

Article

Environmental Degradation of Oxo-Biodegradable Polyethylene Bags

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Abstract: The purpose of the present study is the estimation of the environmental degradation process of oxo-biodegradable polyethylene bags. The degradation process of polyethylene samples, with the addition of a d2w prodegradant, was studied under natural weathering, freshwater (pond), and water in laboratory condition for a period of 48 months. The impact of characteristic parameters of environments on the extent of degradation, monitored by weight changes, mechanical properties, and surface morphology, has been discussed. The degraded polymer samples were also analyzed by FTIR spectroscopy. It was established that the oxo-biodegradable polyethylene samples were hardly prone to degradation in natural freshwater, but more vulnerable to environmental weathering. Abiotic parameters (oxygen, temperature, solar radiation) played a more important role in the degradation process of oxo-biodegradable polyethylene than biotic parameters (microorganisms). Natural weathering led to first fragmentation of the polymeric samples after 18 months, weight loss to 81.6% after 39 months, and complete assimilation after 45 months. In the pond, 48 months incubation resulted in an increase in the weight of the samples (+19%) and a decrease in mechanical properties: tensile strength from 26.31 to 17.35 MPa and elongation at break from 304 to 31%. The biofilm formed on the polymer surface made it difficult for oxygen to reach the degraded material, so oxydegradation in the pond was slower. ATR-FTIR analysis and microscopic observations confirm the degradation taking place in natural environments. No visible degradation changes were observed in the oxo-biodegradable polyethylene after incubation under laboratory water, because of the lack of microorganisms and solar radiation. The degradation of oxo-biodegradable polyethylene in natural environments required a longer incubation time compared to the degradation time declared by the manufacturer.

Keywords: degradation process; pro-oxidant additive; polyethylene; freshwater; pond; natural environment



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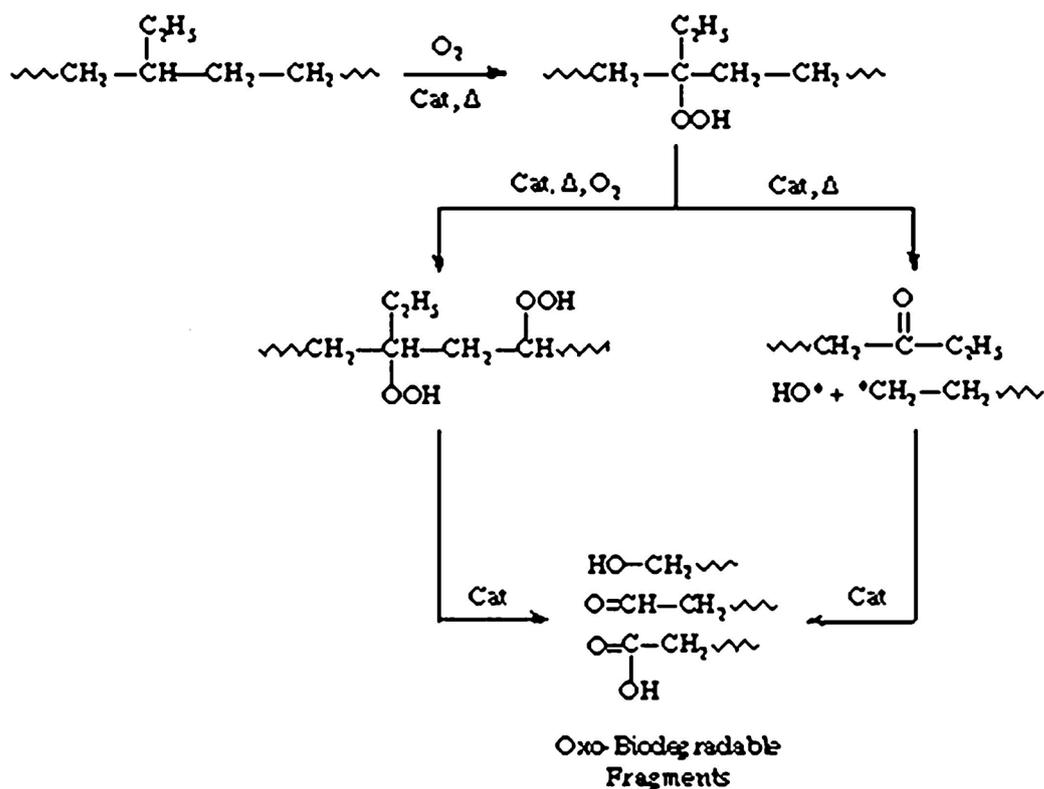
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1. Introduction

Polyethylene (PE) has the largest share of the polymer market, accounting for around a third of the polymer products produced [1]. Globally, 22% of the annual production of plastics enters terrestrial and aquatic environments, where they can stay for decades. One strategy for reducing plastic pollution is to design materials so that they degrade more quickly in air when exposed to heat and UV light. The degradation process can be speeded up by the addition of pro-oxidants (d2w), like transition metals (e.g., Cu, Co, Ce, Mn, Ni, or Fe) in the form of organic complexes or salts to the polyolefin compound, up to 5% by weight. Transition metals may work as catalysts in the thermal- and photodegradation processes of polyolefin. These processes are triggered by oxygen, heat, and UV light, and proceed through radical chain reactions, resulting in low molecular weight oxidation products (oxygen is entered into carbon chain in hydroxyl, peroxide, and carbonyl form). (Scheme 1) [2–6].



Scheme 1. Oxidation mechanism of polyethylene [5,6].

In the case of oxo-biodegradable materials, there are two stages of degradation, namely biotic and abiotic. The abiotic process consists of oxidative degradation, which occurs as a result of pro-oxidants (the polymer breaks down into smaller fragments). The second stage is the biotic process, in which microorganisms transform the oxidation products resulting from the abiotic process into biomass and CO₂. Oxo-biodegradable polymers do not degrade as quickly as biodegradable ones [2–6].

It has been long disputed whether chemical additives work as described by manufacturers, harm the environment, and make plastic recycling more convenient and efficient. Due to these uncertain reports, the parliament of the European Union planned a total ban on ‘oxo-degradable’ materials for the whole EU in 2014. This move was halted in mid-2015, and a resolution was passed to analyze the environmental impact of using oxo-degradable plastics [7,8]. In 2017, the European Commission published a report entitled ‘Study to provide information supplementing the study on the impact of “oxo-degradable plastic” on the environment’. The results of the report were inconclusive [9]. After this analysis, and because of ‘a lack of consistent evidence about the rate of abiotic and biotic decomposition in the environment’, the EU has prohibited the use of oxo-biodegradable materials from the 3 July 2021 [2]. The decision to forbid the use of plastics only applies to European countries and does not apply to the rest of the world.

The degradation testing of oxo-degradable plastics can be carried out through accelerated laboratory tests (UV aging tests with a UV fluorescence or xenon chamber) or under natural environmental conditions (soil, sea, pond, river, natural weather conditions). Accelerated laboratory tests should only be complementary to tests conducted in natural ecosystems, as they do not give a complete picture of the degradative changes in the polymer. In the environment, the speed of degradative change depends on many factors, such as geographical location, climate, or season, which have an impact on the temperature, humidity, or the amount of UV light emitted. Also in the natural environment, different concentrations and types of microorganisms (bacteria, yeast, and fungi) are found, which, although they make the standardization and reproducibility of the studies carried out more difficult, are best practice. However, in the environment, plastic is not the only source of

carbon for micro- and macroorganisms and the biodegradation rate can be overestimated in laboratory tests.

In 2020, a new PAS 9017 specification was developed to provide pass criteria, time-frames, and methods to demonstrate that oxo-biodegradable polyolefin will degrade in the terrestrial environment in the open air (i.e., unmanaged disposal or littering) without forming plastic microbeads. [2]. Each oxo-biodegradable material, which has a different application and varies in composition, also requires a different biodegradation research approach [4].

In recent decades, oxo-degradable and biodegradable materials have been investigated in complex media, like outdoor weathering [10–12], soil and compost [13–17], sea water and freshwater [18–22], and under monitored experimental conditions [23–26], e.g., with identified microbial strains.

Vazquez et al. [10] wrote that prodegradant additive in polyolefin accelerates degradation after natural (4 years) and UV (5 days) accelerated aging processes. The samples with d2w were significantly more degraded than the base polyolefin under same conditions, and the results demonstrate that the chain scission of the polyolefin with d2w is not being improved to an extent that would allow biodegradation.

Chiellini et al. [27] reported 12–48% biodegradation of thermally oxidized (accelerated aging at either 55 °C or 70 °C) oxo-degradable polyethylene films (with d2w) in river water in a 100-day time frame. The biodegradation was assessed by monitoring the amount of CO₂ in a respirometer apparatus.

An Ojeda et al. [12] study aimed to evaluate the abiotic and biotic degradation of polyethylene without and with the pro-oxidant additive (d2w). These materials were exposed to natural weathering and, after a year of exposure, samples of the bags were incubated in substrates (compost, perlite, and soil) at 58 °C and 50% humidity. The biodegradation of the materials was estimated with their mineralization to CO₂. These samples showed a mineralization level of 12.4% after three months of incubation with compost. PE without pro-oxidant additive and exposed to natural weathering showed little biodegradation.

Two studies [23,24] were published in 2021 to examine the correlation between artificial laboratory UV-accelerated weathering and the outdoor exposure of pro-oxidant additive plastics (with d2w) according to PAS 9017: 2020. The temperate accelerated UV-weathering cycle over 14 days demonstrated an approximate correlation to 90 days of outdoor exposure in Florida for the PE film studied.

The biodegradation of plastics generally leads to the creation many microplastics, which remain in the environment (water, soil) for some time. To date, the studies conducted do not allow a credible evaluation of the ecotoxicity of oxo-biodegradable materials on natural environments [28–30]. Further research is required to evaluate the potential effects of the accumulation of transition metals (acting as either catalyst or pro-oxidant) from oxo-biodegradable plastics, especially in the water environment and the organisms living in it.

Today, plastic pollution of the seas and oceans is a huge problem. Plastic litter can enter saltwater through rivers or freshwater. Packaging plastics, before they reach larger saline bodies of water, have their sources in freshwater (rivers, lakes, ponds), where different biotic and abiotic conditions prevail. Before they reach the seas and oceans, the first degradation processes start in freshwater. In this study, an attempt was made to carry out the degradation process in the freshwater of a pond due to the rich biotic life of freshwater organisms. The purpose of this study was to assess the environmental degradation process of oxo-biodegradable polyethylene samples under natural weathering conditions, in freshwater (pond), and under laboratory water conditions. Only abiotic weathering led to fragmentation of the polymeric samples, while the effect of incubation in the pond was biofilm coverage of the sample surfaces. The degradation was carried out in the natural environment to observe how nature would cope and what would happen to the

material if uncontrolled rubbish was deposited in the natural environment (ponds, forests, fields).

2. Materials and Methods

2.1. Environments

The environmental degradation of polymeric materials has taken place in three environments: in the natural weathering, freshwater (pond), and laboratory water.

The degradation of oxo-biodegradable polyethylene under natural weathering conditions was carried out on a polystyrene pad placed in the Rumia's garden (latitude: 54°35' N; longitude: 18°23' E) [31]. The polymer samples placed on the pad were covered with a mosquito net, which allowed free airflow, precipitation, and solar radiation access.

The incubation of polymeric samples in freshwater was performed in Rumia's natural pond [32–34]. The polymer samples were placed in a particular perforated basket, which was suspended on a rope 2 m below the water surface. The perforated structure of the basket allowed the free flow of water and access of microorganisms and enzymes dissolved in the freshwater to degrade the material samples [35].

The natural pond was an extremely micro- and macrobiologically rich environment. In addition to the identified freshwater vegetation, such as reeds, cudweed, grasses, eyelashes, waterweed, duckweed, and water lilies, the presence of carp, trout, pike, and roach was observed, as were plankton, algae, and invertebrates (annelids, leeches). Among other things, the activity of microorganisms contributes to the formation of dead organic matter, which was also observed in the pond.

For comparison, the incubation of the polymer samples was also carried out in distilled water in the laboratory (without solar radiation) to exclude microbial activity and assess the polymers' resistance to hydrolysis. During the entire four-year experiment, the distilled water was not changed, only replenished when it evaporated (the replenished water had a TDS of 0 ppm).

A comparison of the three research environments is provided in Table 1.

Table 1. Comparison of research environments.

Environment	Location GPS	Type of Environment	Description
Natural weathering	54° 35' 0'' N 18° 23' 34'' E	atmospheric air	The polymer samples placed on the pad in the garden were covered with a mosquito net, which allowed free airflow, precipitation, and solar radiation access.
Natural pond	54° 33' 38'' N 18° 22' 11'' E	freshwater	The polymer samples were placed in a particular perforated basket, which was suspended on a rope 2 m below the water surface in the pond.
Laboratory water	54° 31' 35'' N 18° 30' 41'' E	distilled water	The polymer samples were placed in an aquarium with distilled water without solar radiation in the laboratory.

Note(s): Source: own research.

The temperature, pH, and TDS of aquatic environments was monitored throughout the degradation process of oxo-biodegradable polyethylene.

The degradation of the investigated samples lasted for a period of up to 48 months.

2.2. Material

Polyethylene (HDPE) bag samples containing a pro-oxidant additive (d2w—Symphony Environmental—UK), with 0,02 mm thickness, were obtained in "Castorama" market from Rumia, Poland.

The manufacturer had stated on the bag that the 100% oxo-biodegradation process takes place under the right conditions when exposed to external factors such as light, water, or oxygen over a period of up to two years. These tests are usually conducted in an environmental chamber in a laboratory simulating real-life scenarios. The degradation process under such conditions is accelerated and standardized [22]. In this paper, testing

the oxo-biodegradability of polymer plastics in natural environments only complements the research that the plastics manufacturer has conducted.

Polymer film was cut into 150 × 20 mm rectangles. After degradation, the samples were washed, dried at room temperature, and then taken for testing.

2.3. Methodology

The macro- and microscopic observations, weight changes, chemical structure, and mechanical properties of oxo-biodegradable polyethylene were investigated before and after exposure in the natural and laboratory environments.

- The macro and microscopic observations—the polymer samples were observed in a macro (naked eyes) and micro scale (microscopic observation). Macroscopic observations of the polymer surface were analyzed organoleptically using a FujiFilm S2500 HD camera, whereas microscopic observations of the polymer structure were analyzed with the metallographic microscope ALPHAPHOT-2YS2-H Nikon linked to the photo camera Delta Optical DLT-Cam PRO 6.3MP USB 3.0. The micrographs were collected under transmitted light. The images of the polymer samples before and after degradation were compared.
- The changes of weight—the dried polymer samples were weighed on an analytical electronic balance (RADWAG AS 160.X2, repeatability 0.1 mg). The weight of clean and dried polymer samples after incubation in the natural and laboratory was compared with the one before incubation. The final results of the determinations were the average of the five sample measurements.
- The changes of chemical structure—Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to determine the characteristic groups of oxo-biodegradable polyethylene. FTIR spectra were recorded with an attenuated total reflection (ATR Smart Orbit Accessory, Thermo Fisher Scientific, Madison, WI, USA) mode on a Nicolet 380 FTIR spectrometer (Thermo Scientific, Madison, WI, USA) with a diamond cell. A resolution of 4 cm⁻¹ and a scanning range from 600 to 4000 cm⁻¹ were applied, and 48 scans were taken for each measurement.
- The changes of mechanical properties—the tensile strength (MPa) and elongation (%) was measured at room temperature using The Tensile Testing Machine MultiTest 1-xt made by Mecmesin, according to PN-EN ISO 527-1, 3: 2018-19 Standard [36,37]. The final results of the determinations were also the average of the five sample measurements.

3. Results and Discussion

3.1. The Characteristic Parameters of Environments

The experiment was conducted over a period of four years and the parameters of the environments (natural weathering, freshwater (pond), and laboratory water) were measured during the months of sample removal. The average values of the measurements are shown in Table 2.

Table 2. The average parameters of environments from 2018–2022.

Months	Weathering Parameter's		Pond Parameter's				Laboratory Water Parameter's			
	T [°C]	Humidity [%]	T [°C]	pH	TDS [ppm]	Oxygen Content [mgO ₂ /dm ³]	T [°C]	pH	TDS [ppm]	Oxygen Content [mgO ₂ /dm ³]
July	25	40	20	8.7	183	6	26	7.8	42	8
October	12	53	11	8.2	201	8	18	7.7	42	7
January	5	30	4	8.5	192	10	17	8.0	38	7
April	7	30	8	8.6	175	9	17	7.7	48	7

Note(s): The measurement error environmental parameters: T ± 0.2; pH ± 0.01; TDS ± 0.02; Humidity ± 0.1; Oxygen content ± 0.1. Source: own research.

Air is mainly nitrogen (78%) and oxygen (21%), with a small volume of noble gases (1%). Currently, the concentration of air constituents remains relatively constant [38]. The natural weathering of polymers (oxidative degradation) is via their breakdown under the influence of mainly atmospheric oxygen, but also temperature, sunlight, water, and living organisms. Depending on these factors, physical, chemical or biological weathering occurs. All these processes interact with each other, which can contribute to amplifying some of them, e.g., chemical weathering occurs faster when supported by physical weathering. This is due to better penetration of aqueous compounds into the polymer surface. Physical weathering is determined by thermal relations; it occurs most intensively at very high amplitudes of air temperature: daily and annual (seasons). The lower the air temperature, the more intense is the physical weathering (Table 2—January 5 °C). Chemical weathering depends on water conditions and temperature: the higher the temperature and humidity, the more intensive is the chemical weathering (Table 2—July 25 °C). Biological weathering occurs where there is biological activity by living organisms [39].

The temperature of both natural environments varied markedly over the duration of the experiment (from 4 °C to 26 °C) and was dependent on the weather conditions (summer and winter). From the parameters shown in Table 2, it can be seen that the average temperature during the natural weathering was around 12 °C, and 11 °C in the pond. Enzymatic degradation occurs best at higher temperatures (20–60 °C); lower temperatures slow down microbial activity [40]. The average temperature of the laboratory water was the highest compared to the other environments (19.5 °C), as the incubation was carried out in the laboratory.

Atmospheric humidity ranged from 30% to 53% during the natural weathering. The samples were exposed to sunlight on the south side of the garden, where insolation was greatest. Sunshine, precipitation, and direct access to oxygen influenced the decomposition of the test material. Abiotic parameters had the greatest impact on the decomposition of oxo-biodegradable polyethylene [2].

In the biodegradation process the recommended pH value is 5–8; in the test environments the pH values were mildly alkaline and exceeded the upper limit slightly. [40]. The average pH value was 8.5 in the natural pond. Only the growth of photosynthetic organisms in high solar radiation during the summer months was able to raise the pH of natural water (8.7 in July) [41]. The average pH of the laboratory water was 7.8, but there was no solar radiation or microorganisms.

TDS (total dissolved solids) is an indicator of the total content of all mobile charged ions in a water solution. This includes: minerals, metals, and salts dissolved in a given volume of water. The total dissolved solids in water included inorganic salts and organic substances. The average TDS values in the laboratory water were at 42 ppm, indicating a low content of inorganic salts in the water, most likely due to the gradual release of ink from the surface of the labeled samples. In the pond under natural conditions, the TDS values were much higher, in the range of 175–201 ppm, indicating the presence of inorganic salts and organic substances. The pond was a natural water reservoir that is micro- and macrobiologically active. The alkalinity and low temperature of pond could have affected the psychrotrophic bacteria action, which could adjust to such variable conditions.

Oxygen is essential for the life of organisms. The oxygen content in air is 20.98%, while the dissolved oxygen content in natural waters is in the range of 0 to 14 mgO₂/dm³. Waters take up oxygen primarily from the atmosphere. A second source of oxygen in water is that given off by plant photosynthesis. The amount of oxygen from photosynthesis is much less than from the air [42–44]. Table 2 shows the dissolved oxygen concentration in the pond, which ranged from 6 to 10 mgO₂/dm³ and 7 to 8 mgO₂/dm³ in the laboratory water. The amount of dissolved oxygen in the water depends on the temperature of the water depending on the season: the lower the water temperature, the higher the oxygen content. The oxygen content of the water can also fluctuate widely throughout the day. During the day, photosynthesis with the release of free oxygen can occur with strong sunlight and the growth of aquatic plants. Oxygen saturation of the water then occurs, which manifests

itself as foam on the water surface. During the night, photosynthesis does not take place and there is a sharp drop in oxygen content when aquatic organisms breathe heavily. Fish then swim close to the water surface and have an increased respiration rate. Therefore, the dissolved oxygen content in the water should not be less than 3–4 mgO₂/dm³. The oxygen content of the water is at least a limiting factor for the self-purification processes of water bodies (biodegradation). In surface waters polluted with organic substances, dissolved oxygen is consumed in the biochemical decomposition processes of these substances. The greater the water pollution, the lower the oxygen content. When the oxygen content is significantly reduced, disturbances in the biocenosis occur. Mineral substances, e.g., micro- and macroelements, are required for biodegradation, in addition to oxygen, microorganisms, and enzymes [42–44].

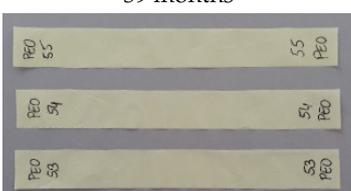
3.2. The Changes of Oxo-Biodegradable Polyethylene during Environmental Degradation

The environmental degradation of the tested polyethylene with d2w additive samples was first assessed visually. Table 3 illustrates macrographs of the polymer surfaces before and after degradation in different environments.

Table 3. Macrographs of oxo-biodegradable polyethylene samples before and after degradation in different environments.

Natural Weathering	Pond	Laboratory Water
before degradation	before degradation	before degradation
6 months	6 months	6 months
12 months	12 months	12 months
18 months	18 months	18 months

Table 3. Cont.

Natural Weathering	Pond	Laboratory Water
		
24 months	24 months	24 months
		
32 months	32 months	32 months
		
36 months	39 months	39 months
		
39 months	45 months	45 months
		
	48 months	48 months

Note(s): Source: own research.

Before degradation, the oxo-biodegradable polyethylene samples were white, matt, thin, and flexible.

The polymer samples decayed most rapidly under natural atmospheric conditions (Table 3). The first cracking of the samples was observed after 18 months of degradation, and after 24 months the cracking covered all the samples in larger fragments. The following months saw increasing fragmentation of the material until month 39, when the defragmentation was greatest. After 45 months, the samples were completely assimilated into the environment. As the tested material contained an added pro-oxidant, the decomposition into fragments was mainly due to abiotic parameters (oxygen, solar radiation, temperature, air humidity), which are most active in atmospheric weathering. These results confirm the importance of abiotic degradation for polymers with d2w additive, as was also emphasized by Ojeda et al. [12].

Macroscopic changes on the surface of polyethylene with d2w additive after incubation in a natural aquatic environment indicated their very sluggish environmental degradation. After six months of incubation in the pond, slightly dark brown spots could be observed

on the surface of the polymer, which became more visible and darker over the next months of degradation. This was a consequence of microbial activity and the gradual biofilm formation on the surface of the samples. The biofilm, on the one hand, hinders the access of oxygen and sunlight to the degradable material, which is very important for the degradation of the oxo-biodegradable polymer. On the other hand, the accumulated microorganisms that form a biofilm on the surface are very close to the degradable material, although this does not necessarily mean that they will degrade it quickly. Biofilm can result in different mechanisms of polymer deterioration, such as fouling, degradation of leaching components, corrosion, hydration, penetration, and changes in coloration [45]. From the 39th month of incubation, there was some loss of material, but there was no fragmentation of the samples in the following months of incubation under natural aquatic conditions.

The decomposition of oxo-biodegradable plastics produces plastic micro particles that accumulate in the natural environment. This has also been confirmed by other authors [46,47]. Microplastics pose a potential risk to flora and fauna [48] and affect microbial communities in the pond.

No visible changes were observed on the surface of the polyethylene with d2w additive samples after incubation under laboratory conditions. Because of the lack of solar radiation and microorganisms in the laboratory test, only chemical hydrolysis could be expected [34].

The macroscopic observations were consistent with the changes in the mass of the polymer samples. The results of the weight changes of the tested oxo-biodegradable polyethylene samples are shown in Table 4.

Table 4. Weight changes [%] of oxo-biodegradable polyethylene samples before and after degradation in different environments.

	Degradation Time [Months]											
	3	6	9	12	18	24	27	32	36	39	45	48
Natural weathering	+0.3	−0.8	−0.7	−1.4	−2.0	−8.4	−20.7	−26.2	−62.0	−81.6	destroyed	
Pond	+0.9	+1.7	+1.5	+3.5	+5.5	+4.3	+5.4	+6.6	+13.0	+19.5	+24.3	+19.1
Laboratory water	−0.2	−0.2	−0.7	−0.8	−0.7	−0.6	+0.8	+1.3	−0.8	−0.8	−0.8	−0.3

Note(s): Source: own research.

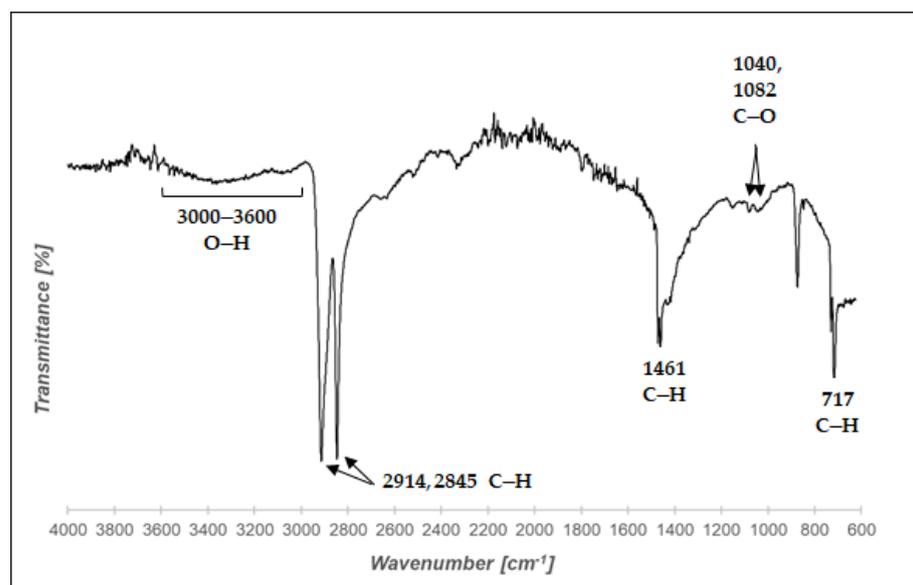
The results of the mass change of the degraded oxo-biodegradable polyethylene differed depending on the environment.

Under atmospheric weathering conditions, a gradual mass loss was observed of 81.6% after 39 months. After 45 months, the samples were completely decomposed in the natural environment. Solar radiation, precipitation, and the presence of oxygen played a central role in the decomposition of the plastic, which caused the activation of the d2w additive and consequent cutting of the polyethylene chain [2,20]. According to the manufacturer, the material should decompose 100% within two years. In the natural environment, the decomposition time of oxy-degradable polyethylene was twice as long.

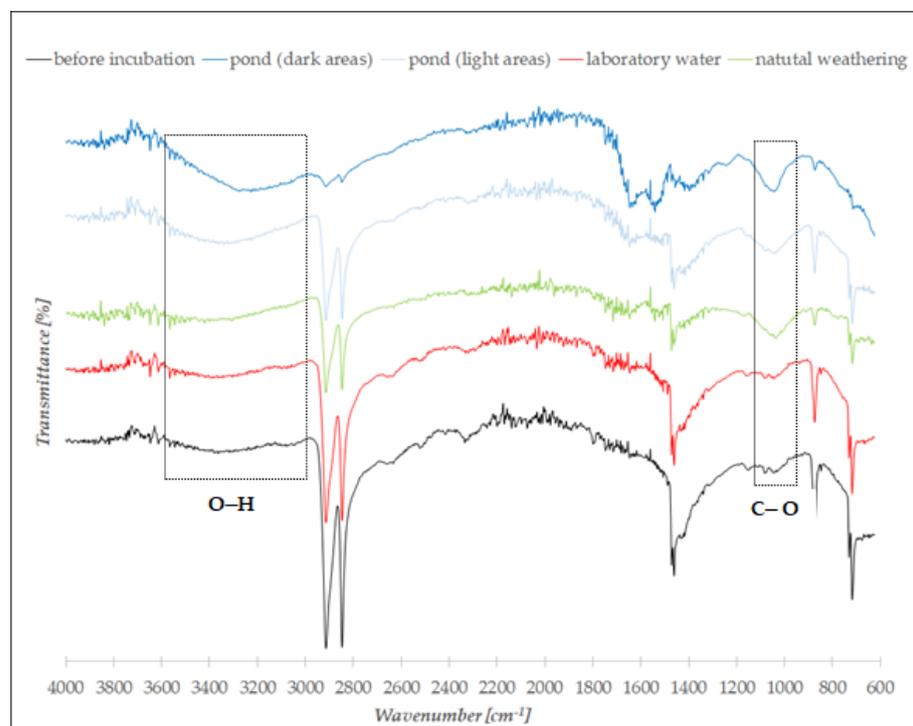
The results of the changes in the mass of oxo-biodegradable polyethylene in a natural pond were interesting. The mass loss of the polymer was expected because of the presence of microorganisms and dissolved enzymes in the water. A gradual accumulation of biofilm observed on the plane of the incubated samples, which consequently led to an increase in mass (19.1–24.3% over a period of 39–48 months). The biofilm formation was sufficiently high that the sample losses observed on the macroscopic images did not affect the weight loss of the samples. The degradation of oxo-biodegradable polyethylene in the freshwater occurred very slowly because the pond had a lower temperature, oxygenation, and less access of sunlight to the degraded material (Table 2). It required a much longer incubation time. The key role that abiotic degradation plays in the biological decomposition of plastic is highlighted by experiments by Rose et al. [20] on artificially aged samples of polyethylene with d2w additive.

During incubation of the test samples in laboratory water in the laboratory, despite a constant temperature (about 18 °C) and oxygenation (about 7 mgO₂/dm³), no significant changes in mass were observed to indicate chemical hydrolysis taking place (from −0.8% to +1.3% over four years of incubation).

The progression of polyethylene with d2w additive degradation was also examined by evaluating the change in its chemical structure after degradation in different environments (Figure 1).



(a)



(b)

Figure 1. ATR-FTIR spectra of the oxo-biodegradable polyethylene samples in the wavenumber of 600–4000 cm⁻¹: (a) before degradation with characteristic peaks; (b) before and after degradation in different environments. Note(s): Source: Own research.

The peaks localized at 2914 and 2845 cm^{-1} belonged to symmetric and asymmetric C–H stretching vibrations. Initially, there is C–H stretching, and then there is a pronounced drop in the peak, corresponding to bond cleavage. This was true for all the samples, especially after degradation in the pond and natural weathering. Further changes occurred at the band (1461 cm^{-1}) related to CH_2 scissoring groups, and at the bands (717 cm^{-1}) indicating CH_2 rocking vibration. The other small absorption, at 1040 and 1082 cm^{-1} , belongs to some C–O bonds that appeared due to the atmospheric oxidation of the investigated polyethylene surface after degradation in natural environments: pond and weathering [49–54]. In the natural weathering environment, abiotic parameters played the dominant degradative role, while in the pond the changes in the incubated polymer were the result of both abiotic parameters and the presence of microorganisms (biofilm penetration) [45]. The absorption found in the range 3000–3600 cm^{-1} indicated the existence of O–H groups (because of the formation of hydroperoxides and alcohols during oxidation reactions), which was more pronounced in the oxo-biodegradable polyethylene after biodegradation in the pond and suggested partial water affinity. The observed changes in the spectra suggested the appearance of oxidation and degradation of the used material [49–54].

Using the results of the FTIR analysis, the carbonyl index (CI) values were calculated according to Equation (1):

$$\text{CI} = \text{Absorbance at } 1713 \text{ cm}^{-1} / \text{Absorbance at } 1464 \text{ cm}^{-1} \quad (1)$$

CI—absorbance ratio of carbonyl and methylene groups. This makes it possible to determine the amount of carbonyl compounds formed during the photo-oxidation process [50,52,55].

The carbonyl index helps to determine the amount of carbonyl compounds created during the photo-oxidation process. Figure 2 shows the carbonyl index results for polyethylene with d2w additive before and after degradation in different environments. A reduction in the carbonyl index was observed in all the samples after degradation in natural weathering, pond, and laboratory water.

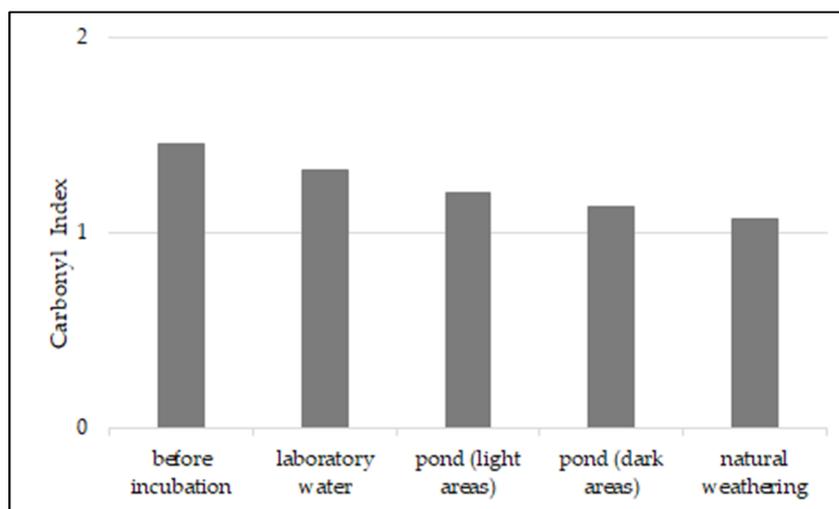


Figure 2. The carbonyl index of the oxo-biodegradable polyethylene samples before and after degradation in different environments. Note(s): Source: Own research.

Referring to the literature [56–58], the carbonyl index after the degradation of the oxy-degradable samples should increase. The authors of the publication [34,50,56,59] showed that an essential part of the oxidation product is neglected as it evaporates into the atmosphere. Because of this, the indicator cannot be regarded as a reliable probe for measuring the degree of oxidation and does not represent the total degradation of

weight changes, mechanical properties and micro- and macroscopic observations of the investigated polymer.

The effect of the degradation process under natural weathering, pond, and laboratory water conditions on the mechanical properties of the polymer tested was also assessed. Changes in the mechanical properties of polyethylene with the d2w additive samples after environmental degradation were investigated by measuring tensile strength at break and elongation. The results are reported in Table 5 and Figures 3 and 4.

Table 5. Mechanical properties of oxo-biodegradable polyethylene samples before and after degradation in different environments.

		Degradation Time [Months]												
		0	3	6	9	12	18	24	27	32	36	39	45	48
Natural weathering	F _m [N]	15.41	9.91	11.66	10.62	9.43	4.30							
	R _m [MPa]	26.31	24.78	29.14	26.56	23.58	10.76				fragmentation			
	E [%]	304	24	53	18	6	1				fragmentation			
Pond	F _m [N]	15.41	15.75	17.13	17.65	15.08	15.00	15.09	13.80	13.47	11.98	10.53	9.64	6.94
	R _m [MPa]	26.31	32.07	42.83	44.12	37.70	37.50	37.74	34.49	32.59	29.95	26.32	24.09	17.35
	E [%]	304	305	261	326	282	255	242	243	264	167	40	35	31
Laboratory water	F _m [N]	15.41	13.20	13.46	16.18	16.61	18.29	17.44	17.29	17.19	15.59	14.76	14.96	15.60
	R _m [MPa]	26.31	33.01	33.66	40.46	41.51	45.72	43.59	43.22	42.98	38.97	36.90	37.40	39.00
	E [%]	304	266	240	321	331	337	346	334	305	305	298	334	339

Note(s): Source: own research.

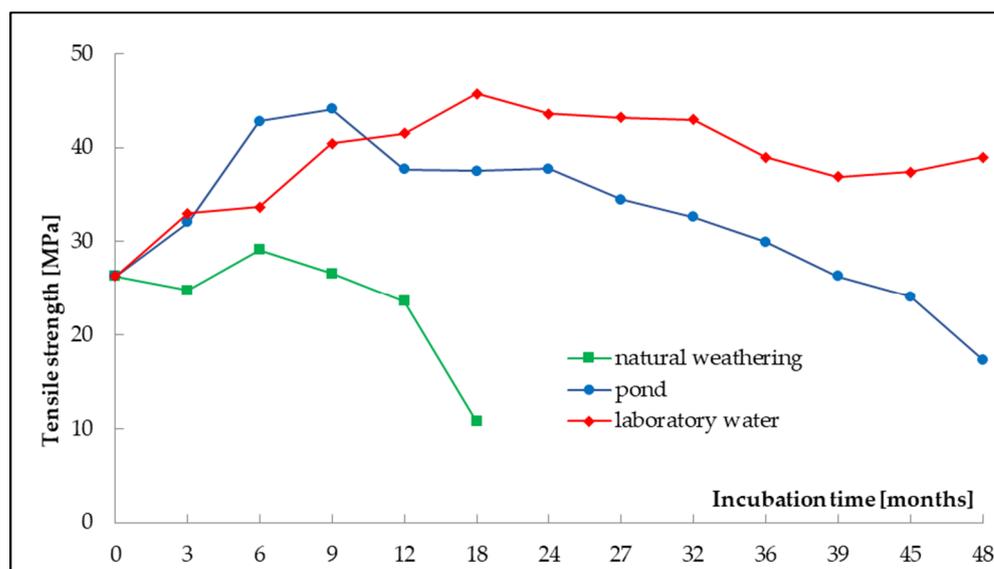


Figure 3. Tensile strength [MPa] of oxo-biodegradable polyethylene samples before and after degradation in different environment. Note(s): Source: own research.

Changes in mechanical properties like tensile strength and elongation at break may give information about the type of changes induced by the chain modifications during degradation. Longer chains can resist the stress better than shorter ones (shorter chains can move easily when they are under stress), then mechanical resistance will be lower if there is chain scission [10].

Analyzing the changes in tensile strength, we can see that the tensile strength was constantly decreasing for oxo-biodegradable polyethylene samples during degradation in natural weathering (to 10.76 MPa), which can be attributed to the activity of solar radiation, precipitation, and the presence of atmospheric oxygen. Changes in the tensile strength could be determined up to the 18th month of natural weathering degradation, as the polyethylene with d2w additive samples fragmented in the following months.

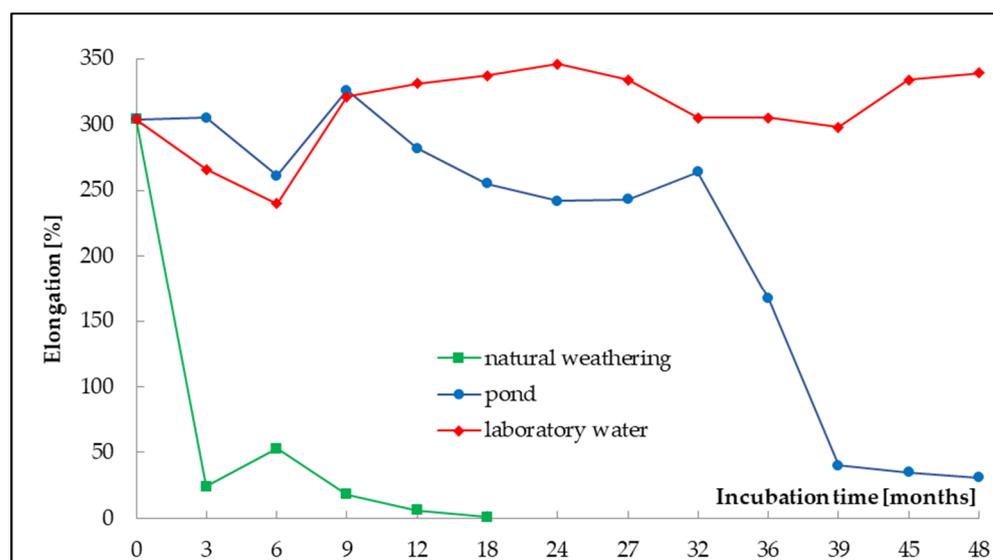


Figure 4. Elongation [%] of oxo-biodegradable polyethylene samples before and after degradation in different environments. Note(s): Source: own research.

In opposition to the degradation of the polymer samples in natural weathering, an increase in tensile strength was noted at the early stages of incubation in natural pond. This may be due to unexpected additional crosslinking through unstable peroxide bridges as a result of the synergistic action of biotic and abiotic factors in freshwater, or by a sort of plasticization effect influenced by low molecular weight fraction generated in the first phase of the oxidative degradation of the polymer matrix. Over the same time, the polymer weight increased [34,57,60]. From the 12th month of exposition of biodegradable samples in the pond, the slowly decrease of tensile strength (to 17.35 MPa after 48 months) was observed (Figure 3). A possible cause was the activity of microorganisms in this environment, which could have influenced enzymatic degradation on the polymer surface. This behavior can also be the result of the superimposed effects of various aging processes, such as chain cracking (leading to a decrease in R_m), or branching and crosslinking (an increase in R_m). During degradation, an initial improvement in mechanical properties is often observed, and only after a sufficiently long period of time is there a deterioration in the film's properties indicating degradation [57,60,61].

In the samples incubated in laboratory water, an increase in tensile strength was observed throughout the incubation period, which could be explained only by water-induced sequencing of the polyethylene chains.

The graph curves in Figure 4 demonstrate that the elongation of polyethylene with the d2w additive samples decreased slowly only during incubation in the natural environment. Also, in the case of the elongation at break, both a decrease and an increase were observed. As with the changes in strength, a trend can be observed: this parameter decreases in a natural weathering environment and increases and decreases in aqueous environments. This means that the initial stages of oxidative photodegradation proceed with a deterioration in the strength of the sample and a decrease in its elasticity, while in aqueous environments the strength and elasticity increase. Increasing the time of environmental exposure results in both a decrease in strength and elongation at break in most samples, so the impact of the degradation taking place is clearly visible [60]. A more significant decrease in the elongation of the samples was noted after degradation under natural atmospheric conditions (from 304% to 1% after 18 months) then after degradation in natural pond (from 304% to 31% after 48 months). An increase in the elongation of the test samples could be observed throughout the incubation time in laboratory water. The results of the reduction in elongation of the samples confirm the findings of the reduction in tensile strength.

Finally, the degradation of the investigated polyethylene with the d2w additive samples was assessed by changes in polymer morphology (Table 6). After degradation in the environments, the analyzed samples were not homogeneously destroyed. Images of the polymer structure varied depending on the analysis site. The most frequently repeated images were those observed under a metallographic microscope.

Table 6. Micrographs of oxo-biodegradable polyethylene samples before and after degradation in different environments.

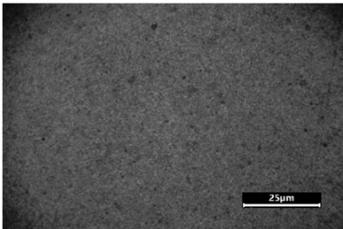
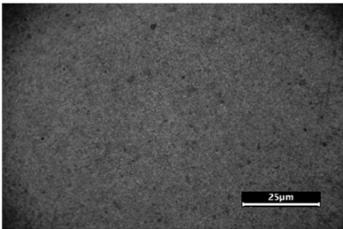
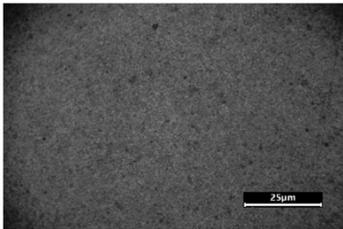
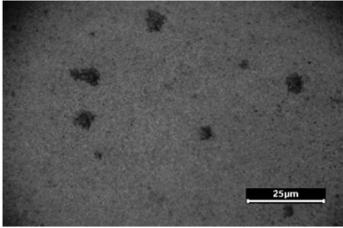
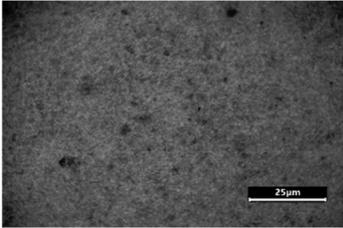
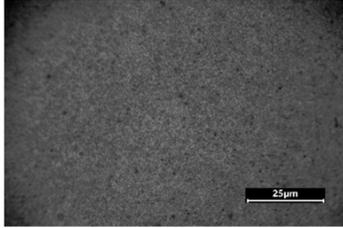
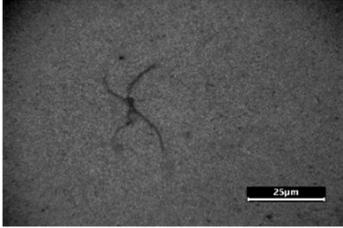
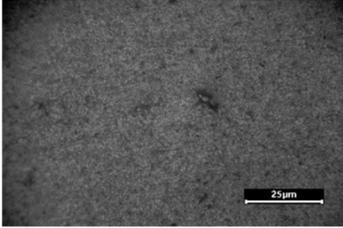
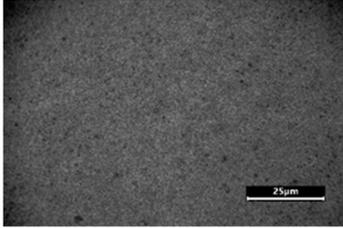
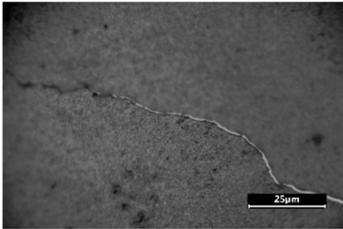
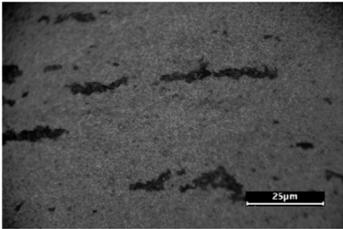
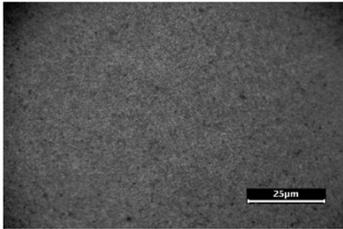
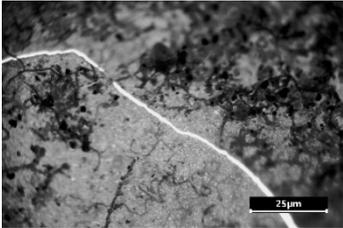
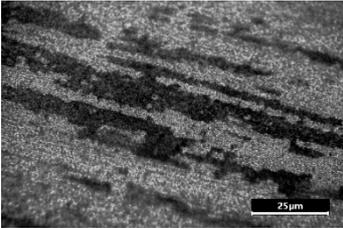
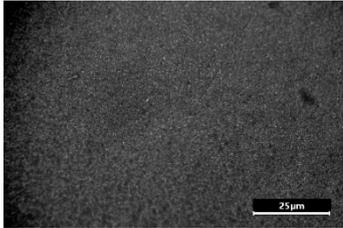
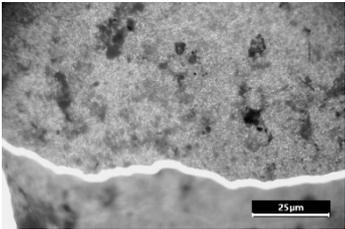
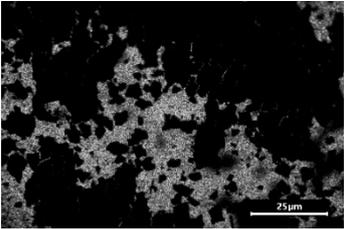
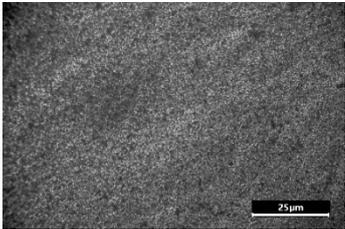
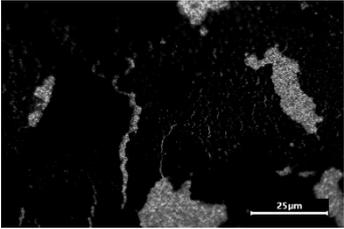
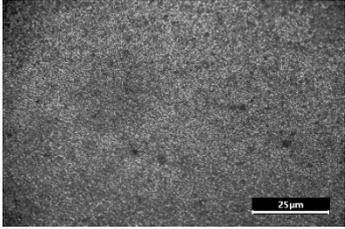
Natural Weathering	Pond	Laboratory Water
		
before degradation	before degradation	before degradation
		
6 months	6 months	6 months
		
12 months	12 months	12 months
		
24 months	24 months	24 months
		
36 months	36 months	36 months

Table 6. Cont.

Natural Weathering	Pond	Laboratory Water
 39 months	 45 months	 45 months
	 48 months	 48 months

Note(s): Source: own research.

The morphology of the oxo-biodegradable polyethylene sample before degradation was homogenous without any oriented phase.

If we take a look at the micrographs, we can see the first slightly different surface degradation of the polymer samples after 6 months of incubation in natural weathering. After 12 months of degradation, the first cracks can be observed on the surface of the samples, which are caused by the presence of oxygen in the atmosphere. During the following months of exposure of the oxo-biodegradable polyethylene in natural weathering, the polymer surface is more degraded, characterized by more frequent and larger cracks, caused by further interference from abiotic parameters (oxygen, solar radiation, temperature, air humidity). In addition, after 36 months of degradation, dark stains appear on the surface of the samples, indicating the presence of microorganisms.

The incubation of the oxo-biodegradable polyethylene samples in the natural pond leads to a gradual appearance of many dark places of different sizes and shapes on the surface (especially after 45 and 48 months), which probably corresponds to created agglomeration of biofilm microorganisms on the surface of incubated samples [62].

It is widely known that microorganisms can form a biofilm on the surface of polymers in any environment. The biofilm is involved in polymer destruction, but its quantity on the surface depends on the bacterial species, temperature, pH, and incubation time [19,63]. Rose et.al [20] demonstrated that different bacterial strains can be employed to evaluate polymer degradation.

The degradation process of the polyethylene with d2w additive samples in laboratory water was unspectacular. Due to the lack of access to light and microorganisms, there have been no marked changes of morphology after 48 months incubation in laboratory water, which cannot unequivocally confirm the occurrence of hydrolytic degradation.

4. Conclusions

Oxo-biodegradable polyethylene in the natural environments is not as “biodegradable” as in simulated laboratory tests. The degradability depends on the particular surroundings. Sunshine, precipitation, temperature, oxygen content, pH and diversity of microorganisms vary across natural environments, which results in different biodegradation rates.

Summarizing the results of the research, the following conclusions can be drawn with regard to the behavior of the polyethylene with d2w additive in investigated environments:

- Natural weathering is an oxidative degradation that produces hydroperoxy, hydroxy, carbonyl groups, and crosslinking. The effects of natural weathering are surface changes, brittleness, weight change, and loss of mechanical properties.
- The results of macroscopic and microscopic observations, changes in weight and mechanical properties indicate a slowly degrading process under natural weathering conditions (39 months), although the manufacturer declared faster degradation (up to 24 months). Natural weathering resulted in a reduction in weight to 81.6% after 39 months and complete assimilation of the samples after 45 months, while the 48-month incubation in the pond led to an increase in the weight of the samples (+19%).
- The enzymatic degradation of the samples in the natural pond was very slow—after 48 months the samples did not fragment, only swelled. The degradative effect of microorganisms was evident in the reduction of the strength parameters of the tested samples. In the pond after 48 months of incubation, the tensile strength decreased from 26.31 to 17.35 MPa and the elongation at break reduced from 304 to 31%.
- Due to the significant fragmentation of the samples, mechanical properties could be determined up to the 18th month of degradation in natural weathering: tensile strength decreased to 10.76 MPa and elongation at break to 1%.
- During the degradation, the initial improvement in mechanical properties and, only after a sufficiently long period of time, the deterioration in film properties indicated that degradation is due to the superimposed effects of various aging processes, such as branching and crosslinking (max. increasing R_m to 45.72 MPa) and chain cracking (leading to a decrease in R_m to 10.76 MPa).
- The microbial biofilm formed, on the one hand, accumulates microorganisms on the polymer surface and, on the other, restricts the access of radiation and oxygen to the oxo-biodegradable plastic, thus slowing down the degradation process.
- FTIR spectroscopy interpretation showed that the degradation process exists in natural environments (atmospheric weathering and freshwater), and the polyethylene with d2w additive appeared to be resistant to hydrolysis during the monitored time in the laboratory. The changes concern C–H groups (peaks 2914 and 2845 cm^{-1}), CH_2 groups (peaks 1461 cm^{-1} and 717 cm^{-1}), and C–O groups (peaks 1040 and 1082 cm^{-1}). The absorbance found at 3000–3600 cm^{-1} indicates the existence of O–H groups due to the formation of hydroperoxides and alcohols during oxidation reactions.
- After incubation under laboratory conditions, no visible degradation changes were observed in the polyethylene with the d2w additive samples. Because of the lack of microorganisms and solar radiation in the simulated laboratory test, only chemical hydrolysis can be anticipated.
- The degradation of the polyethylene with d2w additive in natural environments requires a longer incubation time compared to the degradation time declared by the manufacturer.

Given the high complexity of the natural degradation system, there is no standardization of test procedure for evaluating the biodegradability of oxo-biodegradable polyolefin in the natural environment. Studies carried out show abiotic degradation is a key step to biodegradation—natural weathering led to fragmentation of the polymeric samples. The results of the biodegradation studies in the pond show that samples can persist in the natural environment for years—a biofilm created on the surface of the samples, but the rate of biodegradation was slow.

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