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

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**Abstract.** In the present investigation, the degradation of high-density polyethylene (HDPE) in marine environments, under ultraviolet (UV) radiation and saltwater conditions, was examined. HDPE debris were collected from the coastal areas nearby Korinthos, encompassing a wide range of exposure durations, from relatively intact to several decades of exposure in the marine environment. The debris were examined via several microstructural examinations and additionally tensile specimens were extracted to evaluate the weathering effects on the mechanical properties. The experimental test results revealed a significant decrease in the mechanical properties that ranged according to the estimated exposure of the debris to the environmental exposure. The debris were classified into three different groups, based on the decrease of their mechanical properties, to be used for recycling. This high-end discrimination of the induced damage to the material properties will probably allow for the appropriate recycling of such debris without essential decrease in the mechanical properties, as currently a small portion of the damaged debris are being used during recycling of such materials.

**Keywords: High-density polyethylene; Marine environment; Degradation rate; Natural weathering**

## 1. Introduction

Plastic debris pollution has emerged as one of the most pressing environmental issues of our time, particularly in marine and coastal environments. It is an emerging issue that affects biodiversity and the quality of habitats (Weinstein et al., 2016). Several hundred thousand tons of plastics are discarded into the marine environment every year (Khoo et al., 2021). Single-use plastic products, with little or no value after use, are probably a major reason for widespread plastic pollution. Among the numerous types of plastics, HDPE has gained significant attention due to its wide range of applications and its persistence in the environment (Ainali et al., 2021). In response, numerous voluntary and regulatory initiatives have been adopted. EU Single-Use Plastics (SUP) Directive [EU 2019/904] provides a roadmap of measures and targets to be applied to different products. EU's Circular Economy Action plan, describes the transition to a circular economy that will significantly reduce plastic pollution (Syberg et al., 2021).

## 2. Environmental exposure background

HDPE is one of the most used plastics (polymer) due to its favorable properties such as high chemical resistance, durability, and low 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 valorizing marine litter, it is extremely important to identify the nature and quantify the extent of degradation of such polymers under marine. When the HDPE is being rejected into the marine environment, 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. several decades, has a profound impact on the mechanical properties of the materials (Chamas et al., 2020).

In a marine environment, several HDPE degradation mechanisms can occur, often involving a combination of physical, chemical, and biological processes. Physical factors such as UV radiation, wave action, and mechanical stress can lead to the fragmentation of HDPE into smaller particles, commonly known as microplastics (Barnes et al., 2009). These microplastics undergo further degradation and weathering, resulting in changes in their physical and chemical properties (Singh and Sharma, 2008). Plastics exposed to sunlight undergo photo-oxidation, since high-energy wavelengths of the ultraviolet (UV) spectrum by the polymers is absorbed (Sivan, 2011). Once degradation is initiated, it can proceed through temperature-dependent thermo-oxidative reactions without further exposure to UV radiation.

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.

## 3. Experimental Procedure

The main objective of the present study is to examine the degradation of a dominant polymer type found in all environmental matrices, high-density polyethylene (HDPE), when exposed to ultraviolet (UV) radiation and saltwater conditions. For this purpose, a coordinated action was organized by researchers and volunteers of “OZON” NGO, where numerous HDPE debris were collected from the coasts of Korinthos, as depicted in Fig. 1, ranging from barely intact to decades of exposure to marine environment.

**Figure 1.** Coastal cleanup action aiming at the collection, separation, and record of plastic debris in several coastal areas of Korinthos.

The weathering effects on the surface characterization, morphology and mechanical properties of the specimens were examined with Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and tensile testing.

The debris were initially classified according to the manufacturing date/year and hence, the exposure time was estimated according to the visual inspection of the waste, as can be seen in Fig. 2.

**Figure 2.** Images of the production date of several marine plastic debris for the estimation of their environmental exposure.

Based on the above classification, several tensile specimens were cut off from the available debris to examine the tensile mechanical properties. The procedure to acquire the specimens is illustrated in Fig. 3, where the test specimens had geometrical dimensions according to ASTM D638 (ASTM International, 2017). The tensile specimens were tested in a VTS 10 kN load frame with displacement control of the grips, while a 50 mm extensometer was surface attached at the area of the reduced cross-section.

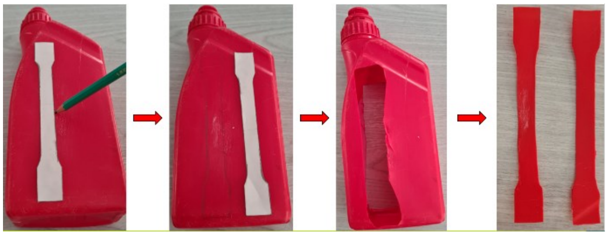

**Figure 3.** Representative example of the acquisition of tensile specimens from marine plastic debris.

## 4. Results and future aspects

Indicative tensile test results can be seen in Fig. 4, where it can be concluded that the tensile mechanical curves differs with the evironmental exposure. In all cases, the maximum (peak) stress from each tensile flow curve is extremely decreased, when compared to the maximum stress of the reference material without any exposure. To this end, a classification was also attempted based on the tensile tests results on the debris that were exposed for a few years and the ones for decades under marine conditions. This degradation was attributed to the different stages of chain-breaking activity of each debris and to the impairment of the microstructure after the initiation of the photo-oxidation process. The final goal of this investigation is the classification of the debris into three different groups, based on the induced damage due to environmental exposure. This classification will enhance the recyclability aspect of these debris, so as to produce reclycled material without extensive decrease in their mechanical properties.

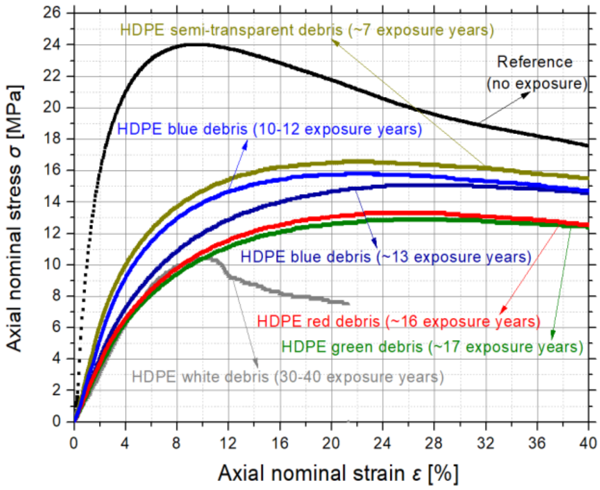

**Figure 4.** Tensile stress-strain curves comparing reference specimens with plastic debris exposed to decades of natural weathering in marine environment.

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