mechanical characteristics (Zhang et al., 2024).

HDPE specimens exposed to natural atmospheric conditions for twelve (12) months (Fig. 10c) showed initial signs of roughness and minor surface cracks, reflecting the beginning stages of photo-degradation and oxidative processes. Similarly, specimens subjected to natural marine conditions (Fig. 10d) for the same duration exhibited surface roughness and the formation of small holes, suggesting the combined effects of hydrolytic and biological degradation.

3.4. Case D: accelerated UV exposure

Fig. 13 shows representative axial nominal tensile stress-strain curves of HDPE specimens subjected to accelerated weathering under UV-A 340 lamps within a custom-built chamber, designed to simulate prolonged UV exposure. The exposure periods were set at 15, 30, 45, 60 and 75 days, with tensile tests conducted at the end of each period to evaluate the material's mechanical performance. The stress-strain curves demonstrate a clear trend of degradation over time. A gradual

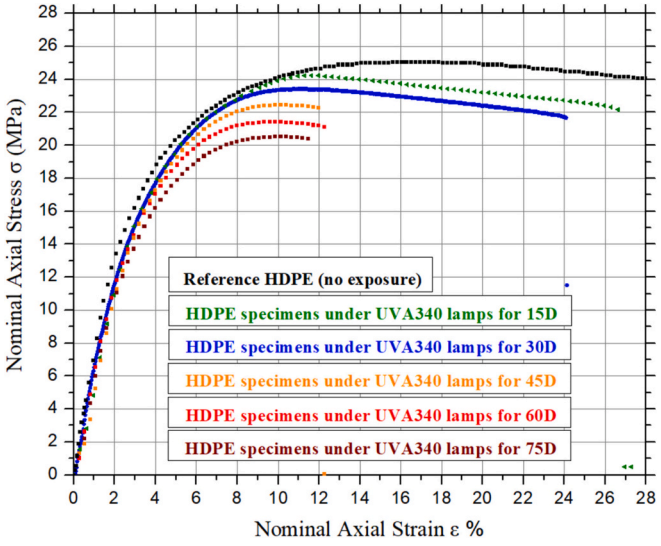


Fig. 13. Representative tensile stress-strain curves of HDPE specimens after exposure to homemade chamber with two UVA 340 nm lamps.

decrease in the ultimate tensile strength (σ_{UTS}) is observed as the exposure duration increases and more specifically, the average σ_{UTS} and standard deviation for the HDPE specimens at different exposure periods were noted in Table 1.

Comparing these data with the average σ_{UTS} values of the reference specimens (unexposed to UV light), exhibit a decrease in σ_{UTS} which can be quantified that initially, after 15 days a decrease of approximately 3 % from the reference value was noted. After 30 and 45 days, the decrease was approximately 7 % and 10 % respectively from the reference value. Finally, after 60 and 75 days, σ_{UTS} was decreased by 14 %

Table 1
Accelerated UV degradation tensile test values.

UV exposure time (days)	Ultimate tensile strength σ_{UTS} (MPa) Average value ± standard deviation
15	24.23 ± 0.44
30	23.24 ± 0.37
45	22.47 ± 0.54
60	21.44 ± 0.96
75	20.53 ± 0.51

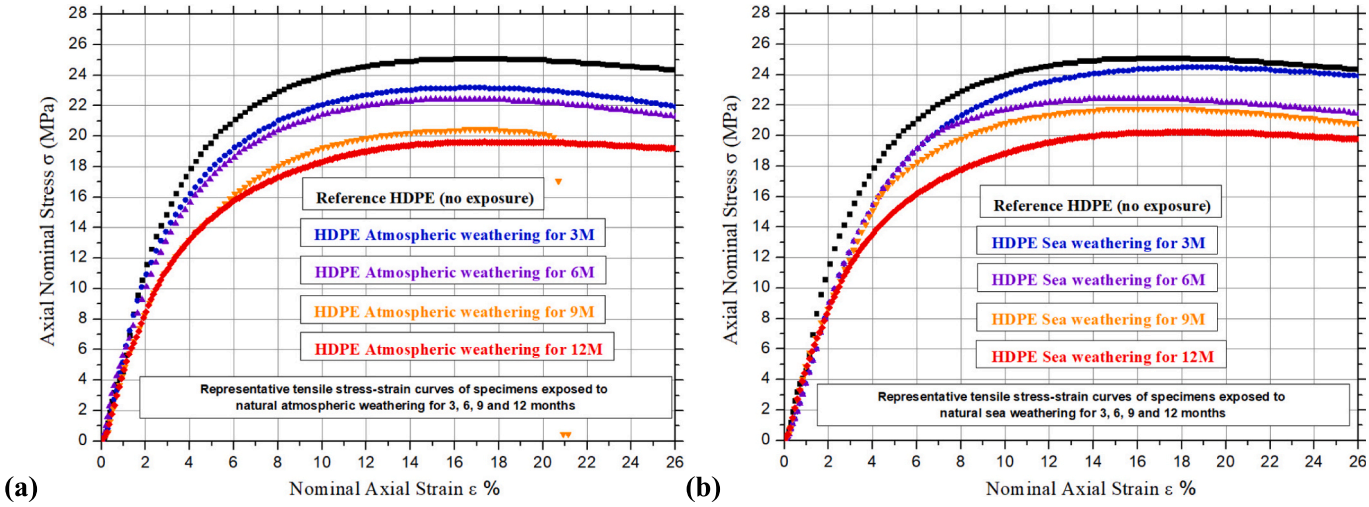


Fig. 12. Representative tensile stress-strain curves comparing pristine HDPE reference specimens & specimens exposed to (a) natural atmospheric and (b) sea weathering conditions for 3, 6, 9 and 12 months.

and 18 %, respectively. This reduction in σ_{UTS} indicates the progressive weakening of the HDPE material due to the photo-degradation effects induced by UV radiation as efficiently showed by (Wypych, 2020). In comparison to the reference specimens (unexposed to UV light), the UV-exposed HDPE specimens show significant alterations in their tensile performance (Yousif and Haddad, 2013).

Accelerated UV weathering (Fig. 10e) resulted in more pronounced surface deterioration over a shorter period. After just 75 days, the specimens displayed significant roughness, flaking, and the initiation of cracks, highlighting the aggressive nature of UV-induced photo-degradation. This accelerated weathering process effectively simulates the long-term effects of natural atmospheric exposure in a much shorter timeframe.

3.5. Case E: artificial saltwater exposure

Fig. 14 shows representative axial nominal tensile stress-strain curves for HDPE specimens subjected to prolonged exposure in artificial seawater without UV radiation. The specimens were submerged for periods of 3, 6, 9, and 12 months, with tensile tests conducted at the end of each period to evaluate the material's mechanical performance. The stress-strain curves demonstrate a gradual decrease in σ_{UTS} as the submersion duration increases, which indicates the progressive weakening of the HDPE material due to the prolonged exposure to seawater. The average σ_{UTS} for the HDPE specimens at different submersion periods an almost linear decrease was noted up to approximate 20 MPa (almost 22 % decrease) for the twelve (12) months exposure. These percentages illustrate the progressive decrease in ultimate tensile strength due to seawater exposure, like the findings in (Yousif and Haddad, 2013). The reference curves exhibit higher tensile strength and ductility, confirming the detrimental impact of prolonged seawater submersion on the HDPE's structural integrity.

Specimens submerged in artificial seawater without UV radiation (Fig. 10f) exhibited a distinct pattern of surface degradation. The surfaces demonstrated smoother characteristics in comparison to the other cases, but eventually, at a higher magnification (×1500), some flaking was noted. This indicates the primary influence of hydrolytic processes and chemical interactions with seawater ions, absent the photo-degradation component.

4. Discussion

In this section, the findings from the various weathering techniques applied to HDPE specimens were exploited to delve into a detailed analysis. The discussion was structured to compare the degradation effects observed under different conditions and to draw correlations that help in understanding the broader implications of HDPE degradation in marine environments. Specifically, the degradation behaviour observed in natural atmospheric conditions (Case B), natural sea conditions (Case C), accelerated UV exposure (Case D), and controlled saltwater exposure (Case E) was furthered explored. The comparative analysis between natural and accelerated weathering methods was highlighted, focusing on the degradation rates and the corresponding mechanical property changes. The aim was to correlate the observed degradation patterns with the environmental factors involved, providing a comprehensive understanding of the mechanisms driving HDPE deterioration.

The rationale for comparing natural atmospheric weathering with accelerated UV weathering lies in the need to understand how UV radiation, a significant factor in atmospheric weathering, influences HDPE degradation. Natural atmospheric weathering encompasses a variety of environmental factors such as UV radiation, temperature fluctuations, and oxygen exposure. Accelerated UV weathering isolates the UV component to study its direct impact on the polymer's degradation. This comparison helps to determine if accelerated laboratory conditions can effectively simulate natural weathering processes and predict long-term material performance.

Similarly, comparing natural sea weathering with artificial seawater weathering is essential to assess how the controlled conditions in a laboratory setup mirror the complex and variable natural marine environment. Natural sea weathering exposes HDPE to a combination of factors, including salinity, wave action, biological activity, and fluctuating temperatures. In contrast, artificial seawater weathering provides a controlled environment to isolate the effects of saltwater on HDPE without the interference of UV radiation and other natural variables. This comparison helps to validate laboratory simulations and understand how each environmental factor contributes to the overall

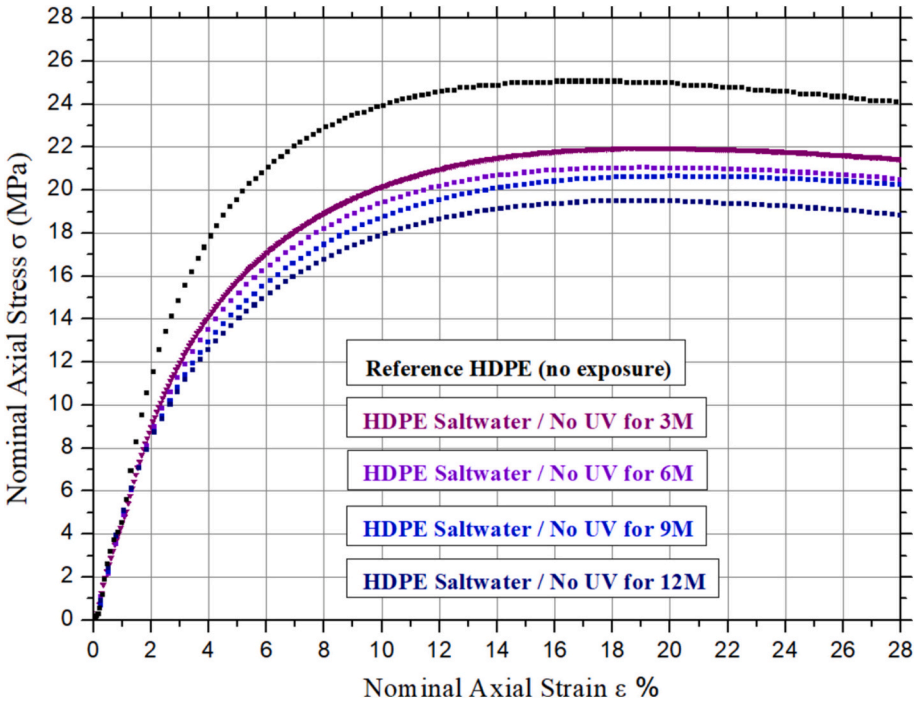


Fig. 14. Representative tensile stress-strain curves of HDPE specimens after exposure to artificial seawater for 3, 6, 9, and 12 months, respectively.

degradation process. By conducting these comparative analyses, a better understanding of the reliability of accelerated and controlled weathering tests in predicting the real-world behaviour of HDPE is achieved, and more effective strategies for mitigating plastic pollution in marine environments can be developed.

4.1. Correlation between the two UV degradation cases

In this investigation, two of the examined degradation conditions (Cases B and D) of HDPE were natural atmospheric weathered, while the accelerated degradation was performed by using a UV chamber. To compare the effects of these two weathering techniques, tensile tests were conducted to evaluate the σ_{UTS} of the HDPE specimens over varying exposure periods. Fig. 15 presents the average tensile stress-strain values for each exposure time, of these weathering techniques. The data points from these experiments were fitted with linear regression model to analyse the degradation trends over time. The resulting linear regression equations provide insight into the degradation rates under both weathering conditions. Comparing these two weathering methods, it is worth noting that a correlation can be drawn regarding their degradation rates. Specifically, the σ_{UTS} average values of 45 days under accelerated UV degradation (Case D) correspond to 6 months of natural atmospheric weathering (Case B). Accordingly, 60 and 75 days of Case D weathering conditions correspond to approximately 9 and 12 months of Case B weathering conditions respectively. This comparison is important, because it demonstrates that accelerated UV weathering can effectively simulate and predict long-term natural atmospheric degradation, thereby validating the accelerated testing methodology. Establishing these correlations provides a reliable basis for using accelerated tests to simulate real-world degradation of HDPE, enhancing the understanding of material performance, and aiding in the development of more durable polymeric materials.

For both weathering techniques, the degradation rate of the HDPE specimens was found to follow the linear equation of the type:

$$\sigma_{UTS} = a + b \cdot x \quad (1)$$

The interpretations of the variables in the linear regression equation are ultimate tensile strength (σ_{UTS}) in MPa, which is the goal to be predicted, x is the independent variable, representing the exposure time in months (it is the value that affects the dependent variable), a is the intercept of the regression line (is the value of y when $x = 0$, which is the initial ultimate tensile strength before any exposure to weathering) and b is the slope of the linear equation that represents the rate of change of the tensile strength per month of exposure. To this end, the negative slope indicates that the tensile strength decreases as exposure time increases.

By establishing these linear regression equations, it is possible to predict the residual mechanical properties of HDPE after specific exposure times that their calculation results based on the experimental data can be seen in Table 2. These predictive models are valuable for estimating the long-term durability of HDPE materials in real-world applications, where both natural and artificial weathering conditions may play a role.

4.2. Correlation between the two sea water exposures

Similar with the above UV correlation exposure, this correlation addresses the sea exposure weathering Cases C and E for HDPE material, and the available results are compared in an attempt to uncover a correlation on the degradation rate between them. The objective was to

Table 2
Equation and database for the degradation rate formula.

$y = a + b^*x$				
	Natural atmospheric weathering	Accelerated UVA340 weathering	Natural sea weathering	Accelerated artificial saltwater weathering
	σ_{UTS}	σ_{UTS}	σ_{UTS}	σ_{UTS}
a	25	25	25	25
b	−0.42643	−1.75862	−0.39111	−0.57089

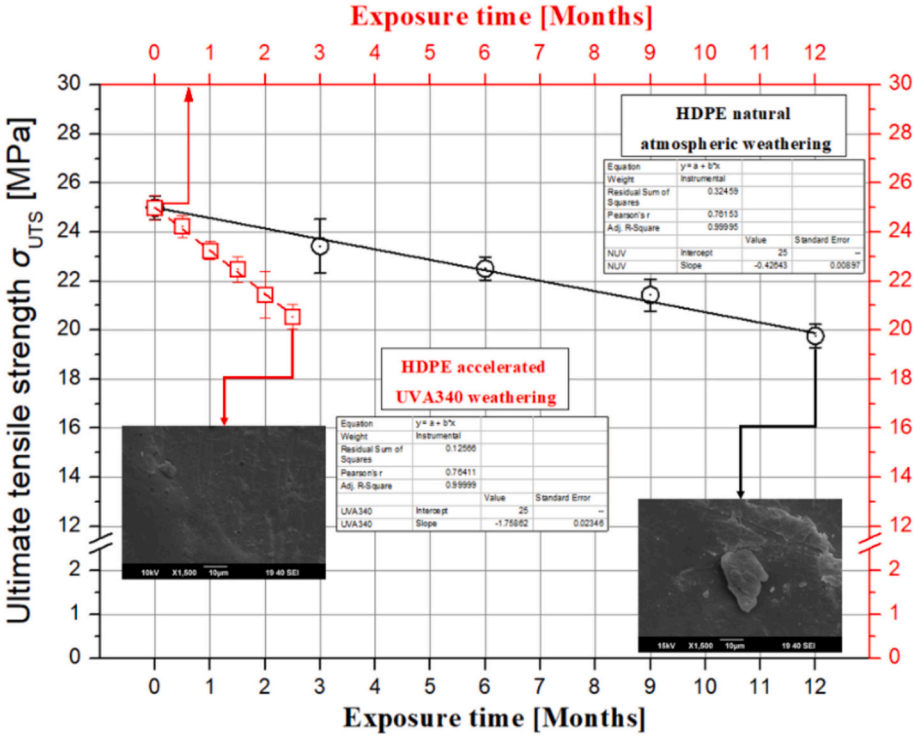


Fig. 15. Ultimate tensile strength σ_{UTS} results as average values for the different exposure times to natural atmospheric weathering and accelerated UVA340 weathering, respectively.

understand how these different conditions impact the material properties over time and to establish predictive models for degradation. Fig. 16 presents the tensile stress-strain curves for HDPE specimens exposed to natural sea conditions and those subjected to artificial saltwater exposure. Similar to the previous subchapter, linear regression models were applied to the experimental data to quantify the degradation rates under both exposure conditions (Table 2). For both weathering techniques, the degradation rate of the HDPE specimens was found to follow the linear Eq. (1).

The negative slopes indicate a decrease in σ_{UTS} over time, signifying material degradation. The comparison of these slopes reveals that the artificial saltwater exposure has a steeper decrease slope, indicating a faster degradation rate compared to natural sea weathering, similar to the findings by (Yousif and Haddad, 2013). There can be various factors that can contribute to steeper degradation in artificial saltwater conditions, but one of the most important is the chemical composition. The artificial saltwater solution is designed to mimic the ionic composition of natural seawater but in a more concentrated and controlled manner, which might accelerate the chemical degradation processes. Also, the laboratory setting ensures a consistent and uninterrupted exposure to saltwater, potentially leading to more aggressive degradation compared to the natural marine environment where conditions can vary. Finally, the exclusion of UV radiation in the artificial setup focuses the degradation purely on chemical and physical interactions with the saltwater, which might intensify the saltwater's impact on the HDPE specimens (Wang et al., 2023). In contrast, natural sea weathering includes mechanical stresses from waves, fluctuating temperatures, varying salinity, and biological activity, which collectively contribute to a more complex but slightly slower degradation process. Further research is warranted to conduct a more in-depth investigation into this matter.

By fitting these linear regression models, the residual tensile properties of HDPE can be predicted after various exposure periods. These models are particularly useful for estimating the long-term durability of HDPE in marine applications, providing valuable insights for the design and maintenance of marine infrastructure and products.

4.3. Generalization potential

In Fig. 17, all natural and artificial weathering Cases were grouped, to perform a comprehensive analysis of the degradation rates observed in the different weathering scenarios compared to HDPE debris collected from the coasts after decades of atmospheric and sea weathering. By analysing all these cases, it is possible to integrate the findings to provide a unified understanding of HDPE degrades over time under various environmental conditions. The focus will be on σ_{UTS}, as it was noted as a reliable key indicator of assessing material degradation. Linear regression models were employed to quantify the degradation rates and to explore potential correlations between the different cases.

Initially, a total approximate 59 % damage to σ_{UTS} properties can be observed, over 35 years span, which demonstrates how different degradation mechanisms (e.g., photo-oxidation, hydrolysis, wave action, biological and chemical degradation) can affect the mechanical propertied of HDPE (Wang et al., 2023). Of course, it is remarkable that even after at least 35 years, the mechanical properties haven't been reduced extensively, and the debris collected were found almost intact. Only through SEM analysis, it became clear that micro-plastics had detached from the initial material.

Fig. 17a was separated into three (3) regions; The first one was the lightly damaged HDPE, which included the unexposed specimens, along with Cases B, C, D and E. For that region, and additional Fig. 17b was provided, to further zoom in on the data regarding the mentioned degradation cases. Afterwards, the other two sections included marine HDPE debris, separated into the first two decades of degradation and lastly the highly degraded debris, after more than thirty years of degradation. For all regions, linear regression models were applied to the experimental data to quantify the degradation rates under both conditions. Confirming the findings of the previous subchapters, all sections were found to follow the proposed Eq. (1). Complementary, SEM images were adjusted for each section, to provide an overall demonstration of the surface deterioration over the years.

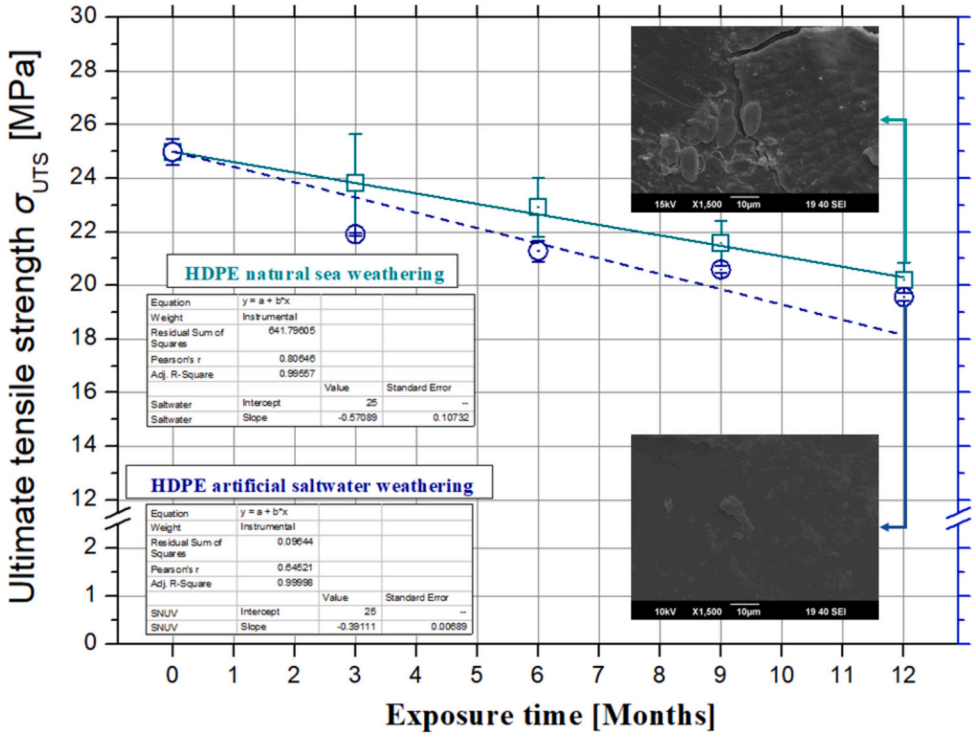


Fig. 16. Ultimate tensile strength σ_{UTS} as average values for the different exposure times to natural sea weathering and accelerated artificial saltwater weathering.

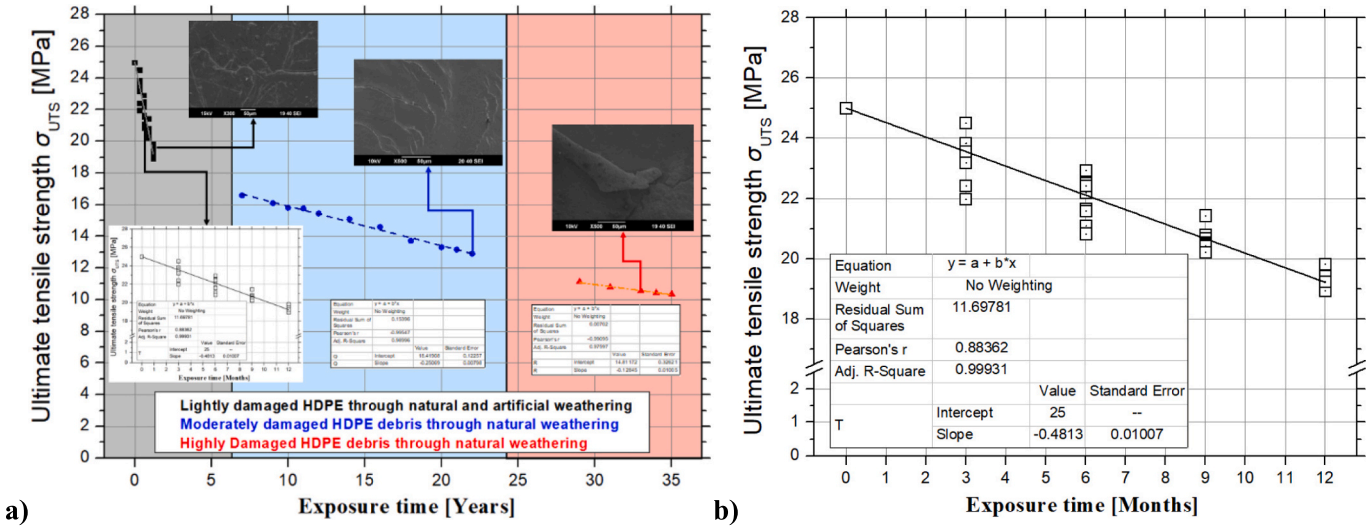


Fig. 17. a) Ultimate tensile strength σ_{UTS} values for all the different investigated cases and classification into three different groups regarding σ_{UTS} decrease value and respective decrease rate and b) σ_{UTS} decrease trendline only for all the investigated cases B, C, D and E.

4.4. Challenges and limitations

Throughout the implementation of the present investigation, several challenges, limitations, and obstacles were encountered, which impacted both the experimental procedures and the interpretation of results. These issues primarily relate to environmental variability, the preparation of specimens, the retrieval of samples from natural environments, and the limitations inherent in accelerated testing methods. All of them can be briefly described below:

a) Environmental variability: One of the major challenges was the unpredictable and highly variable environmental conditions in the natural marine settings. The HDPE degradation in marine environments is influenced by multiple factors such as fluctuations in temperature, salinity, UV radiation exposure, and biological activity. These factors varied not only with the location of the sample collection but also with seasonal changes during the collection period. Such variations made it difficult to ensure consistency across all field samples, which may have introduced variability into the degradation patterns observed.

b) Challenges in manufacturing HDPE specimens: One of the main obstacles was the difficulty in producing HDPE specimens during the injection moulding process. Creating uniform, defect-free samples that accurately represented the desired material properties was challenging. Issues such as material inconsistencies, incomplete moulding, or potential failures in the moulding process occasionally led to the production of specimens that did not meet the required standards for testing. These necessitated additional rounds of specimen preparation and quality control, increasing both the time and complexity of the experimental process.

c) Retrieval and monitoring of specimens in natural marine environments: Another significant obstacle involved the retrieval and continuous monitoring of specimens placed in marine environments. Ensuring that specimens remained in the intended locations without being displaced or lost due to wave action or sea currents required frequent checks and adjustments. Additionally, continuous monitoring of specimens exposed to controlled natural environments was necessary to track their tensile strength degradation rates.

d) Limitations of accelerated weathering tests: While for the purpose of the present investigation accelerated UV weathering methods was exploited to predict the long-term natural degradation, this technique has specific limitations. Accelerated weathering methods simulate long-term exposure by increasing the intensity of certain environmental factors, such as UV radiation. Nevertheless, these methods cannot perfectly replicate the complex combination of factors experienced in natural environments. As a result, the degradation patterns observed in the laboratory might not fully reflect the actual long-term HDPE behaviour in real-world marine conditions, limiting the generalization potential of the experimental results. Additionally, the accelerated protocol was performed by using continuous UV exposure experimental testing, while the natural weathering protocol involved cycles of sun exposure and recovery, which could possibly further affect the tensile properties degradation rates.

e) Long-term natural exposure and consistency of samples: Maintaining consistency over extended exposure period was another challenge, particularly for the samples subjected to long-term exposure in natural conditions (e.g., the possibility for specimens to be exposed for a period higher than twelve months). While the present investigation covered a range of weathering conditions (including one summer and one winter season), longer exposure period of exposure would provide further insights into the HDPE degradation. Additionally, ensuring that samples were not subject to unexpected external interference (such as extreme weather events) was a persistent challenge during outdoor exposure tests.

Nevertheless, the present investigation provides a detailed analysis of the HDPE coastal-induced degradation behaviour under different exposure conditions, which is essential for understanding the long-term impacts of marine plastic waste. The degradation categorization performed in the present investigation paves the road for future investigations and research into the degradation and recyclability prospects of other plastic types in coastal areas. The classification of degradation damage into distinct groups based on chemical and mechanical changes will allow future researchers to assess and compare plastic waste degradation across a range of environments and polymers.

Overall, this research provides valuable insights into the HDPE degradation mechanisms in marine conditions, offering predictive models for material performance and informing strategies to mitigate plastic pollution. By examining the degradation trends and identifying key factors influencing the degradation rates, valuable insights were offered that can guide future studies and the development of more durable HDPE materials. Future studies should focus on exploring the effects of additional environmental variables and developing more resilient polymer formulations to withstand prolonged exposure to harsh marine conditions.

5. Conclusions

The present investigation offers a comprehensive evaluation of HDPE degradation under various weathering conditions, including among all, natural atmospheric exposure, marine exposure, accelerated UV radiation, and artificial seawater submersion. Several important contributions were made to understand the long-term HDPE degradation behaviour in marine environments, are summarized as follows:

- Key chemical and structural HDPE transformations was identified through FTIR spectroscopy and SEM analysis, including the formation of carbonyl groups and the appearance of surface cracks, that are indicative of photo-degradation and hydrolytic processes, which were absent in unexposed samples and only became prominent after environmental exposure.
- The primary degradation mechanisms identified include photo-degradation, thermo-oxidative degradation, hydrolytic degradation, and biological degradation. Among these, photo-degradation emerged as the most influential factor in σ_{UTS} deterioration, particularly under UV exposure.
- Correlation between different weathering methods: the establishment of a correlation between natural atmospheric weathering and accelerated UV exposure in terms of σ_{UTS} decrease. For instance, one and half (1½) month of accelerated UV exposure is equal to approximately six (6) months of natural atmospheric degradation. Such correlations offer practical information regarding the material performance under varied environmental exposure.
- Across all four (4) investigated HDPE cases, σ_{UTS} degradation followed a linear decrease rate over exposure time of the form ($y = a + b * x$). The proposed equations are extremely helpful to predict σ_{UTS} under various environmental exposure conditions.
- HDPE specimens exhibited significant degradation across all weathering conditions, with ultimate tensile strength decrease (σ_{UTS}) ranging from approximate 8 % over 3 months to 60 % over 35 years exposure. These findings underline HDPE's vulnerability to prolonged environmental exposure, particularly in marine environments.

CRediT authorship contribution statement

Nikitas Lourmpas: Writing – original draft, Methodology, Investigation, Data curation. **Paraskevas Papanikos:** Writing – review & editing, Investigation, Conceptualization. **Eleni K. Efthimiadou:** Writing – review & editing, Methodology, Investigation. **Anastasios Fillipidis:** Methodology, Investigation. **Demetris F. Lekkas:** Resources, Funding acquisition. **Nikolaos D. Alexopoulos:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. (the Authors declare no Competing Financial or Non-Financial Interests).

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Data availability

Data will be made available on request.

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