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DEGRADATION OF PLASTICS IN SEA WATER IN LABORATORY

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ABSTRACT: When these materials are thrown as waste, biodegradable plastics are used to lessen the environmental implications. These compounds, however, have the potential to be introduced into natural ecosystems due to poor management methods and environmental contamination. The efficacy of biodegradable and oxodegradable polymers in marine environments is assessed using a respirometric laboratory test in this study. Plastic probes, both pre-exposed to simulated weathering and without prior exposure, were inoculated with a marine organism over 48 days. This procedure was carried out with the assistance of a continuous aeration system, which also aided in the absorption of the ensuing CO2 emissions. Following the test, an assessment was done regarding the samples' loss in mechanical qualities. The biodegradable plastic had a higher percentage of mineralization (10%), whilst the polyolefins showed no significant difference (range from 2.06% to 2.78%) regardless of the presence or absence of pro-oxidants or previous abiotic deterioration. In contrast, when exposed to UV light, the oxodegradable plastic had a considerable loss in elongation at breakage (>68%). The results show that the polymers under examination are more susceptible to physical breakdown, with much slower rates of biodegradation. These entities may fragment as a result of a combination of numerous mechanisms preceding their significant biodegradation. Although the materials may be useful in certain waste management settings, it is critical to limit the formation of microplastics by ensuring their exclusion from marine environments.

Keywords: Mineralization, Oxodegradable, Marine Environment, Polylactic Acid

1. INTRODUCTION

Plastics have become vital materials in modern times, with applications in a wide range of industries including food, building, medicine, and automobiles. The combination of low cost and desirable characteristics, such as lightweight construction, excellent durability, and versatility, has resulted in a constant growing trend in their use. Nonetheless, due to their low potential for disintegration in the natural environment, inappropriate disposal and waste management of plastic items provide a considerable difficulty. The accumulation of plastic waste has significantly degraded the marine ecosystem.

Plastic waste has the potential to harm marine species once it enters these habitats. There have been documented cases of numerous affects on marine species, such as feeding disturbances caused by ingestion, entanglement accidents, and asphyxiation induced by waste materials. Plastics have been found in or on different marine creatures, including seabirds, turtles, and mammals.

Numerous biodegradable polymers have been offered as a feasible option to mitigating the negative environmental

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implications of plastic waste. Compostable and oxodegradable plastics are the two most common forms of plastics on the market today. Biodegradable polymers are created by adding pro-oxidant compounds into ordinary plastics, such as cobalt (Co) and manganese (Mn) salts. Biodegradable alternatives, such as those described, are used to replace more degradable polymers, such as polyethylene and polystyrene. When exposed to UV light or at high temperatures, the activation of pro-oxidants produces free radicals, which then damage the polymer chain. This mechanism converts high-molecular-weight compounds to low-molecular-weight equivalents. Microorganisms are expected to engage in metabolic processes to break down the resultant oligomers and smaller molecules, culminating in mineralization of the material and conversion to carbon dioxide (CO2).

Compostable polymers are specifically designed to degrade during composting under specific conditions, such as a thermophilic temperature range, a moisture content of 50% to 60%, and the presence of microbial species. Ecovio®, a biodegradable plastic derived from polylactic acid (PLA), and Ecoflex®, an aliphatic-aromatic copolyester composed of butanediol, terephthalic acid, and adipic acid, are among the plastics included in the list.

Despite their documented disintegration under aerobic conditions, the methods by which biodegradable and oxodegradable polymers degrade in marine environments remain unknown. Plastic deterioration can be assessed in situ by direct exposure to maritime conditions. It should be emphasized, however, that this test is not especially designed to assess biodegradation. Instead, it usually entails significant investments and the adoption of specific monitoring procedures to reduce the chance of sample loss. As a result, the ASTM D6691-09 recommendations aim to provide a standardized test technique for evaluating the aerobic biodegradation of plastic materials in the marine environment. This method employs either a predetermined microbial community or a natural sea water inoculum to evaluate plastic biodegradation under controlled laboratory settings.

The ASTM D6691-09 standard is used in this study to assess the biodegradation and mechanical property deterioration of conventional, oxodegradable, and compostable plastics. This device allows for the replication of marine conditions in a controlled setting. The approach used in our study evaluates the impact of pre-existing abiotic deterioration on the samples produced by simulated weathering.

2. MATERIALS AND METHODS

In natural saltwater, the biodegradation of polymers was evaluated in a laboratory setting using the ASTM-D6691-2009 technique. The use of a marine microbial consortium allows for the assessment of the level of aerobic biodegradation of plastic compounds in saltwater. The test was accomplished by implementing four successive phases. 1) preparing and selecting plastic samples; 2) obtaining a saltwater sample enriched with inorganic nutrients; 3) subjecting materials to the inoculum; 4) using a respirometric apparatus to quantify CO2 generation over time; and 5) determining the level of

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biodegradability. Following the test, the loss in elongation at break was used to assess the deterioration of both biotic and abiotic plastics.

Tested Materials

The researchers investigated three types of plastic materials: Ecovio®, a biodegradable plastic, low-density polyethylene (LDPE), and two polyethylene variations, LDPE and OXOLDPE, with and without the inclusion of pro-oxidant chemicals. AGUSA, a Mexican firm, used polyolefins and contained the d2w® pro-oxidant component from Plásti-cos Degradables S.A. de C.V. (México), a Symphony Environmental subsidiary. BASF-México provided biodegradable plastic materials. BASF's polylactic acid (PLA) and the copolyester Ecoflex® are mixed to form an aliphatic-aromatic combination. To simulate degradation induced by usage, UV light exposure, and temperature changes, the polymers were partitioned into probes measuring 150 10 mm. Following that, half of each plastic type was subjected to abiotic oxidation in a weathering chamber already constructed at the institution, as described in a prior work. The specimens were exposed to a temperature of 50 C, a relative humidity of 80%, and a radiation range of 300 to 460 nm for a total of 216 hours. The time necessary for the abiotic degradation process to reduce OXOLDPE elongation at break to near-zero levels was calculated. Before starting any writing project, it is necessary to choose the appropriate template based on the dimensions of the page. The template provided is just for printing on bespoke paper and measures 21 cm by 28.5 cm.

Preparation of Inoculum

The seawater used in this experiment came from Tuxpan's Barra Norte beach in Veracruz, Mexico (Figure 1). Four hours after being collected, the seawater was delivered to the laboratory in sterile containers. The salinity of the sample was determined to be 50.5 1.2 mS/cm, and the pH was 7.85 0.07. To assess degradation, two reactors with a volume of 2 liters each were used. These reactors were filled with 1.2 liters of saltwater that had been supplemented with inorganic fertilizers. The saltwater was supplemented with NH4Cl at a concentration of 0.5 g/L and KH2(PO)4 at a concentration of 0.1 g/L. Following that, the reactors were incubated for 48 days at a temperature of 30 C 1 C. During the respirometric test, the experimental approach required maintaining a steady airflow into the reactors.

Aeration System Used to Assess Biodegradation

The appropriate polymers were added to the reactors containing modified saltwater. The mass of each plastic substance is shown in Table 1. As a positive control, cellulose was used, while reactors holding only modified seawater served as blank samples. As indicated in Table 2, three duplicates of each plastic and control were established. Following that, the specimens were attached to a respirometric apparatus (shown in Figure 2), which consisted of a series of traps designed to catch the CO2 created during the plastic's disintegration. To maintain aerobic conditions, a steady stream of saturated air free of CO2 was delivered.

Carbon dioxide (CO2) traps were made from NaOH solutions with a concentration

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of 0.25 N. Following that, the specimens were titrated biweekly with a 0.5 N hydrochloric acid (HCl) solution on two consecutive occasions. Equation (1) was used to calculate the mineralization (%) of the samples' biodegradation.

$$\text{Mineralitation}(\%) = \frac{C_{test} - C_{Blank}}{C_i}$$

In this case, Ci denotes the total amount of polymer-C supplied to the test reactors in milligrams (mg). Cblank signifies the average CO2 generation measured in mg in the blanks that only contained the inoculum. Finally, Ctest denotes the average amount of CO2 produced in the replicates for each material.

Assessment of Degradation by Tensile Tests

Similarly to prior studies, the assessment of tensile elongation at the point of fracture was performed to estimate the level of deterioration, taking both abiotic and biotic factors into account.



Figure 1. The beach location chosen for seawater sampling. Tuxpan Beach is located in Veracruz, Mexico.

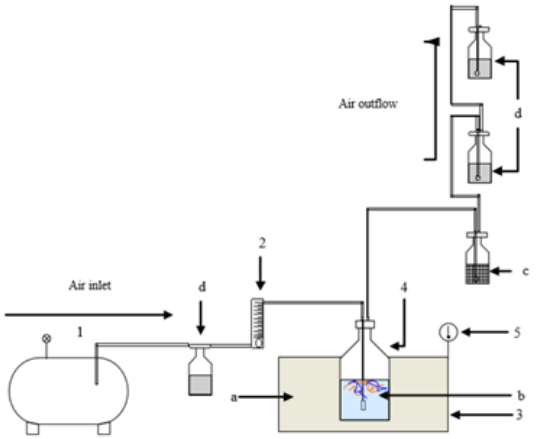


Figure 2. Respirometric system. (a) Distilled water, (b) Seawater with inorganic nutrients and plastics, (c) Silica trap, (d) NaOH solution trap, 1) Compressor, 2) Flow regulator, 3) Water bath, 4) Reactor, 5) Thermometer.

Table 2. Types of plastic used in the experiment, with and without oxidation

Treatments	Sample mass (mg)
Cellulose	1000
LDPE	807
LDPE-O	807
Ecovio®	810
Ecovio®-O	810
OXO-LDPE	926
OXO-LDPE-O	926

Table 1. Mass of each plastic utilized in the test.

Plastic	With oxidation	Without oxidation
LDPE	3	3
OXOLDPE	3	3
Ecovio®	3	3
Total	9	9

The measurement was carried out in accordance with the ASTM D882 standard [18]. The Lloyd LFPlus, produced by AMETEK Lloyd Instrument Ltd. in the United Kingdom, was used in this study. The testing velocity was kept constant at 300 mm/min, with a 30 mm space between the grips. The experimental setup ensured that the conditioning and testing operations were carried out under controlled atmospheric conditions, namely at a

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temperature of 24 C with a 1 C tolerance and a relative humidity of 50% with a 10% tolerance. Equation (2) was used to get the % REB, or residual elongation at break.

Tukey's multiple range test (MRT) and analysis of variance (ANOVA) were performed on the tensile test results at a 95% significant level. The biodegradation stage was removed from the statistical analysis because to its non-normal distribution.

3. RESULTS AND DISCUSSION

Biodegradation

After 48 days of testing, the cellulose reactors had a mineralization rate of 68.3%. The cited statistic is comparable with previous composting research, which found a degradation rate of 80% in 90 days and 100% in 317 days. This figure indicates the respirometric system's effective performance. There was no noticeable difference in the mineralization levels of the two polyolefins—one with a pro-oxidant addition or prior degrading treatment and the other without. Mineralization rates observed varied from 2.06% to 2.78%. Ecovio®, on the other hand, demonstrated a success rate of 10.11% for oxidized samples and 10.38% for non-oxidized samples, as shown in Figure 3.

There has been no comparable research to allow for a comparison of these outcomes. However, previous research has demonstrated that these plastics biodegrade in a variety of conditions. Mineralization values of 2% to 2.5% for low-density polyethylene (LDPE) and 7% to 10% for oxidized low-density polyethylene (OXOLDPE) were obtained after a 90-day incubation period at 45 C in soil. After 352 days of deterioration, OXOLDPE had a mineralization rate of 16%, while LDPE infected with Rhodococcus rhodochrous had a mineralization rate of 9% after 317 days. The findings of the experiment reveal that the amounts of mineralization reached for LDPE and OXOLDPE are consistent with previously published values.

Degradation by Elongation at Break

Statistical investigation indicated statistically significant (p 0.05) differences between the polymers. According to the MRT analysis, there are five homogeneity groups, with LDPE and LDPE-O having the lowest REB percentages of 9.3% and 17.1%, respectively. The OXO-LDPE material attained a performance level of 29.11%, while the Ecovio® material performed similarly with and without oxidation. During the experimental method, the OXO-LDPE-O variation saw the greatest degree of elongation loss, resulting in a large reduction in mechanical resistance of 67.85% (Figure 4).

Given that both biotic and abiotic factors influence elongation at break, it is not suitable to compare the biodegradation rates determined by respirometric testing to these variables. In contrast to previous findings, oxidized OXOLDPE showed a greater drop in elongation at break. However, the current study found that Ecovio® had the highest level of biodegradation. Natural marine ecosystem deterioration is a complicated and intricate phenomenon impacted by a variety of factors such as the composition and number of living species, soluble salts, temperature, dissolved oxygen levels, UV radiation, and water flow rate. There is a

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scarcity of knowledge on the degradation of plastics by sea salts. Nonetheless, soluble sea salts have been shown to influence the chemical and physical properties of concrete and anticorrosive coatings. Furthermore, studies have shown that certain microorganisms, such as bacteria, fungus, and other microbes, can develop biofilms on plastic surfaces. These biofilms have the ability to release enzymes that aid in the modification of the physicochemical properties of the plastic substance.

In contrast to untreated polyolefins, polyolefins that had previously been oxidized by exposure to UV and excessive temperature demonstrated a marked proclivity for further degradation, as evidenced by consistently higher values of%REB. Plastic deterioration by light is a well-known phenomena, and once began, it frequently persists, allowing subsequent biotic and abiotic processes. Because Eco-vio, a kind of PLA, performs non-enzymatic hydrolysis, the degrading mechanism found varies from the normal chemical interaction reported in polyolefins. Previous ultraviolet (UV) radiation exposure had no effect on the object's deterioration. Compostable plastic had a higher mineralization % than both polyolefins, indicating a faster rate of decomposition. The results of this study indicate that the respirometric strategy used in this experiment is a useful tool for undertaking a more streamlined and cost-effective evaluation of the performance of various plastic materials. The values found for all of the plastics are comparable to those previously reported for direct exposure in marine environments.

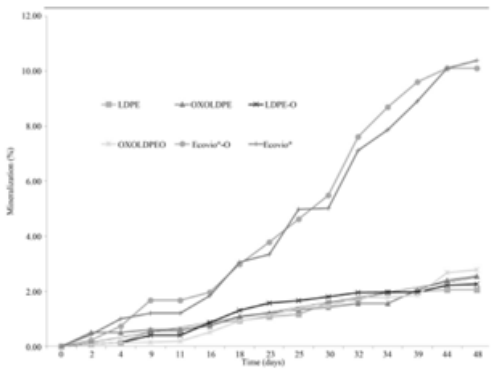


Figure 3. Mineralization of plastics produced by biodegradation in natural saltwater

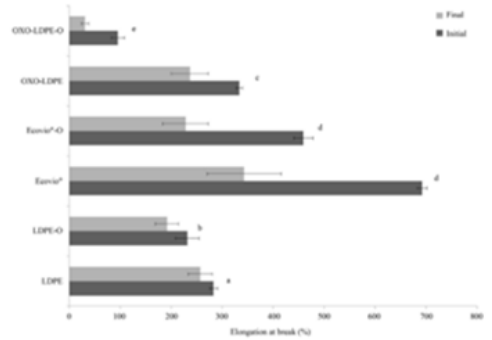


Figure 4. The percentage of elongation at the point of fracture after laboratory marine exposure. To distinguish between the ANOVA and MRT tests, distinguishing typographic variants are used. There are five distinct types of homogeneity.

4. CONCLUSIONS

Adoption of biodegradable polymers is one potential solution to the difficulties caused by plastic waste. In general, these materials are intended to degrade when exposed to waste management conditions, primarily. It is critical to remember that the loss of physical integrity, namely the loss of elongation upon break, is not intrinsically good. When the rate of fragmentation exceeds the rate of biodegradation, the creation of microplastics is possible.

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A plethora of literary works have documented the presence of microscopic plastic particles in the water, as well as their subsequent passage through the food chain during the composting process. However, it is likely that the new materials will end up in natural environments due to improper disposal methods, inadequate waste management strategies, or people wrongly believing that they will biodegrade in any environment.

Regardless of the introduction of a pro-oxidant component or prior treatment in a weathering chamber, we observed low marine biodegradation for the polyolefins under consideration in this study. Furthermore, in the current study, the biodegradable plastic showed essentially negligible marine biodegradation. Nonetheless, the observed decrease in elongation at break indicates that all of the polymers' mechanical characteristics deteriorated. In this situation, it is clear that the addition of the additive, together with abiotic UV oxidation, resulted in additional degradation of the polymers when exposed to the maritime environment.

The data indisputably show that complete disintegration of plastics, including those classified as biodegradable, cannot be assured in the absence of further degrading processes. It is important to highlight, however, that these findings cannot be extended to genuine decline in marine ecosystems. It is critical that persons who use these materials understand their inherent limitations and qualities, and that they use them in situations that match their specific characteristics. As a result, negative repercussions such as the production of microplastics can be efficiently mitigated.

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