

## Experimental investigations on polyethylene and polyethylene terephthalate microplastics' degradation. A review

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**Abstract.** A topic of high interest, the plastic degradation in the environment, is approached in this work, to serve for future research. The problem of plastics pollution became critical with the exponential development of plastic materials industry in last decades. Soil and water are primarily polluted, then degradation to microplastics leads to spatial distribution of plastic debris in all ecosystems. Slow natural degradation and pollutants accumulation on the plastic particles are responsible for environment unbalances. This work follows the new research about the induced degradation methods, abiotic and biotic, pointing out the most notable results. Most research took place in laboratories, but promising results of some biotic methods will hopefully lead to industrial scale-up.

**Keywords:** microplastics; degradation; polyethylene; polyethylene terephthalate.

### 1. Introduction

Since the industrial revolution, the industry evolved exponentially in all directions of development, including the environmental protection sector. Although most of present technologies are advanced and innovative, the industry still faces the main negative aspect of its activities, the environmental pollution. The impact of pollution has been amplified with the increase in the consumption of resources as well as of secondary goods derived.

An obvious example is represented by the plastics industry, which due to its many attractive physical and chemical properties such as elasticity, hardness and durability, have led to a dramatic increase in production up to market oversaturation despite the known social and environmental consequences.

The usefulness of plastics materials is overshadowed by the negative implications of the slow degree of degradation and their accumulation in the environment as waste and plastic debris [1].

Thereby, the subject of environmental pollution soon became a main issue due to the major and irrevocable repercussions on all ecosystems. So involuntarily, with the industry development, new forms of pollution also developed. One of these forms is represented by the microplastic pollution. This type of pollution is caused by the fragmentation of polymeric materials into particles smaller than 5 mm in size, as a result of the action of mechanical, chemical and biological factors [2].

Microplastics can be classified into two categories: primary and secondary, depending on the source and mechanism of formation. Primary microplastics are polymeric fragments resulted in the textile and personal

care goods industries, while secondary microplastics are polymeric particles resulting from the fragmentation of plastics in the environment [1].

The accumulation of small plastic particles in aquatic ecosystems was first reported in 1970 and the scientific term "microplastics" was first used by Thompson's work [3], since 2004. These fractions of polymeric material are less dense than the water, therefore they float and move along global water bodies carried by water and air eddies. In addition, microplastics can accumulate toxic contaminants on their hydrophobic surface and can be ingested by many aquatic organisms leading to ecological imbalances [4].

This form of pollution is extremely difficult to handle and control due to the many variables involved in the process, since its prevention solutions are extremely limited.

The aim of this work is to present the state-of-the-art of research for plastics induced degradation, with accent on polyethylene (PE) and polyethylene terephthalate (PET) polymers.

### 2. Factors affecting the polymers degradation

Degradation is an irreversible process leading to significant changes in the structure of a material, reflected in one or more properties, and caused by the action of environmental conditions [5]. Due to a wide variety of external factors such as exposure to UV radiation, wind, waves, seawater and bacteria, polymeric materials undergo various simultaneous processes leading to cracking, surface erosion, abrasion, and fragmentation into small particles [6].

Mainly, the degradation of plastics is strongly influenced by the nature of the polymer, the presence of

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various additives in the material, and normally can follow two directions: biotic or abiotic [5].

### 3. Mechanisms of polymers degradation

#### 3.1. Abiotic degradation

Depending on the nature of the responsible agent, the degradation of polymers by abiotic phenomena can be classified into: photodegradation, thermal degradation, ozone-induced, hydrolytic and mechanical degradation [7-9].

Photo-oxidative degradation is the decomposition process caused by the action of light. The process is considered one of the primary sources with consequences on the plastics substrate in different environmental conditions. Most of the synthetic polymers are susceptible to degradation initiated by sunlight or UV radiation [8].

Thermal degradation occurs through the fragmentation of plastics due to structural changes caused by temperature variation. In case of high temperatures, degradation is initiated by a thermo-oxidative reaction. However, for a plastic to be degraded thermo-oxidatively, enough energy in the form of heat is needed to break the chemical bonds [1].

Ozone-induced degradation is determined by the presence of ozone in the atmosphere, which, even in small quantities, causes an acceleration of the aging / degradation process of plastics materials. Exposure of polymers to ozone results in the formation of unstable intermediates that eventually lead to the decomposition of the macromolecule [8].

Hydrolytic degradation occurs on plastics containing heteroatoms in the main polymer chain, including polyaddition or condensation polymers such as polyesters, polyamides or polyurethanes, this category of polymers showing a high susceptibility to the hydrolytic process [9].

Mechanical degradation involves fragmentation under the influence of mechanical stress forces [8]. These processes can be initiated by the action of waves and tides when the plastic is present in marine environments but also by the abrasion produced with sediment particles on the coast [9].

Currently, the main widespread processes of plastic degradation are considered: the exposure to UV light, the fragmentation under the influence of mechanical forces, and the photodegradation, all leading to irreversible changes in the chemical, physical and mechanical properties of the polymeric material [10].

#### 3.2. Biotic degradation

Biodegradation use the systemic functions of some microbial species to convert polymeric substrates into smaller molecules that can be subsequently degraded into simple compounds as carbon dioxide and water. The efficiency of the biotic degradation process performed by the microorganisms is directly associated with key properties such as molecular weight and crystallinity degree of the material. Thus, polymer degradation is achieved with the formation of new products due to mineralization, a process in which simple final molecules are obtained, such as carbon

dioxide, water or methane. Biodegradation can be achieved under aerobic or anaerobic conditions, these determining the final products of degradation process.

Because of their chemical and physical characteristics, plastics materials are difficult to degrade through biotic mechanisms because they are solid materials, and the process must be initiated at the surface. The intrusion of microorganisms into the plastic structure is a very slow process and the rate of degradation depends mainly on the of the plastic's surface area [11]. In addition, this resistance comes mainly from the high molecular weight of the polymer, strong C-C bonds and extremely hydrophobic surface, which acts as a barrier, very difficult to be attacked by microorganisms [10].

### 4. Experimental studies on polymer degradation

Every year, a European report is issued, analyzing the production, the demand, and the waste management of plastics materials. The aim of this report is to evaluate the polymer industry from an economic point of view but also from the perspective of the material's life cycle. In 2018, a global plastic production of approximately 359 million tons was reported, a huge amount of 25% of post-consumer plastic waste being directed to landfills, and the rest being distributed for recycling or energy recovery. It is a worrying fact, that to these statistics one can add the quantities of plastic waste distributed spatially in the environment as the result of anthropogenic actions [12]. Due to the slow degradation rate, these plastics debris accumulate in marine and coastal areas, in sediments, but also in pelagic and benthic biota on the entire surface of the planet. Over time, these debris, under the simultaneous or individual action of various environmental factors (temperature, saline environment, UV radiation, mechanical forces, etc.) show structural and compositional changes because of degradation. Although the degradation of these materials takes place slowly, in time, they are the subject to the newest form of pollution, the microplastics pollution.

Depending on the sources and formation mechanisms, microplastics are classified into two categories: primary (deliberately introduced by the anthropogenic factor) and secondary (fragments smaller than 5 mm resulting from the degradation of polymers) [13].

Distributed in a wide range of markets, the 51.2 Mt of plastics manufactured and used in 2018 are, in order: polypropylene (PP  $\approx$  10 Mt), low density and linear low density polyethylene (PE-LD / PE-LLD  $\approx$  9 Mt), high and medium density polyethylene (PE-HD / PE-MD  $\approx$  6 Mt), polyvinyl chloride (PVC  $\approx$  5 Mt), polyurethane (PUR  $\approx$  4 Mt), polyethylene terephthalate (PET  $\approx$  4 Mt) and polystyrene (PS  $\approx$  2 Mt) [12].

Regarding the scientific field of research studies on polymeric products, as expected, the paperwork number is proportionate with the size of manufacture market and their degree of use.

In most cases, the degradation of plastics occurs in aquatic environments given to their spatial distribution mainly in water bodies. Thus, for a better overview of

the degradation mechanisms, it is useful to classify plastic materials into polymers with main chain consisting only of C-C atoms and polymers with heteroatoms in the main polymer chain. This aspect directly influences the directions and mechanisms of plastic degradation [13].

According to these two aspects, this paperwork aims to highlight the recent scientific studies on abiotic and biotic degradation mechanisms, as well as the implications in microplastics formation for two of the most known and used polymers: polyethylene (PE) and polyethylene terephthalate (PET) given to their widespread use in daily products.

#### 4.1. Abiotic degradation methods

The best known and important direction of abiotic plastics' degradation is the photo-oxidation, a process involving complex sequential steps in which the main polymer chain is cleaved by light, heat or a combination of those, to form free radicals which, following the reactions with oxygen, lead to chain scission, branching and new oxygen-containing functional groups. Moreover, beside this type of mechanism, other types of mechanisms such as: thermal degradation, hydrolysis or mechanical degradation may also occur individually or simultaneously [13].

All these mechanisms acting in the natural environment, or in simulated natural conditions or in

artificial conditions, have been studied to understand the starting point of the degradation process of polymers.

High interest was expressed by polyolefins group due to its widespread in almost all market segments.

Regarding the polyethylene case, following numerous studies, the principle of mechanism and the degradation scheme was determined and defined. This process initiates with the absorption of light by chromophore groups and with the formation of free radicals undergoing different successive reactions at structural level that eventually lead to the fragmentation of the plastic material.

Depending on the UV wavelength specific to each type of polymer (polyethylene example-300 nm) and the action of other factors, plastics undergo changes in both structural and physical-chemical properties [7].

Currently, there are several types of polyethylene on the market manufactured according to the different quality requirements from which, the best-known types are high density polyethylene (HDPE) and low density polyethylene (LDPE). For them, a variety of scientific studies regarding the type of degradation and their consequences was performed. The most notable paperwork about polyethylene degradation, individually or in comparison with other polymeric materials and their results are summarized in Table 1.

**Table 1.** Experimental studies concerning the PE abiotic degradation

Polymer	Degradation type / Experimental conditions	Highlights	[Ref]
PE	a) exposure to artificial saline environment followed by 8 weeks in a batch reactor, in dark, under stirring at 125 rpm rate and constant temperature 19 °C b) exposure to artificial saline environment and UV radiation - same conditions (a) and additionally exposure to UV radiation (wavelength = 254 nm and 400 $\mu\text{W}\cdot\text{cm}^{-2}$ intensity of the lamp)	<ul style="list-style-type: none"> <li>In the eight weeks of exposure there were no noticeable variations in the molecular weight of polymers; instead, the formation of new functional groups was observed when comparing FTIR-ATR spectra indicating that the most significant transition begins only after the sixth week of exposure.</li> <li>In comparison, UV exposure did not result in considerable spectrum changes and the formation of new functional groups was attributed to the action of the saline environment.</li> <li>SEM analysis of the morphology and structure of the polymer did not indicate significant changes, but it was noted that in the presence of a saline environment cracks and cleavages begin to appear due to inorganic ions that can act as catalysts for oxidation reactions.</li> </ul>	[14]
LDPE, HDPE, PP, PLA	Thermal degradation - thermogravimetric analysis in inert gas atmosphere at temperature between 303 and 973 K, with different heating rates	<ul style="list-style-type: none"> <li>The degradation process depends on the heating rate, thereby a higher rate implicitly leads to an earlier start of polymer degradation.</li> <li>From the thermogravimetric analysis it was observed that the shape of the mass loss curve does not change with the variation of the heating rate.</li> <li>Although from the obtained data it appears that the degradation takes place in a single stage (continuous degradation) in fact, the thermal degradation takes place through multiple parallel or series cleavage reactions.</li> <li>Thermal degradation starts with weaker bonds of the polymer chain, leading to the formation of monomers and oligomers.</li> </ul>	[15]
HDPE	Photo-degradation under stress: - exposure to uniaxial stress of 0, 2.5, 5 and 7.5 MPa at approximately 30 °C and 5 $\text{W}/\text{m}^2$ irradiation intensity	<ul style="list-style-type: none"> <li>The tensile stress of HDPE may show an inhibitory or an accelerating effect, depending on the aging time and the level of stress to which the material is exposed.</li> <li>The accelerating effect in the early stages of degradation can be attributed mainly to the progressive increase of the molecular orientation degree and packing state in amorphous regions, while the inhibitory effect in later stages is due to the formation of closely stacked structures with a declining free volume, low mobility of small molecules and the reactive properties of the polymer chain.</li> </ul>	[16]

Polymer	Degradation type / Experimental conditions	Highlights	[Ref]
		<ul style="list-style-type: none"> <li>In the presence of oxygen and light, the chain scission is random and preferentially occurs on the longest chains.</li> <li>The photo-oxidation process, at the tested stress levels, does not change the crystallinity of the polymer samples.</li> <li>The successive self-nucleation and annealing technique (SSA) used in this study can be more efficient compared to other techniques for the analysis of the aging behavior manifested by HDPE subject to mechanical stress forces.</li> </ul>	
<b>HDPE, LDPE, PE-BIO, PE-OXO</b>	UV-B radiation - exposure to UV-B lamps ( $3.5 \times 10^{-4}$ W/cm <sup>2</sup> at 280 și 320 nm) for 60 days	<ul style="list-style-type: none"> <li>The degradation of some unmodified and modified (PE-BIO and PE-OXO) LDPE and HDPE polymers was evaluated from the perspective of the changes occurred on the carbon index, vinyl index, crystalline phase fraction and dichroic ratio.</li> <li>The initiation of the degradation process starts with the formation of hydroperoxides due to the action of UV-B radiation which leads to new functional groups formation such as hydroxyl, and carbonyl.</li> <li>Because carbonyl and vinyl groups are the main products of photo-oxidation, their index is used to evaluate the effect of UV radiation on polymers degradation.</li> <li>The carbonyl index of HDPE and LDPE increased from the fifth day indicating a rapid initial degradation and gradually, progressing until the cleavage of the main polymer chain in day 60.</li> <li>For modified polymers, the exposure of PE-BIO to UV-B radiation shows changes only after 30<sup>th</sup> day due to the presence of stabilizers and plasticizers, the same applies for PE-OXO polymer which exhibits a more resistant behavior due to prooxidants.</li> <li>The vinyl index indicates an approximately linear increase for LDPE, HDPE and PE-BIO due to the breaking of tertiary carbon branches which leads to the formation of vinyl groups while the PE-OXO polymer shows no change due to oxidizing agents and transition metals which acts as inhibitors.</li> <li>The crystallinity degree depends mainly on the former polymerization process and exhibits different behavior depending on the linearity and type of polymer.</li> <li>The dichroic ratio increases for all four polymers in the first 30 days, suggesting that the cleavage of the branches from the main polymer chain leads to the reordering, parallel to the stretch direction of the polyethylene films, until there is no branch available to break or reorder.</li> </ul>	[17]
<b>HDPE</b>	Photo-degradation - UV exposure at different temperatures until the polymeric material breaks	<ul style="list-style-type: none"> <li>Exposure to UV radiation shows acceleration trends with increasing temperature and UV irradiation rate.</li> <li>The main consequence of HDPE photo-degradation is the cleavage of the polymer chain and the formation of new functional vinyl, carbonyl, or hydroxyl groups.</li> <li>There is a linear relationship of the degradation rate up to a certain irradiation rate (40% UV) after which the rate is lower than estimated, aspect not yet explained but assigned to the additives presence.</li> </ul>	[18]
<b>Nylon, PE, PET, PP</b>	UV Radiation - 6.5 months exposure to marine water (changed once a week) and UV radiation	<ul style="list-style-type: none"> <li>Following tensile stress experiments, the samples showed a loss of elasticity after 2.5 months of exposure, thus decreasing the toughness and increasing the rigidity of the polymer (PET and PP samples were the most affected).</li> <li>Changes in surface textures were observed due to the cracks and fissures appearance, because of photooxidative degradation.</li> <li>The thermal proprieties were affected leading to the weakening of the material.</li> </ul>	[19]

All studies mentioned in Table 1 have confirmed changes in the polymer properties due to the action of various degradation factors.

Degradation in the aquatic marine environment is a research topic of great interest given the global problem of too many plastic debris ending up in water bodies every year. Following the exposure to an artificial saline environment and UV radiations, it was found that new oxidized groups formed in the polyethylene spectrum

led to changes in the PE surface, an aspect confirmed by the SEM analysis. In addition, the validation of the results was performed by Raman analysis of the environment in which the samples were exposed, confirming the presence of organic matter [14]. Another study [19], also in saline environment, evaluated the changes on four types of polymers: Nylon, PE, PP and PET. Following the study conducted for 6.5 months, it was found that polymer degradation is initiated by

various mechanisms and the main property affected is elasticity. After comparing the SEM analysis results, it was evident that the structure of the polymers begins to crack and break after long periods of exposure.

For thermal degradation processes, it is confirmed that an increase of temperature accelerates the degradation process [15].

Most studies regarding the exposure to UV radiation indicate the direct dependence of the wavelength and intensity of radiation as defining variables for the degree of polymer degradation. The addition of mechanical forces leads to irreparable structural and compositional changes [16-19].

Another common polymer is polyethylene terephthalate (PET), used mainly for bottling liquids. Although it has an ester bond that could be easy to split, the structure of PET has a higher resistance to degradation due to its aromatic ring. However, at long exposure times to UV light, the material deteriorates and turns yellow. Research has suggested that PET photooxidation involves the formation of hydroperoxide species following the oxidation of  $-CH_2-$  groups adjacent to the ester bond, which have a defining contribution in the photodegradation process of PET [7].

Table 2 indicates the most significant studies regarding PET degradation under abiotic condition.

**Table 2.** Experimental studies concerning the PET's abiotic degradation

Polymer	Degradation type / Experimental conditions	Highlights	[Ref]
PET	Hydrolytic	<ul style="list-style-type: none"> <li>This type of degradation is promoted in crystalline materials, having relatively low molecular weight, by temperatures around the glass transition temperature (<math>T_g</math>).</li> <li>The hydrolysis process affects the mechanical properties of the material and leads to the formation of microplastic particles.</li> <li>Degradation is increased in specific conditions, such as acidic or alkaline environment but also in the presence of certain metal ions.</li> <li>Hydrolysis under natural conditions induces a slow degradation and manifests itself predominantly on the material's surface.</li> </ul>	[20]
	Photolytic degradation	<ul style="list-style-type: none"> <li>Photolytic degradation is initiated when the PET is exposed to radiation close to the UV region, degradation that occurs by Norrish I or II type mechanisms.</li> <li>The Norrish type I reaction is based on the formation of radicals during the cleavage of the ester bond while the Norrish type II reaction takes place intramolecularly, by the formation of polymer chain terminations in carboxylic acid and vinyl groups.</li> <li>Although the crystalline regions of polymers are less affected by degradation, it has been shown that PET can directly absorb UV radiation, cleaving the polymer chain and causing changes in mechanical properties and molecular weight.</li> </ul>	
	Accelerated weathering	<ul style="list-style-type: none"> <li>This type of degradation is an artificial one, carried out in well-established conditions to stimulate the simultaneous action of different degradation mechanisms that usually take place in nature.</li> <li>Currently there are two types of simulating systems for accelerated weathering: q-UV and q-sun, the former being useful for simulating aggressive test environments while the last is more useful for simulating natural-like conditions.</li> <li>In both normal and accelerated weathering, the material undergoes changes in the molecular mass, crystallinity, color, and mechanical properties.</li> <li>It is certain that the degradation under normal conditions is much slower than that under accelerated conditions and the estimation of the life cycle of the material is difficult, due to the dynamics of natural phenomena.</li> </ul>	
	Hydrolytic - 150 days of water exposure at varying temperatures from 10 to 80 °C	<ul style="list-style-type: none"> <li>PET can undergo hydrolytic reactions when immersed in water at high temperatures causing cleavage of chains and decrease in molecular weight</li> <li>Hydrolysis induces a chemo-crystallization process having effect on the crystallinity of the polymer during the aging process</li> <li>The PET fragmentation is strongly affected by the water temperature</li> </ul>	[21]

Sang *et al.* [20] conducted a comprehensive assessment of the degradation process of PET under different simulated natural or artificial environmental conditions. The study results showed that PET is a material which degrades very slowly under natural environmental conditions, however the process is initiated and propagated over time with significant consequences on the properties and structural characteristics of the material, actions that lead eventually to microplastics formation. In another study of hydrolytic degradation of PET conducted at

temperatures between 110 and 80 °C [21], a high degradation rate was observed, and since the experiments were carried out at a temperature higher than the glass transition temperature ( $T_g$ ), a chemo-crystallization process was initiated, resulting in increase of the polymer crystallinity. These aspects led to changes in the strength properties of PET with molecular weight decreasing below 17 kg / mol, where embrittlement began to develop in the microstructure of the polymer.

#### 4.2. Biotic degradation methods

In essence, biological degradation is based on chemical processes, the only difference being that the source of initiation is the action of microorganisms. Biotic degradation depends on various factors and manifests itself at different structural levels [8].

Microbial species able to degrade polymeric materials are quite rare in nature [9], and in general, biodegradation is very slow due to high molecular weight, strong C-C bonds, and extremely hydrophobic surface [10].

The biotic mechanism of degradation occurs in sequential stages: biodegradation (alteration of

properties), bio-fragmentation (release of the polymer into a simpler form by enzymatic cleavage), assimilation (uptake of molecules by microorganisms) and mineralization (production of mineral compounds [22]).

The most known microorganisms associated with plastics biodegradation are bacteria (from the genus *Bacillus*, *Micrococcus*, *Paenibacillus*, *Pseudomonas*, *Rahnella*, *Staphylococcus*, etc.) and fungi (from the genus *Aspergillus*, *Chaetomium*, *Mucor*, *Penicillium*, etc.) [23].

A series of recent studies on the microorganisms' potential for the degradation of different types of polyethylene, is summarized in Table 3.

**Table 3.** Experimental studies concerning the PE biodegradation

Polymer	Degradation type / Experimental conditions	Highlights	[Ref]
LLDPE	Biodegradation by <i>Microbulbifer hydrolyticus</i> IRE-31 - exposure to marine broth, 2216 agar media and incubation at 37 °C, 220 rpm; 7-, 20- and 30-days cultivation	<ul style="list-style-type: none"> <li>• FTIR analysis indicated the formation of hydroxyl and carbonyl groups which are a clear indication of oxidation occurred on the polymer surface.</li> <li>• After first cultivation period (7 days), the surface of LLDPE was affected, and the presence of copper sulfate in the culture medium accelerated the degradation process.</li> <li>• In the following incubation periods (20, respectively 30 days), the surface of the material degraded exponentially until crevices formed and confirmed the microbial attack.</li> <li>• This study is among the first to evaluate the biodegradation capacity of strains microorganisms isolated from marine environments as a prediction of the plastics degradation in the marine environment.</li> </ul>	[24]
HDPE	Biodegradation by <i>A. flavus</i> PEDX3 strain - exposure to fungal media for 30 days	<ul style="list-style-type: none"> <li>• The biotic action of the fungus indicated changes on the polymer surface starting with the 28th day of incubation.</li> <li>• The polymer recorded a mass loss of approximately 4%.</li> <li>• FTIR analysis indicated the presence of hydroxyl, carbonyl and ether groups, evidence of initiation.</li> </ul>	[25]
HDPE	Biodegradation by marine bacteria - incubation at 30 °C for 3 months	<ul style="list-style-type: none"> <li>• From the isolated bacteria to which the plastic was exposed, 10 of them proved to be effective and the highest percentage of weight loss recorded was about 40%.</li> <li>• After only one week of exposure, there was an increase in the degree of turbidity of the media environment, an increase attributed to the formation of a biofilm and biodegradation residues, an aspect confirmed in the following weeks.</li> <li>• FTIR analysis indicated the presence of oxide groups: mainly ketone groups and carbonyl esters.</li> <li>• Most efficient bacteria belong to the genus <i>Bacillus spp.</i> and <i>Pseudomonas spp.</i>, and have shown that marine bacterial strains have a biodegradation capacity without additional treatment or pro-oxidant additives.</li> </ul>	[26]
PE	Biodegradation by <i>Zalerion maritimum</i> - exposure to media for 208 days in the dark at a rate of 120 rpm stirring	<ul style="list-style-type: none"> <li>• After 14 days of exposure, the polymer deteriorated by 43% in terms of mass variation.</li> <li>• The spectra of the ftir-atr analysis indicated the presence of carboxyl, hydroxyl, phenolic and amide groups but also of other groups suggesting a reduction of the <i>Z. maritimum</i> lipids and proteins content.</li> <li>• The results of optical and electron microscopy showed that the polymer surface had degraded, and irregularities and biological material residues appeared.</li> </ul>	[27]
LDPE	Biodegradation by <i>Pseudomonas aeruginosa</i> ISJ14 - exposure to media for 20, 40 and 50 days of incubation at a 180 rpm stirring rate at 35 °C	<ul style="list-style-type: none"> <li>• After incubation, it was observed that <i>P. aeruginosa</i> adhered to the polyethylene surface, forming a biofilm and leading to the initiation of biodegradation process.</li> <li>• After 60 days of exposure, the polymer suffered a mass loss of 6.5%, which means that the strain needs approximately 462 days to degrade half of the polymer mass.</li> <li>• SEM analysis indicated surface changes: erosion, cracks, and crevices as a result of 60 days of biological exposure.</li> <li>• FTIR analysis indicated new peaks in spectra associated with the formation of new functional groups and new intermediates products.</li> <li>• The hydrophobicity and initial crystallinity (23%) of the material decreased significantly indicating the effective action of this strain for polyethylene biodegradation process.</li> </ul>	[28]

Polymer	Degradation type / Experimental conditions	Highlights	[Ref]
PE	Biodegradation by bacterial strains from the Guts of Plastic-Eating Waxworms - exposure to media for 7, 14, 21, 28 and 60 days at 120 rpm stirring rate and 30 °C	<ul style="list-style-type: none"> <li>• 8 bacterial strains were isolated, two of which (YP1 and YT1) had a serious impact on polymer hydrophobicity, by reducing it which implicitly led to a decreased resistance to degradation processes.</li> <li>• The appearance of carbonyl groups is an essential sign in polyethylene degradation process.</li> <li>• Mass loss analysis indicated a reduction percentage of approximately 11% (YP1) and 6% (YT1) after 60 days of inoculation.</li> <li>• Degradation of polyethylene was confirmed not only by bacterial growth on polyethylene films, but also by the key reactions identified similar to abiotic ones.</li> </ul>	[29]

From the presented studies evaluation, it appears that the biotic degradation of polymeric materials is performed selectively, only by certain types of microorganisms and generally takes place quite slowly. The action of bacteria or fungi is manifested mainly on the surface of the polymer, an aspect confirmed by the structural changes identified by the SEM analysis. Another confirmed aspect was that the biodegradation process begins with the formation of new functional groups such as hydroxyl, carboxyl or carbonyl, groups that lead to a series of subsequent reactions that eventually cause the plastic fragmentation.

The highest degradation yields were recorded by the species *Aspergillus flavus* (40%) and *Zalerion*

*maritimum* (43%). In addition, in most of these studies, the simulated biodegradation process was accompanied by favouring conditions such as: temperature (up to 37 °C), stirring (up to 180 rpm) and incubation periods between 7 and 90 days.

An important studied aspect of the polymers' degradation, biotic or abiotic, is following their classification into polymers containing only carbon atoms in the main chain and those polymers containing heteroatoms in the main chain. In Table 4, it is presented a summary of the research aimed to evaluate the biodegradation of PET materials which contain heteroatoms in the main chain.

**Table 4.** Experimental studies concerning the PET biodegradation

Polymer	Degradation type / Experimental conditions	Highlights	[Ref]
PET	Biodegradation by <i>Streptomyces</i> - exposure to media for 18 days at 28°C under 120 rpm stirring rate	<ul style="list-style-type: none"> <li>• PET powder samples with dimensions between 212 and 500 µm experienced a percentage of degradation directly dependent on the size of the particles, the 212 µm registering a yield of approximately 70% while the 500 µm samples approximately 50%.</li> <li>• GC analysis of the sample extract filtrate with the highest degradation rate indicated the presence of ethylbenzene and hexamethylcyclotrisiloxane as major components of the metabolite.</li> <li>• In addition, the degradation of PET into very small molecules also results from the identification of metabolite components that did not exceed a carbon number in the chain greater than 15</li> <li>• When compared with the study performed under the same conditions on PET films, only a slight change in the polymer surface was observed, indicating that a chopper of the material can streamline and accelerate the degradation process.</li> <li>• The combination of physical processes (milling) with biological ones (biodegradation) can lead to efficient results and solutions regarding the degradation of plastics material.</li> </ul>	[30]
	Biodegradation by <i>PETase</i> enzyme displayed on the <i>Pichia pastoris</i> yeast - exposure to biocatalytic cell for 18 h at 30°C	<ul style="list-style-type: none"> <li>• The use of a biocell composed from the display of the bacterial enzyme called PETase on the surface of a yeast indicated satisfactory results for the degradation of some commercial polymeric polyethylene terephthalate materials.</li> <li>• The experiments performed indicated that the newly created biocell can degrade various highly crystalline polymeric products showing a satisfactory yield.</li> <li>• Additionally, the advantage of this type of process consists in the possibility to scale the process at the industrial level and that biocell can be reused up to 7 times without suffering notable biological activity changes.</li> </ul>	[31]
PET, PLA	Biodegradation by rhizosphere microorganisms - exposure for 6 months to inoculated soil with bacterian and fungal suspension	<ul style="list-style-type: none"> <li>• Both materials (polyethylene terephthalate and polylactic acid) underwent property changes and best strains for soil inoculation were <i>A. Sulfonivorans</i> (bacterium) and <i>Clitocybe sp.</i> (fungus) for PLA and <i>S. Plymouthica</i> (bacterium) for PET, respectively.</li> <li>• In strength tests approximately all the inoculation variants of the tested soil led to a decrease in the resistance of the polymer film and the best results were obtained by combining several types of microorganisms.</li> </ul>	[32]

Polymer	Degradation type / Experimental conditions	Highlights	[Ref]
		<ul style="list-style-type: none"> <li>The FTIR analysis showed that following exposure of biological action of various strains, the carbonyl index, the one susceptible for the initiation of degradation, has increased or remained constant apart from the soil inoculated with <i>Clitocybe sp.</i>, as well as the combination of: <i>Clitocybe sp.</i> + <i>M. Giganteus</i> for PLA and <i>L. Laccata</i> for PET and respectively in the presence of <i>Autochthonous</i> strains and <i>B. napus</i>.</li> <li>In the mass loss analysis, the PET polymer did not register significant changes over time for any of the tested inoculation combination while the PLA polymer showed a loss of approximately 17 % when exposed to a soil inoculated with <i>L. Laccata</i> + <i>M. Giganteus</i>.</li> <li>The performed tests indicated a partial inhibition of plant growth for the experiments in which they were present in the inoculated soil with different strains.</li> <li>Also, the presence of the two polymers in the soil led to certain changes: in the presence of the PLA polymer, the abundance of microorganisms increased, and the soil became more acidic, while in the presence of the PET polymer the number of microorganisms decreased.</li> <li>However, the best system that can be used for biodegradation of PLA and PET in the soil are the inoculation systems with <i>M. Giganteus</i> and <i>L. Laccata</i> in which plants can also be present.</li> </ul>	

Biodegradation of polymeric materials with heteroatoms in the main chain, as the case of PET, has a higher susceptibility to biodegradation comparing with materials containing only carbon in the main chain. From the summarized paperwork it seems that, the same as in PE studies, only certain types of microorganisms and experimental conditions can facilitate a fast and efficient biodegradable process.

The study testing the potential of *Streptomyces*-type microorganisms in aqueous environment [30] indicated that a fragmentation of the polymeric material up to 500 µm in size can lead to a biodegradation yield of about 50 % in 18 days, while for a fragmentation up to 212 µm the process yield can reach a rate of up to 70 %.

On the other hand, the testing of the biodegradation capacity of plastics in inoculated soil [32], indicated significant performance when mixing various rhizosphere strains of bacteria and fungi in soil with and without plants growing.

The most innovative method, however, is the manufacture of a biocell capable of degrading plastics, an option that can be extrapolated at industrial scale and in which the biocell can be reused up to 7 times.

#### 4. Conclusions

It is certain that the degradation of polymeric materials is a complex process that occurs through both abiotic and biotic processes because of the external factor's action on plastic material properties. In addition, these types of materials need extremely long periods of time to be degraded.

Research studies are mostly performed at laboratory scale, using small amounts of plastic. Nowadays, scaling to industrial degradation process is promising, but still at the beginning of its development, so the best option is to recycle or recover energy from plastics.

The plastic materials decompose in the end, but the worrying issues regarding their degradation in natural environments are the high degree of spatial distribution of plastic debris in all ecosystems, low recycling level,

and the most important, the microplastics formation and then, their global spreading. This type of pollution will lead to major environmental imbalances, due to their introduction into the food chain and already confirmed presence in various systems: air, water bodies and even in the digestive tract of animal species, especially marine ones.

#### Conflict of interest

Authors declare no conflict of interests.

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*Received:* 30.08.2022

*Received in revised form:* 26.09.2022

*Accepted:* 27.09.2022