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Effect of Environmental Conditions on the Carbonyl Index Using Specific Area Under the Band (SAUB) Method During Degradation of Commercially-Available Plastics

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Abstract

Plastic waste is ubiquitous in the environment and may undergo different degradation mechanisms, such as photooxidation, thermooxidation, and hydrolytic degradation. However, there is still a lack of understanding, especially for plastics used in real-world applications, of which environmental compartment they degrade faster, leading to accelerated production of microplastics when improperly disposed of on land or at sea. This study evaluates the degradation of the commonly used plastics, namely: High Density Polyethylene (HDPE), Low Density Polyethylene (LDPE), and Polyethylene Terephthalate (PET), in two different environmental media (air and seawater). The Specified Area Under the Band (SAUB) method is used to calculate the carbonyl index (CI) to assess the extent of plastic degradation. This study will serve as a baseline for the fate of plastics ending up in marine ecosystems, providing valuable insights into the long-term impacts of plastic pollution on the environment.

The results of this study show that the degradation of HDPE does not vary between the two environments ($p>0.05$). Meanwhile, LDPE and PET exhibit higher degradation rates in air as compared to seawater ($p<0.05$). The degradation process of these two plastics in the air is accelerated by increased UV, temperature, and oxygen availability.

The differences in HDPE, LDPE, and PET degradation behavior in air and seawater could be attributed to the different chemical structures and properties of these plastics, as well as the environmental media to which they are exposed. This study highlights the degradation patterns of plastics once they enter the various ecosystems during their end-of-life fate, which results in the expedited production of microplastics in the environment.

Keywords: Photooxidation, FTIR-ATR Spectroscopy, SAUB.

Introduction

The global plastic production reached 390 million tons in 2021 and is expected to reach 34 billion tons by 2050 [1, 2]. The rise in plastic production is attributed to its versatility, durability, and affordability, making it a popular choice for various industries [3-6]. However, the non-biodegradable nature of plastic waste when improperly disposed of has led to significant environmental concerns [3, 4]. The increasing amount of plastic waste has resulted in pollution of land, water bodies, and air, causing harm to ecosystems and wildlife [3, 7]. Efforts are being made to promote recycling and develop sustainable alternatives to reduce plastic's negative impact on the environment [3]. However, only 9% of plastic waste is recycled, 69% is incinerated or disposed of in landfills, and 22% is leaked into the environment [4, 7, 8]. Mismanaged waste often leads to plastic ending up in oceans and rivers, where an estimated 8 million metric tons of plastic enter the ocean annually [4, 9, 10]. In the Philippines, 945,000 metric tons of plastics are discarded directly into the environment, with 745,000 metric tons entering the ocean [9]. These plastics can be exposed to environmental factors, such as ultraviolet radiation, temperature, and oxygen, and also to the action of winds, currents, and tides which contribute to the breakdown of plastics into microplastics and nanoplastics [11-16].

Plastics can be degraded via biotic and abiotic degradation [17]. Abiotic degradation degrades the plastic which alters its physicochemical properties which several mechanisms are reported such as photooxidation, thermo-oxidative degradation, and hydrolytic degradation [18]. Plastic waste degrades first via photodegradation, then by hydrolysis, and then followed by thermo-oxidative degradation [3, 7]. Photooxidation is one of the primary causes of plastic deterioration in the environment, which occurs when the UV radiation breaks down the chemical bonds in the plastic, leading to the formation of free radicals [19, 11, 20-22]. These free radicals then react with oxygen, causing further degradation of the plastic into smaller fragments [17, 22, 23]. Hydrolytic degradation happens when a polymer is in contact with water [24, 25]. Hydrolysis is a chemical reaction where water molecules break down the polymer chains, resulting in the degradation of the material [25]. This process occurs due to the interaction between water molecules and the polymer's chemical bonds, leading to a gradual breakdown of its structure over time [25]. Thermooxidation is the degradation of plastics due to exposure to high temperatures and oxygen [26, 27]. These processes can lead to the breakdown of polymer chains, resulting in a loss of mechanical strength and structural integrity [28, 29].

The differences in the degradation mechanisms of plastics are due to the different environments they are exposed to and the chemical composition of plastics. Faster deterioration in the air environment (e.g. plastics that are stranded on the shorelines) than in seawater (plastics that float or sink at the bottom of the ocean) was observed for most plastics [3, 28, 6, 30, 31]. The greater degradation in air compared to the seawater environment can be due to the higher temperature and higher UV irradiance in the air environment because of the absence of fouling [32, 28, 30, 31]. Seawater reduces photooxidation of the plastics because of the lower oxygen availability in the medium, the increase in refractive index of the medium, which causes light intensity to decrease and the formation of salt crystals on the surface of the polymer [6, 28, 31].

Commercially-available plastics differ from virgin pellets in terms of their initial degradation process that takes place during its manufacturing process and their additives. The transfer of the chemical defects, which are precursors of oxidation, to the amorphous phase of the polymer occurs during the annealing and slow cooling of a crystalline material [33]. Internal impurities such as chromophoric groups - unreacted monomers, carbonyl groups, and hydroperoxide groups - are introduced from the polymerization process of the plastics, and its degradation is initiated by UV radiation [31, 34, 35]. Additives such as filler, stabilizers, and plasticizers can contain heavy metals such as chromium, cadmium, and lead, which are used to prepare the additives [36]. The most common additive is UV stabilizer which protects the materials from deterioration when exposed to the UV radiation [37]. The degradation under the UV light has shown to promote the release of additives into the aquatic environment [38].

The changes in the plastic's composition during the degradation process can be measured using infrared spectroscopy. Infrared (IR) spectroscopy is a reliable, fast, cost-effective, and a non-destructive method for measuring the chemical changes of a material [39]. Chemical changes in the polymer can be observed by the formation of carbonyl products, with wavenumbers ranging from 1680–1850 cm-1and the formation of hydroxyl products in the wavenumbers 3100-3800 cm-1 [39-43]. Carbonyl products such as ketones, aldehydes, carboxylic acids, and esters (Mylläri et al., 2015), cause the most apparent change in the IR spectra and by measuring the amount formed in a plastic can indicate that the polymer has been degraded and will facilitate further degradation [17, 43].

The carbonyl index (CI) is used to measure the progress of the deterioration of plastics [19, 39, 43]. It is a quantitative measure that indicates the level of carbonyl groups present in the plastic material [19, 39, 44]. The carbonyl index is often calculated by dividing the peak area of the carbonyl region by the peak area of a reference peak, such as an internal standard or a specific compound [43]. This ratio provides a quantitative measure of the relative concentration of carbonyl groups in a sample. However, due to the lack of standardization, it is important for researchers to clearly define and justify their chosen method when reporting carbonyl index values. Some papers have used the ratio of the peak heights, but that data is insufficient since there are various carbonyl products with overlapping peaks that are formed, such as carboxylic acid, aldehydes, and ketones. A study by Almond et al. has suggested using the specified area under the band (SAUB) method to calculate the CI for polyolefins [28, 30, 45-47, 39]. The SAUB method takes into account the entire spectral region associated with carbonyl absorption, providing a more comprehensive measure of carbonyl content. This approach allows for a more accurate and reliable calculation of the carbonyl index for polyolefins, enhancing the comparability and reproducibility of results across different studies [39].

This study focuses on the degradation of High Density Polyethylene (HDPE), Low Density Polyethylene (LDPE), and Polyethylene Terephthalate (PET). The aim is to compare the degradation patterns of the different plastics when exposed to different environmental media under accelerated aging conditions using the SAUB method. Almond et al. developed the SAUB method specifically for polyolefins, and this study will identify the appropriate peaks for PET to be used in the CI calculation [39]. Commercially available plastics were used in this study because there are few studies that use these materials, which are frequently discarded and contribute significantly to plastic waste pollution. This work focuses on the changes in plastics that can be observed when they are exposed to different environmental conditions: air, which mimics the plastic waste with the absence of the fouling of the medium (i.e. on the surface of the terrestrial environment and the beach), and seawater, which represents the ocean's surface. By simulating these environments, we aimed to understand how exposure to air, UV radiation, and seawater would impact the chemical properties of these commonly used plastics. Further, this study will serve as a baseline on the fate of commercially available plastics in the environment.

Materials and Methods

Plastic Samples

Commercial products shown in Figure 1 were selected as representative materials in this study. For HDPE, a jug is selected as it is mainly used for food packaging. For LDPE, a foam sheet is selected as it is used to insulate packaged materials, and for PET, a soft drink bottle is used. The plastic materials are cut into small pieces such that the longest axis is approximately 6 mm.

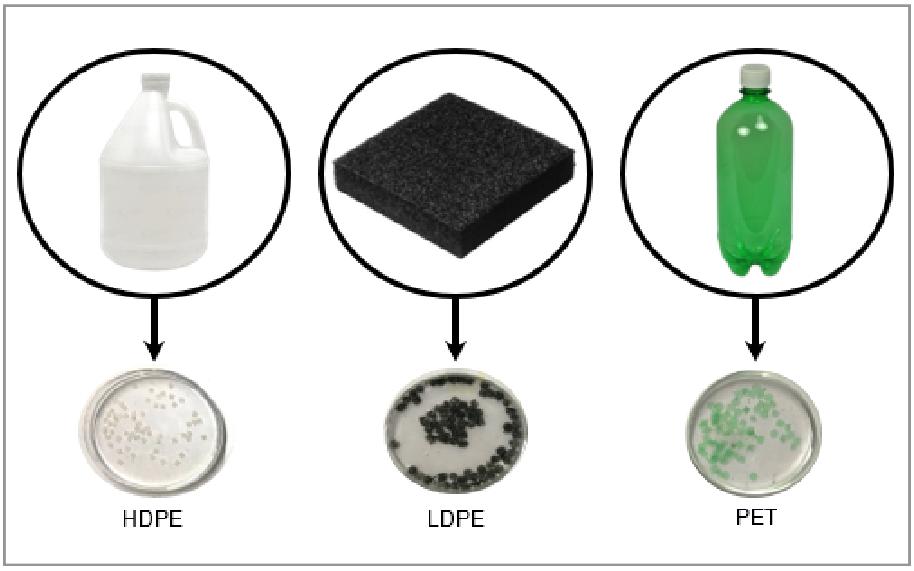

Figure 1: Commercially-Available Products: (from left to right) HDPE jug, LDPE foam sheet, and PET bottle.

Experimental Design

The samples (Figure 1) were exposed to two environmental settings: (1) in air and UV and (2) in seawater and UV. A modified environmental chamber (Figure 2) was used to expose the plastics to the effects of UV and the environmental media on their degradation. The modified environmental chamber allows the control of the exposure conditions and accurately measure the degradation of the plastics.

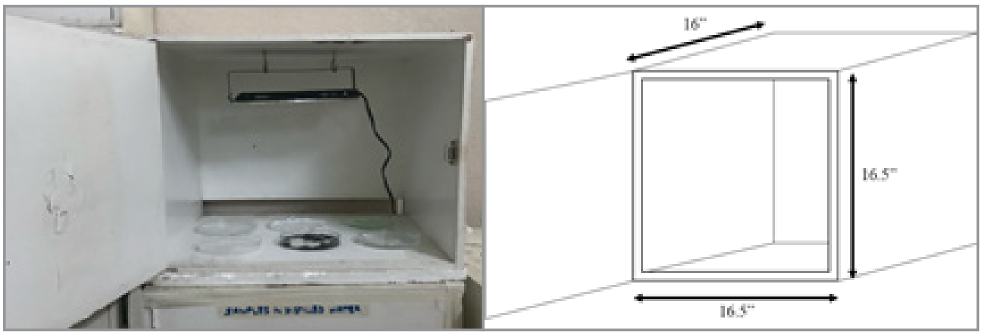

Figure 2: Actual modified Environmental Chamber Equipped with UVA340 Lamp (left); Dimensions of the Chamber (right).

Sample Exposure

The samples were submerged in filtered seawater on a petri dish. These were transferred into the modified environmental chamber equipped with a UVA340 lamp (Figure 2). The aging experiment, with a period of 5 months (one month was 30 days, which was defined as a cycle), was conducted with continuous UV irradiation with an irradiance of 1.36 Watts/m2. Ten plastic pellets for each treatment were randomly removed from every cycle and dried with absorbent paper. These were further dried at 60 °C and stored in petri dishes in the dark.

FTIR-ATR Spectroscopy

The analysis is performed using Nicolet™ iN™ 10 MX (Thermo Fisher Scientific Inc.) FTIR with a Germanium ATR tip. The spectral range is in 4000 to 400 cm-1, and the spectra resolution was obtained using 16 scans per spectrum at 8 cm-1 resolution. The room temperature is 25°C and relative humidity of 60%.

Each side of the sample was measured at 3 points (in a diagonal position), of which two points are at the end point of the samples and 1 point is in the center (Figure 3). This method ensures that the entire length of the samples is accurately measured.

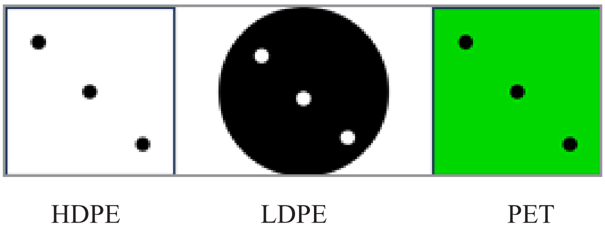

Figure 3: Measurement Points

Estimation of Carbonyl Index

The carbonyl index was used in this study to determine the degradation of the polymers in different environmental media. The SAUB method (Specific Area Under the Band) was employed to calculate the carbonyl index for the PE samples. The equation of the CI is:

$$Carbonyl\ Index = \frac{Area\ under\ the\ carbonyl\ region\ (1850-1650\ cm^{-1})}{Area\ under\ the\ reference\ peak\ (1500-1420\ cm^{-1})} \text{(Eq. 1)}$$

The carbonyl index for PET was calculated by the same equation but with a different wavenumber range, as the carbonyl region for PET is at 1680–1800 cm-1 and the reference peak that is used is centered at 730 cm-1. Thus, the CI calculation for PET is:

$$Carbonyl\ Index = \frac{Area\ under\ the\ carbon\ yl\ region\ (1800-1650\ cm^{-1})}{Area\ under\ the\ reference\ peak\ (775-675\ cm^{-1})} \text{(Eq. 2)}$$

There were no baseline corrections done on the data as they can potentially skew the CI. The area under the peaks was measured using a software, QTIPlot. This software allowed for accurate determination of the peak areas by fitting the data to a Gaussian distribution curve.

Statistical Analysis

The Shapiro-Wilk Test was used to assess the normality of the data. The data with normal distribution were tested with two sample independent t-test while data with non-normal distribution were tested with a nonparametric test, the Mann Whitney U Test. The outliers were not included in calculating the CI. The statistical analysis was done in Minitab v. 17.

Results and Discussions

HDPE

The distinct peaks for HDPE samples are three intense methylene doublet bands with peaks in 718 cm-1 and 728 cm-1 for CH2 rocking deformation, 1460 cm-1 and 1472 cm-1 for bending formation, and 2845 cm-1 and 2915 cm-1 for asymmetric and symmetric stretching [48, 49]. During the initial stage of UV irradiation, HDPE already exhibited changes in the carbonyl region (1650 – 1850 cm-1) shown in Figure 4. The carbonyl peak is centered at 1712 and 1735 cm-1 which is the peak for the formation of ketones and esters, respectively [40, 50]. HDPE also exhibited changes in the 1620-1650 cm-1 which indicates the unsaturation in the plastic [11]. Moreover, it was also observed that the hydroxyl products are also formed in the wavenumber of 3100 – 3800 cm-1 for all of the samples, however, due to the interference of the formation of salt crystals to the samples submerged in seawater, the carbonyl region is the focus for this study.

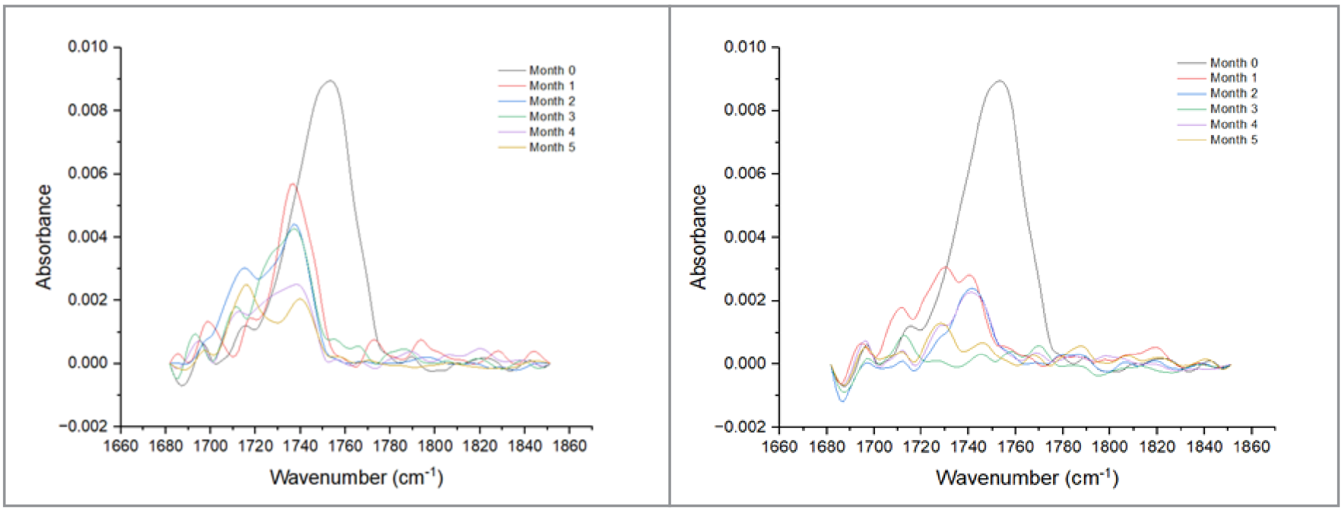

Figure 4: FTIR Spectra of Carbonyl Region of Irradiated HDPE in Air (above) and Seawater (below).

The presence of carbonyl groups at the start of the experiment suggests that the material already exhibited an initial stage of degradation since the material is not a virgin plastic. Pure polymers differ from commercial plastics due to the unsaturated sites (i.e. vinylidene, hydroperoxides, and ketones) that remain after the polymerization process which are susceptible to further photolytic attacks [44, 13, 51]. These impurities or structural defects can act as chromophores which are readily oxidized by radicals and can be converted to a more stable UV-absorbing carbonyl group through Norrish I or Norrish II reactions [52]. The Norrish I mechanism is the formation of carbonyl groups while Norrish II mechanism is the production of vinyl and hydroxyl or hydroperoxide species [53].

It can be observed that there is a peak shift throughout the exposure to UV which can be due to the simultaneous formation of various carbonyl groups, such as ketones, carboxylic acids, esters, and lactones (Figure 4). During the degradation of HDPE, ketones (1715 cm-1) are formed in the initial stage, while carboxylic acids (1714-1716 cm-1), esters (1735-1740 cm-1), and lactones (1780 cm-1) are formed in the secondary stage [40]. The reaction of hydroxy and alkoxy radicals with ketones leads to the formation of carboxylic acids and esters, respectively (Yang & Ding) [49]. The peak shift suggests that the concentration of alkoxy radicals increases over time, favoring the formation of esters over carboxylic acids.

The carbonyl index for HDPE is in Figure 5, where the degree of degradation does not differ in the two environments (p>0.05). This suggests that the photooxidation process of HDPE is not significantly influenced by the specific environmental conditions. It can be observed that there is a downward trend for the CI of HDPE in both environments. After 5 months of exposure to the polymer in the air, the CI decreases until it reaches 0.056 ± 0.045 while the sample in seawater also follows the same trend with CI of 0.062 ±0.030. The decrease in CI can be due to the release of plastic particles on the surface and the formation of carbon monoxide by the decarbonylation of the acyl radical produced in Norrish I reaction [47].

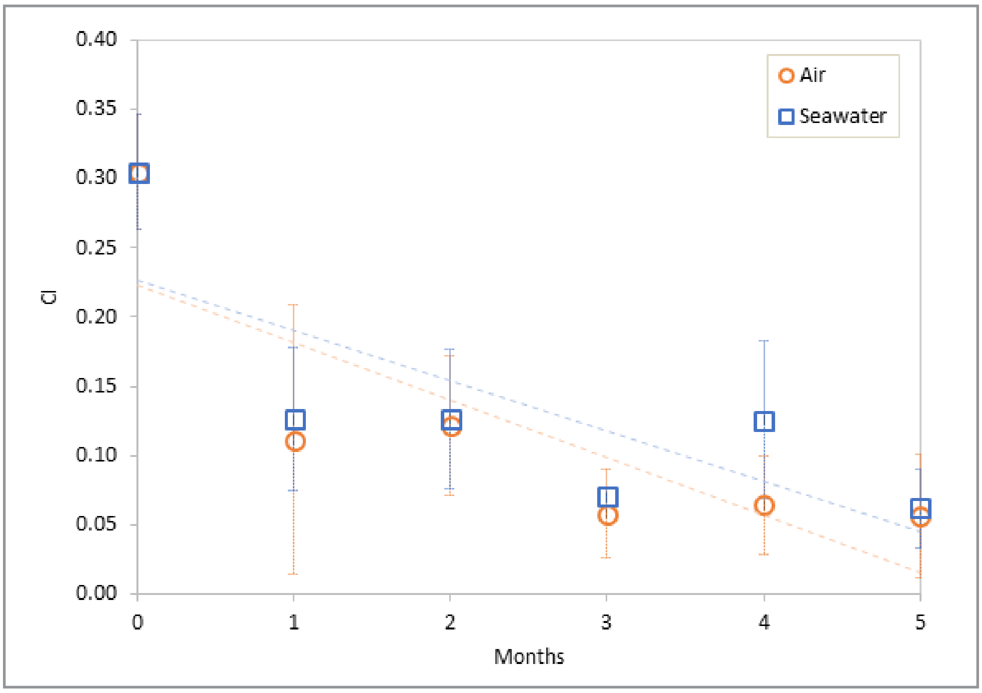

Figure 5: Carbonyl Index Values of HDPE in Air and Seawater Environments

LDPE

LDPE has peaks at 730 cm-1 for CH2 deformation, 1462 cm-1 for CH scissor bending, and methylene doublet band at 2848 cm-1 and 2916 cm-1 [54]. LDPE has the same degradation products as HDPE, namely vinyl, carbonyl, and hydroxyl products. The deterioration of LDPE is mainly by photooxidation which allows the formation of free radicals that may react freely with atmospheric oxygen and can form carbonyl groups [6]. The peak of carbonyl products of LDPE is centered at 1733-1735 cm-1 (Figure 6) which is the formation of esters and aldehydes [44]. The results are similar with Yagoubi and Abdelhafidi, where they found that aldehydes had the highest concentration for weathered LDPE, followed by ketones, carboxylic acids, then esters through curve-fitting in the range of 1680-1850 cm-1 [54].

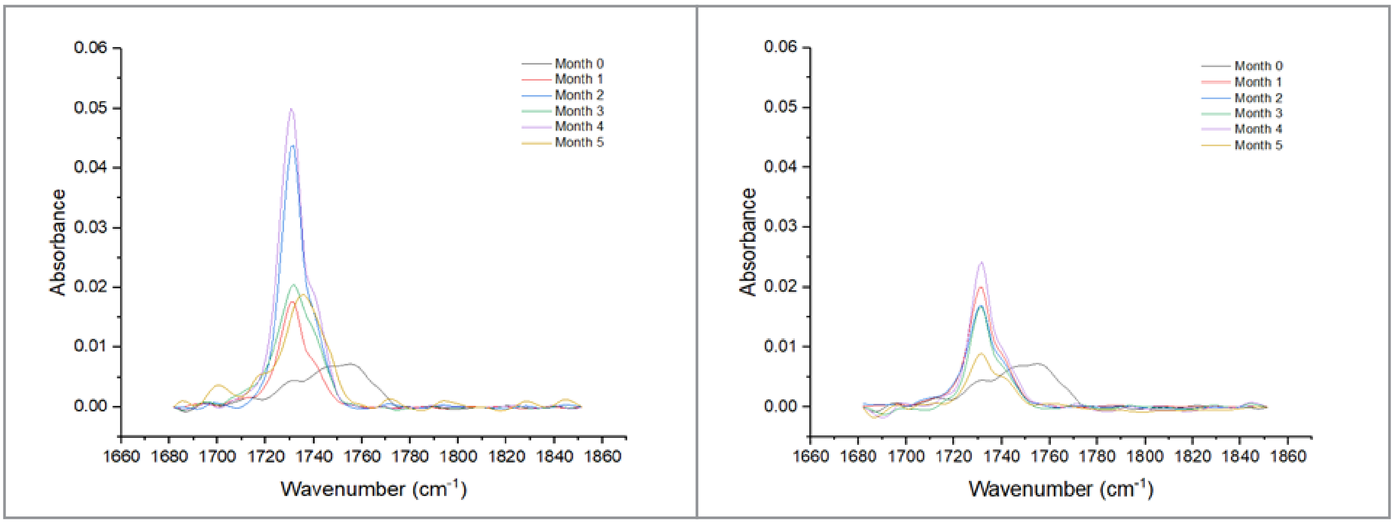

Figure 6: FTIR spectra of carbonyl region of irradiated LDPE in air (above) and seawater (below).

The CI of LDPE in air is greater than in seawater ($p<0.05$) which is shown in Figure 7. This suggests that the degradation of LDPE in air is more pronounced as indicated by the increasing CI observed in the samples. LDPE photooxidation is greater in air than in seawater environments due to the higher temperature, UV irradiance, and oxygen availability in the air [28, 6, 55]. The salt present in seawater increases the refractive index of the seawater thus lowering the light intensity [6].

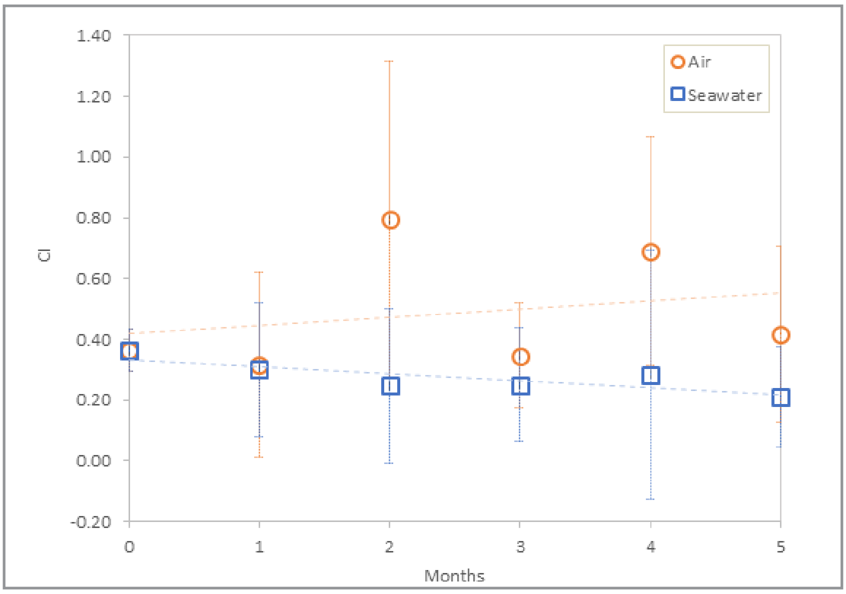

Figure 7: Carbonyl index values of LDPE in air and Seawater Environments

PET

There are five main distinct peaks for a PET which are 723 cm-1 for aromatic C-H bond stretching, 871 cm-1 for aromatic C-H bond stretching, 1017 cm-1 for ether aliphatic C-H bond stretching, 1245 cm-1 for ether aromatic C-C-O bond stretching, and 1715 cm-1 for ketone C=O bond stretching [26, 56]. PET degrades by hydrolytic cleavage and photooxidation initiated by UV light [57, 24]. The oxidation of PET will yield carbonyl products in the wavenumber 1700-1785 cm-1 [58]. The carbonyl index of PET is centered at 1712 cm-1 which is assigned to the C=O stretching of ketone where the samples in air experiences an increasing intensity and widening of the peaks over the course of exposure to UV (Figure 8) [58].

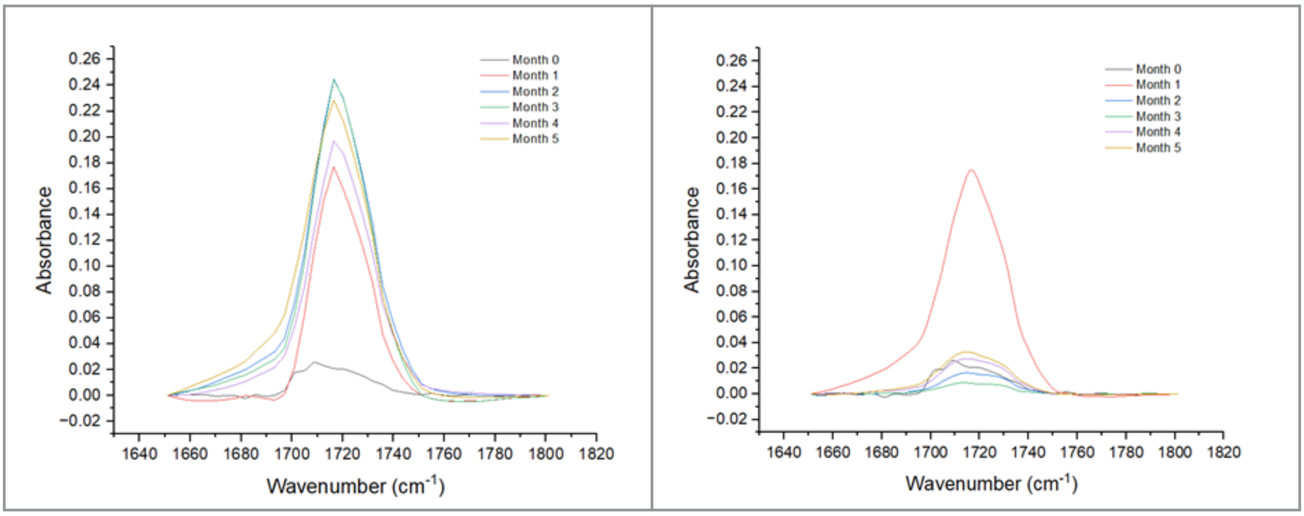

Figure 8: FTIR Spectra of Carbonyl Region of Irradiated PET in Air (above) and Seawater (below).

The continuous increase in carbonyl products in PET samples exposed to UV in air indicates a persistent degradation process, which may be attributed to the direct impact of UV radiation on the polymer structure. In the air, the free radicals formed during the photooxidation of PET react readily with oxygen and the formation of degradation products mainly composed of carboxyl end group, particularly of perester or anhydride (Fagerburg and Clauberg, 2003) [59]. This is evident by the CI of the samples (Figure 9) where PET degrades faster in air than in seawater ($p < 0.05$).

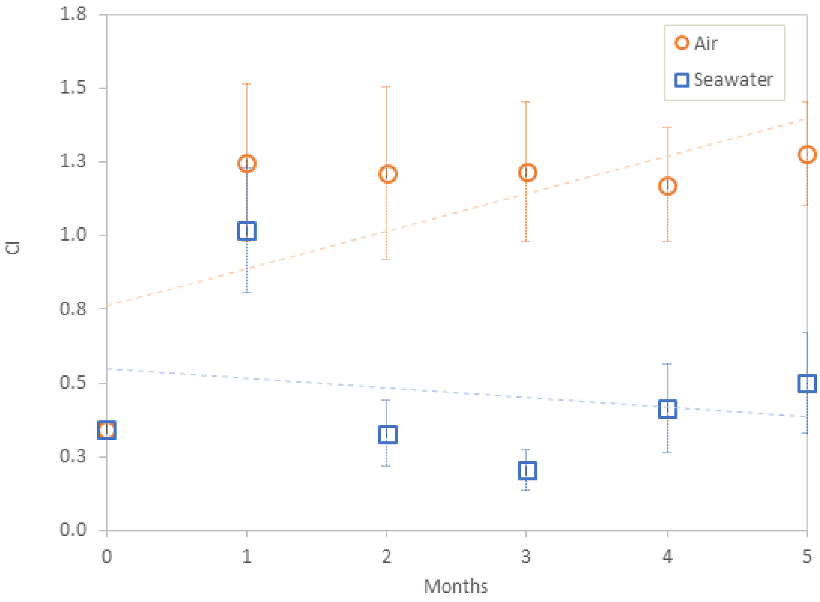

Figure 9: Carbonyl Index Values of PET in Air and Seawater Environments

The faster degradation is primarily due to the presence of oxygen in the air, which accelerates the breakdown of PET molecules. Additionally, greater exposure to sunlight and higher temperatures can further enhance the degradation process [28, 30]. Higher temperature and UV irradiance may be the factors that have affected the degradation that leads to faster deterioration in air than in seawater. Seawater may have slowed down the photooxidation due to the low concentration of dissolved oxygen in the medium [28]. The nonlinear degradation of PET in seawater can be due to the hydrolysis of PET which produces terephthalic acid and glycol [58]. The decrease of CI for samples in seawater can also be attributed to the release of the PET particles degraded on the surface of the plastics during the photooxidation process [32].

Difference between the CI values of the Plastics

PET has the highest CI values during the course of the experiment compared to the PE samples, and the increase in CI of PET, particularly in air samples, can be attributed to perester or anhydride formation (Fagerburg and Clauberg, 2003). Among the PEs, LDPE has higher CI values than HDPE, with the difference in degradation rate due to LDPE's lower crystallinity, which allows for more amorphous regions in its structure and a higher frequency of reactive branch points [60-63]. An increased surface area of LDPE foam sheets can also result in higher CI values compared to HDPE. Crystallinity protects against oxidation and oxygen permeability decreases as crystallinity increases [40, 64]. High crystallinity causes light scattering and reflection, reducing the distance that light can penetrate [41]. As a result, LDPE is more susceptible than HDPE to environmental factors such as heat and UV radiation, resulting in faster degradation.

Environmental Implications

Plastics that find their way into the environment are subjected to a variety of environmental elements, including temperature, oxygen, and ultraviolet radiation (UV). They are also subjected to the action of winds, currents, and tides, which move the plastics back and forth from the ocean to the shore and vice versa. [11-13]. These factors contribute to the breakdown of plastics into smaller particles, which can be ingested by a wide range of marine organisms [19, 65-47]. Furthermore, as these plastics degrade, toxic additives and plasticizers may leach out into the environment. Persistent organic pollutants or POPs in the seawater are adsorbed into the surface of the meso or microplastics [18]. When these particles with POPs are consumed by marine organisms, it can cause digestive system disruption and reduce the absorption of nutrients [49, 18, 68]. This can lead to malnutrition and weakened immune systems, which can have detrimental effects on their health and can also bioaccumulate up the food chain, potentially impacting human health as well [69].

Although the degradation of LDPE and PET is slower in seawater, there is still degradation occurring on the plastics, which requires action in whatever environment the plastics are discarded in. Microplastics are most likely produced by stranded plastics on beaches, emphasizing the importance of beach cleanups as an effective mitigation strategy. The removal of plastic items from beaches and nearshore areas has the potential to reduce the amount of debris and microplastics entering the ocean.

Conclusions

The nature of the plastics, as well as environmental conditions, will have a significant impact on degradation patterns. The degradation process is complex, particularly for commercially available plastics, which may undergo initial degradation due to chromophoric defects that can serve as unsaturated sites for the propagation of degradation products. A jug of HDPE degrades similarly in both environments, whereas LDPE foam sheet and PET bottle degrade faster in air than in seawater. Increased oxygen availability and UV irradiance may cause faster degradation in the air medium, promoting photooxidation of these plastics. The faster degradation between the plastic types is as follows: PET > LDPE > HDPE. This means that PET plastic bottles will degrade faster than the other materials studied, particularly when stranded on beaches or in the terrestrial environment with direct sunlight exposure. As a result, waste that becomes stranded on beaches or in the shoreline will produce microplastics more quickly. Consequently, efficient beach clean-ups can be a useful mitigation technique to reduce the amount of waste that ends up in our ocean.

Declaration of Competing Interest

All authors declare that they have no competing interests.

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