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A scoping and critical review of properties, standards, and regulations of oxo-biodegradable plastics

Juan C. Salcedo-Reyes^{*1}, Octavio A. Castañeda-Uribe², Luis D. Gómez-Méndez³, Aura M. Pedroza-Rodríguez³, Raúl A. Poutou-Piñales³

Edited by

Angela Johana Espejo Mojica
editorus@javeriana.edu.co

1. Thin Films & Nanofotonics Group, Physics Department, Faculty of Sciences, Pontificia Universidad Javeriana, Cr. 7 No. 40-72, Ed. 53, Lab. 402b, PC 110-23, Bogotá, D.C., Colombia.

2. School of Engineering, Science and Technology, Universidad del Rosario, Bogotá, Colombia.

3. Grupo de Biotecnología Ambiental e Industrial (GBAI), Departamento de Microbiología, Facultad de Ciencias, Pontificia Universidad Javeriana, Cr. 7 No. 40-72, PC 110-23, Bogotá, D.C., Colombia.

*salcedo.juan@javeriana.edu.co

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Abstract

Based on recent scientific-technical developments referring to the transformation and biodegradation mechanisms of plastic compounds, progress has been made both in the conceptualization of relevant definitions and in the development of technical standards that allow determining, in a more precise and reproducible way, the ratio of biodegradability of a determined material. From these advances, they have developed, furthermore, the so-called oxo-biodegradable plastics, in which pro-oxidant additives are added to the raw polymer in such a way that allow an optimal abiotic transformation process (photo/thermo oxidation), producing the fragmentation of the material under suitable conditions for its simultaneous or successive biotic degradation (enzymatic oxidation). Although, currently, oxo-biodegradable plastics are widely used in different applications such as, for example, in agriculture and single-use plastics, until very recently a technical standard was developed that allows determining the relative degradation ratio of different types of plastics under abiotic and biotic conditions. This process implies that for producers to be able to use specific terms of bio-degradation and oxo-biodegradation for advertising purposes that claim to offer an environmentally friendly product, the relevant entities must carry out metrological tests in light of the new definitions and technical standards. Furthermore, a large amount of specialized literature has been generated in which the bio-degradation ratio of oxo-biodegradable plastics is determined in very specific environments and conditions. This review gives a detailed account of the different definitions and scientific concepts involved in oxo-/bio- degradation and shows how these concepts have evolved over time. It also shows the evolution of the technical standards, which, in general, are adapted to the new scientific and technical developments in the field of plastics. Finally, a detailed analysis of results reported in the scientific literature shows the dependence of oxo-biodegradation on different parameters (UV radiation, temperature, exposure time, type of enzymes), specific environments (soil, composting, waste, recycling, etc.), different types of plastics (LDPE, HDPE, LLDPE, pro-oxidant additives) and, finally, on different analytical techniques used (FTIR, DSC, TGA, SEM, tensile test).

Keywords: oxo-biodegradable plastics; pro-degradant additives; mineralization; thermo- oxidation; photo-oxidation; enzymatic oxidation.



1. Introduction

Materials science and engineering have been some of the cross-cutting themes in modern society's scientific and technological development. One example of materials' impact on social evolution was the social problems generated by the extensive use of natural rubber during the 19th century. Conflicts that lasted until Charles Goodyear, in 1839, improved the properties of natural rubber through a process called vulcanisation [1], in which rubber is heated together with sulphur and

lead, generating artificial rubber that served to mitigate the social conflicts generated by the cultivation and harvesting of natural rubber. Today, vulcanisation is obsolete because of the serious environmental pollution problems it causes.

Almost all technologies available today are related to the possibility of designing, manufacturing and characterising artificial materials with improved physicochemical properties compared to their counterparts natural materials. In this sense, polymer science responds to the need to produce plastics, fibres and elastomers with better mechanical, optical, electrical, magnetic and biological properties, guaranteeing, as far as possible, a low environmental impact. From the point of view of the circular economy [2] and the green economy [3], materials science and engineering have become crucial for new materials development able to adapt to new concepts of regeneration and restoration.

1.1. Standardization of the plastic term

Historically, standards bodies have defined the basic concepts related to plastics technology as a constantly evolving discipline. The American Society for Testing and Materials (ASTM) has generated standards in different areas of technology [4]. In 2020, ASTM D883-20A "Standard Terminology Related to Plastics" was published, defining plastic as a material composed primarily of one or more organic polymeric substances of high molecular weight and which, in its final stage, is in a solid state in spite during manufacture it may be a fluid. The standard suggests that rubber, textiles, adhesives and paints could be conceptualised eventually as plastics; however, they are not, showing an inconsistency in the definition. Another example is the International Organization for Standardization (ISO) technical standard 472: 2013, which states that plastics are materials whose main component is a polymer that could have moulded as a fluid along the manufacturing stages. However, elastomers, which meet this definition, are not considered plastics. In addition, from a scientific and engineering point of view, efforts have been made to define the term plastic. The polymer division of the International Union of Pure and Applied Chemistry (IUPAC) set the plastic term generically to refer to a polymeric material that may contain other substances intended to improve performance and reduce manufacturing costs. However, it is not appropriate to indistinctly use the plastics term as a synonym for polymers. Furthermore, in polymer engineering, plastic is any material able to be treated as a fluid.

The above definitions are just a few examples of the great challenge of standardising the terminology used in plastics technology. At present, there are inconsistencies and contradictions between some standardisation entities. It is striking that in materials science, plastic is a macromolecule that has the property of being thermoplastic, while in terms of phase, it is a viscous solid at temperatures below the glass transition temperature [5]. The latter definition is, in our view, the most appropriate for the context of the present review.

1.2. Plastic compounds

In 1953, H. Staudinger received the Nobel Prize for his work in polymer development [6]. Since then, the discovery of new manufacturing methods and polymer-based materials has grown exponentially. The properties of polymers and their applications are extremely broad, leading to various approaches to their classification. Today, polymers are commercially available in a wide composition variety, forms and properties. Polyolefin Blends are obtained by mixing different polyolefins in order to obtain different physicochemical properties of the resulting material (molecular weight, shape memory, rheological, etc). The concept is based on the idea that a specific property of the resulting material is a superposition of the corresponding property

of the initial miscible polymers. When the initial materials are not miscible with each other, we speak of a polymer composite, which are materials that contain two or more phases (chemical and physical) with well-defined borders. A plastic compound or polymeric compound is formed, on the other hand, by a polymeric matrix with physical-chemical properties altered by the introduction of specific additives at low concentrations [7]. From ISO 472, a plastic compound is formed by the intimate mixture of a polymer or polymers with other ingredients such as fillers, plasticizers, catalysts and colorants [15]. Precisely based on their properties, polymers classification involves four broad categories [8]: *i*) Thermoplastics, that can be moulded and remoulded by heating. Thermoplastics can be processed into a desired shape through many processes, the most common of which are injection molding and extrusion; *ii*) Rubbers, or elastomers, are network polymers that are lightly cross-linked and are reversibly stretchable to high extensions; *iii*) Thermosets are network polymers that are heavily cross-linked to give a dense and rigid three-dimensional network that do not melt on heating; *iv*) Liquid-crystal polymers (LCPs), are a subset of thermoplastics that can be main-chain LCPs (in which the chains are aligned closely parallel to each other) or side chain LCPs. In particular, the mouldability (due to temperature effects) of thermoplastics is the fundamental basis for the recycling concept of this class of polymers, as their shape modification can give a new use. In general, thermoplastic is often simplified as plastic materials, of which polyethylene (PE) stands out as the simple form.

From the chemical composition, polyolefins or poly(alkane) are a particular class of thermoplastic polymers whose monomers are alkenes which, in turn, are monomers formed by hydrogen and carbon atoms joined by double covalent bonds. Propylene, ethylene, isoprenes, and butenes are examples of olefins that are obtained from natural coal or petroleum sources, and therefore PE, HDPE, LDPE, LLDPE, and PP are examples of polyolefins [9].

In 1963, Karl Ziegler and Giulio Natta received the Nobel Prize for their work on the use of catalysts, complexes derived from aluminium and titanium tetrachloride in the manufacture of polyethylene and polypropylene (PP), respectively [10], in a process actually known as polymerisation. This development promoted the mass production of so-called polyolefins (PE, PP, ethylene-propylene rubber EPM) due to the low production cost obtained by using various catalysts based on metal complexes, such as Aluminium, Magnesium and Zinc. The mass production of plastics gave rise to the so-called “patent application fair” [6], in which different industrial producers improved synthesis processes to obtain PE with improved physicochemical properties. At this early stage, organic polymers differed from organometallic (hybrid) polymers in that the last ones contained metals in their molecular structure, whereas today are considered petroleum-based plastics.

Currently, PE synthesised based on metal compound catalysts (hybrid PE) is available in an ample composition, molecular structures, presentations and physicochemical properties. PE production is estimated at 100×10^9 kg per year, of which 27 % is low-density polyethylene (LDPE), 44 % is high-density polyethylene (HDPE) and 29 % is linear low density polyethylene (LLDPE). To a large extent, current PE synthesis uses the Ziegler-Natta and Phillips methods, the single-site catalyst method and the co-catalyst method [11]. All synthesis methods use transition metals as catalysts, increasing the number of residual metals and environmental risk due to their potential toxicity. In order to mitigate the environmental impact of synthesis methods, green polymer chemistry has designed and generated strategies to reduce the use of residual metals without compromising their physicochemical characteristics. This type of plastic, obtained from green chemistry, falls into the engineered PEs category, which has a low production volume at a high cost. Due to these industrial conditions of engineered PE, we find ourselves, once again, with a “patent application fair” in which the different industrial producers of plastics demand the benefits of their original synthesis methods (usually showing a reduction of residual metals) without, until

very recently, the existence of a standard that demonstrates all these benefits. In this context, catalytic residues (swarm contamination) are an intrinsic factor in the production of plastics because they are in “relatively” low concentrations.

1.2.1. The role of additives in plastic compounds

One of the most common strategies for controlling and improving the physicochemical characteristics of polymers has been the addition of additives, in different concentrations, to the molecular structure during or after the manufacturing process. The process of adding essential ingredients to polymers in order to improve the physicochemical characteristics is called compounding and, in general, the result (additives mixed to the base polymer) is called a polymeric compound. Thermoplastic compounds or plastic compounds are typically prepared by mixing organic and/or inorganic compounds depending of the properties that should be improved. Inorganic additives are of many types, ranging from natural minerals to synthetic minerals to specialized materials with directional physical properties [12]. Plastic compounds are proprietary products of polymer manufacturers and depend on their specific use. The additives provide resistant polymers to oxidation at high temperatures, flexibility-colour retention, resistance to ultraviolet radiation, antimicrobial resistance and impact resistance. From the point of view of their use, additives are accelerators or promoters (The crosslinking reaction rate may be too slow for some commercial processes and the reaction may exceed the oxidation resistance time for the elastomer compound), defoamers (prevent foaming during manufacturing and the formation of holes in the final product), anti-degradants (stabilisers against oxidation, ozone and light), antioxidants (also sometimes called anti-degradants) [12]. More than 50 % of the total PE production incorporates different types of additives, such as i) coupling agents that increase the chemical interaction with the material, ii) cross-linking agents, flame retardants that prevent combustion mainly during raw material transport, iii) plasticisers that improve flexibility, strength and handling properties, iv) retardant vegetable oils to prevent webbing during manufacturing, and v) vegetable or artificial inks.

On the other hand, using metals such as cobalt, nickel, manganese, silver, palladium, molybdenum, chromium, tungsten, and cerium has significantly increased environmental pollution as toxic waste [13]. The International Cadmium Association (ICdA) reported that when using cadmium and zinc-based stabilizers to slow down the degradation process of PVC, exposure to heat or sunlight releases 300 ug of cadmium per g of PVC, contaminating marine ecosystems. A similar situation occurs with lead and zinc-based additives [14]. Given the negative impact of metal-based additives on ecosystems and human health, there is a need to develop reliable analytical measurement protocols and reliable information sources to identify and quantify the additives and to know the specific concentrations used in a given polymeric compound.

1.2.2. Regulations regarding the use of plastic compounds

Beyond the catalytic processes for the production of plastic compounds, it is necessary to consider the life cycle of this important type of material, which is present in almost all human activities. Generally, after multinational companies such as Exxon-Mobil, Dow, Ineos, Polimeri Europa, Chevron-Phillips, Formosa plastics, among others, patented their production processes and the additives they use fabricate PE in the form of a pellet. Pellet is sent to the production plants (with a high risk of combustion) in which it is heated (thermoplastics), shaped and added with some other additives, depending on the final product desired. During this process, the compounds are subjected to extreme conditions (temperatures greater than 190 °C and high mechanical stresses) that, eventually, can alter properties such as chemical resistance and durability [15]. At the

developing and disseminating point, there are uncountable amounts of legislation regulating both the type of compound and the additives that the product contains. These regulations arise from specific cases. For example, pharmaceutical companies use plastic compounds to design devices such as inhalers, ampoules, diffusion membranes and drug dispensers; the contamination of the pharmaceutical product from both the presence of toxic additives and from the chemical reaction between additives with the pharmaceutical products has been demonstrated [16]. Generally, this problem arises because *i*) the plastic compound is chosen based on its engineering properties, without considering the chemical elements present in it, *ii*) the use of obsolete analytical techniques, typical in the field, such as gas chromatography, with flame ionization detector (GC/FID), [17] for the identification of toxic elements. A first joint effort of producers to regulate the presence, the toxicity degree and the use of appropriate analytical methods for different types of polymeric compounds only took place until 2008 [18].

Regulation regarding the chemical content of plastic compounds is motivated mainly by two general risks: *i*) the contamination risk in ecological systems and human beings, and *ii*) the risk of hazards due to the industrial application of the material (electronic, pharmaceutical and food industry). Based on the recent interest in the negative impact of the different plastic compounds, both on human health and on ecological systems, several government entities have focused on determining the toxic substances (endocrine disruptors, carcinogens, etc.) that polymers and their additives generate during their life cycle. For example, toxic plasticisers have been detected in environmentally friendly systems and pharmaceutical products [19]. The general regulations issued by TSCA (US Toxic Substances Control Act, 1976) and REACH (Registration, Evaluation, Authorization and Restriction of Chemicals of the European Parliament, 2006), despite being completely generic, may eventually prohibit or attenuate the commercialization of products manufactured with polymeric complexes.

On the other hand, the regulations about the use of plastic compounds for pharmaceutical applications, materials used in electronic equipment and materials that will be in contact with any food are agreed upon by different government agencies. For example, *i*) EU Directive 2002/96/EC WEEE (Waste Electrical and Electronic Equipment) establishes additive concentration limits of a product in the electrical and electronic industry that is recyclable (reusable). *ii*) EU Directive 2003/11/EC ROHS (Restriction of the use of certain Hazardous Substances) restricts the use of six toxins in electronic equipment. *iii*) EU Directive 2002/72/EC (relating to plastic materials and articles intended to come in contact with foodstuffs) establishes basic rules and provides a list of appropriate plastic compounds for the manufacture of materials that are in contact with food. *iv*) EU Directive 2002/61/EC (Aryl Amine Breakdown Products in Azo Dyes), *v*) EU Directive 67/548/EEC Carcinogenic and Regulated Dyes. *vi*) FDA and CFR – 21 CFR Parts 175-178 regulating the use of certain adhesives, coatings, paper, and polymers. *vii*) USEPA – Methods 606, 506-1 and 8061 that regulates the use of certain plasticizers. *viii*) ANVISA-RDC No. 91 of 11 May 2001 establishes the general criteria and classification of packaging materials and equipment contacting with food.

Contrary to regulations for pharmaceutical and food contact use, inexplicably, most PE compounds have not been regulated. The use of different types of PE in the manufacturing of plastic bags is a clear example of this. In this case, the bag manufacturers implement a process model in which they initially buy the polymer compound (without detailed specifications) from a supplier who, in principle, guarantees adequate properties of the PE based on the final product. Subsequently, additives are included to improve the impact resistance properties, and guarantee the integrity (no gaps or cracks formed), that makes that they do not stick together (anti-blocking performance), and that exhibit good optical properties (transparency, color, opacity) [20]. Ultimately, it is crucial

to mention that these fabrication processes of plastic compounds are not static, implying that producers periodically change fabricating protocols and additives types without prior notice. This process model makes it impossible to predict what kind of chemical complexes will be present in an entity of the final product, which imposes a challenge in the traceability process of these materials. Additionally, this traceability problem is compounded by the fact that analytical techniques have not yet been defined for the precise determination of all the chemical compounds present in these materials. Currently, it has been proposed to use the method of gas chromatography with a mass selective detector (GC /MSD) [21]; however, the implementation of these techniques types entails restrictions in detection time and costs.

2. Degradation mechanisms of plastic compounds

Although, from ASTM D883 – 22, degradation is defined as a deleterious change in the chemical and/or physical properties (crazing, cracking, erosion, discoloration and phase separation) of the plastic compounds under specific environmental conditions, from a chemical point of view, degradation, under aerobic conditions, results in the mineralization of the plastic compound to carbon dioxide and water and, under anaerobic conditions, methane. Transformation, on the other hand, involves only a restricted number of oxidative reactions in such a way that the basic structure of the polymer chains remains essentially intact [22].

The degradation process of the different types of plastic compounds is mediated by different physical, chemical or biological mechanisms that, in general, begin by breaking the polymer chains, modifying, in this way, the mechanical, optical, and electrical properties of the material. The transformation of thermoplastic materials can be defined as a modification of the material, on a molecular level, produced by different mechanisms, which include [23]: *i*) loss of mechanical properties (viscoelasticity, stiffness, fragmentation, surface erosion), *ii*) depletion in resistance to the chemical attack of the material, *iii*) change in optical properties (discolouration, transparency, reflectance), *iv*) formation of carbonyl functional groups. The material is transformed, in principle, into a low molecular weight material (generally expressed in Daltons, $1 \text{ Da} = 1.66 \times 10^{-27} \text{ kg}$), highly amorphous, forming small pieces of the material (with dimensions ranging from mm to nm). Despite the large number of studies related to the transformation of polymers, there is still a vast amount of problems in the theoretical foundation and in the technical implementation that lead to contradictory results with their corresponding low traceability [24].

Depending on the nature of the degradation mechanism, they are classified into photo-transformation, oxidative transformation, microbial degradation, and oxo-biodegradation [25].

2.1. Photo-transformation

Transformation process of material produced by its direct interaction with electromagnetic radiation, mainly with radiation comprised in the visible region (wavelengths between 400 nm and 780 nm) and ultraviolet (UVA: 400 nm and 315 nm, UVB: 315 nm and 280 nm, UVC: 280 nm and 100 nm) of the electromagnetic spectrum. In this transformation mechanism, also known as photolysis, the radiation interacts directly with polymer chains so that, eventually, this interaction can cause molecular bonds to break, typically C–C bonds with an energy of 3.6 eV ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$) and C–H bonds with an energy of 2.84 eV. Hence, the Einstein-Planck equation, the 344 nm radiation has enough energy to break the C–C bonds of a polymer chain, while the 194 nm radiation has enough energy to break the C=C bonds, and the 284 nm radiation has enough energy to break the C–H bonds of a polymer chain. The photo-transformation of PE

occurs by its interaction with radiation of approximately 300 nm. The breaking of molecular bonds produces a series of macroscopic alterations in the physicochemical properties of the material. The main effects are: *i*) the change in the optical properties of the material that turns yellowish *ii*) the excision of the material into small fragments proportional in size to the loss of molecular weight *iii*) significant variation in stress coefficients at the breaking point and the deformation at the breaking point.

In the framework of polymer litter management, the use of solar radiation is proposed to induce photo-transformation, especially radiation in the UV-range of the solar spectrum. **Figure 1** shows the direct solar spectrum (ASTM G173) under conditions of an air mass of 1.5 (the air mass coefficient defines the ratio of the distance travelled by radiation through the atmosphere and the distance it travels at the zenith). In general, photolysis is the main transformation mechanism of material when its inherent polymeric structure absorbs radiation with a wavelength greater than 300 nm. Unlike most polymer compounds, PE does present an inherent absorption at the wavelengths present in the solar spectrum. In Figure 1, the UV/VIS absorption spectrum of LDPE is shown. LDPE absorb radiation with a wavelength smaller than 300 nm.

Considering that the breaking of the polymer chains definition states in terms of the number of rupture of chemical bonds in the material, the quantum efficiency of the breaking of the chains definition states as the ratio between the number of dissociated chemical bonds and the number of incident photons. In general, for all polymers, the quantum efficiency of the chains breaking is less than 1.0×10^{-2} , which states that it is a relatively inefficient process. To improve the quantum efficiency of polymer chain breaking, different type of additives has been developed, defining photodegradable plastics.

2.2. Oxidative transformation

In a very specific context, oxidative transformation can be defined as the introduction, through chemical reactions, of oxygen into the molecular structure of the polymer chains of the material, so that C=O bonds are created, which are a particular class of the so-called carbonyl functional groups.

Hence, these chemical reactions produce the reduction of the molecular weight of the material by breaking the polymer chains. In this context, the oxidation of the material occurs through a reaction in several stages, in which free radicals are created that interact with the oxygen incorporated into the molecular structure, inducing the breaking of the bonds of the polymer chain.

In a more general context, it is important to place the oxidative transformation of polymers within the framework of advanced oxidation processes (AOP), defined as a phenomenon in which highly oxidative/reductive species are generated and used, mainly free radicals, which induce the oxidation/reduction of organic molecules. Oxidation (reduction) definition states as the tendency of a molecule to gain (loss) electrons. Said tendency is measured in terms of the oxidation-reduction (Redox) potentials. When the Redox potential of a molecule is positive, it is said to be an oxidizing agent (the molecule tends to gain electrons), while if the potential is negative it is said to be a reducing agent (the molecule in question tends to lose electrons). Carbonyl functional groups are good reducing agents (they are easily oxidized) whilst among the most effective oxidizing agents are (in descending order): Fluorine (F), Hydroxyl radical (OH•), Atomic Oxygen (O), Ozone (O₃) and Hydrogen peroxide (H₂O₂). When the catalyst is a metal oxide, its redox potential depends mainly on the energy of the valence band (**Figure 2**) [26]. The interaction of oxidizing agents with polymer chains induces their breaking and, therefore, the oxidative transformation of the material. AOP's define different methods to produce highly oxidizing agents

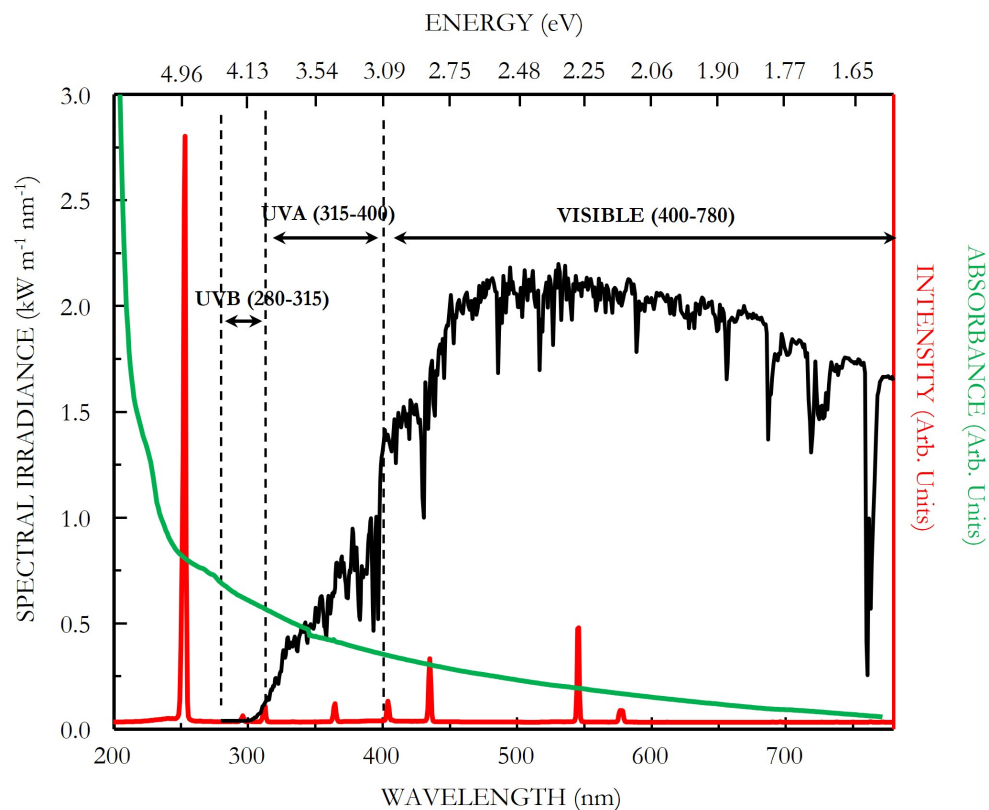


Figure 1. Solar spectrum (black line) where the wavelength of UVB, UVA and the visible region are shown. The corresponding energy is shown in eV. Emission spectrum of Fluorescent UV Lamp/Hg Arc Lamp (red line). See ASTM G15 – 16. UV/VIS absorption of LDPE (green line).

from different methods that generally involve a catalyst activated by absorption of radiation or heat. In this sense, in the field of polymer science, they talk of photo-initiators that trigger the production of free radicals in a reverse process to the Ziegler-Natta and Phillips polymerization methods. In any oxidation-reduction process, three stages can be identified: *i*) Initiation: induced by some external agent such as radiation, temperature or mechanical stress. *ii*) Propagation: Free radicals generated in the first stage initiate a series of secondary chemical reactions independent of the initiation mechanism. Reaction of free radicals with oxygen and formation of peroxide radicals that, finally, is responsible for breaking polymer chains.. *iii*) Termination: the reaction, ideally, ends with the production of CO_2 and H_2O .

AOP's have implementations in a wide variety of technologies, including the remediation of wastewater, the removal of aerosols in the atmosphere and, in particular, in the transformation/degradation of different types of polymers. Alkaline ozonation, ozonation with hydrogen peroxide, Fenton processes, electrochemical oxidation, non-thermal plasmas, photolysis and (semiconductor) photocatalysis are some examples of AOP [27]. In particular, when a polymer chain interacts with $\text{OH}\cdot$ it induces its breaking by different processes (successive or simultaneous): *i*) hydrogen abstraction, *ii*) OH addition or substitution, and *iii*) electron transfer.

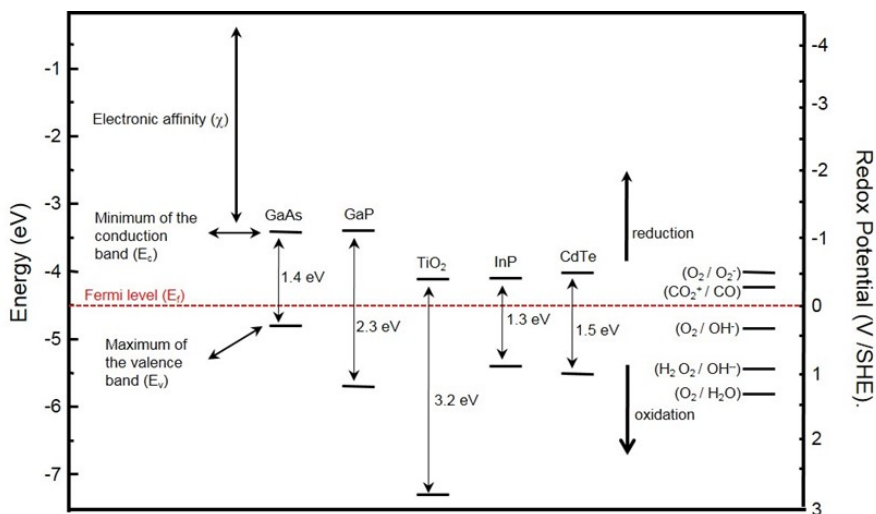


Figure 2. Energy diagram of the main physical parameters of different crystalline semiconductors concerning their redox potential. The metallic oxide TiO_2 is one of the most efficient oxidizing agents with trigger energy of 3.2 eV. The Redox potential of some important molecules is shown.

2.2.1. Thermo-oxidative transformation

Degradation process induced by heat absorption. Thermal oxidation produces, in general, a breakage of the polymer chains mediated by free radicals (generally peroxides) and, therefore, the production of small fragments of the material together with volatile organic compounds and soot [28]. Despite its multiple limitations, thermo-oxidation has been a widely used technique in the matter of plastic degradation through two possible simultaneous mechanisms: *i*) random breakage of the polymer chains, causing reduction of the molecular weight of the material, and *ii*) breakage of C-C bonds at the ends of polymer chains, generating volatile products.

2.2.2. Photo-oxidative transformation

Process of oxidative transformation of polymers activated by the absorption of radiation by a catalyst (oxidizing agent) incorporated into the polymer chains or, eventually, incorporated as additives to the structure [29]. The catalysts used to produce photo-oxidative transformation effects are transition metals (Ti). The wavelength necessary to activate the oxidation processes depends exclusively on the physical characteristics of the catalyst (energy spectrum) and is independent, in general, of the photolysis processes. Radiation absorption conducts the catalyst to an excited state in which it can, under certain conditions, transfer electrons to the material inducing the production of free radicals, the addition of oxygen in the polymer chains and their subsequent breaking, producing fragmentation into small pieces of material, which produces a synergistic effect between photo-oxidation and biodegradation [30].

2.2.3. Photo-thermo-oxidative transformation

Polymer transformation process in which oxidative transformation is produced by absorption of radiation and heat simultaneously in a synergistic process of mutual acceleration. One of the main characteristics of this type of transformation is that once radiation induces oxidation, through thermo-oxidation, the production of free radicals is maintained even if the incident radiation is restricted [31].

2.3. Microbial degradation

Degradation process generated by the action of enzymes produced by different microorganisms such as bacteria, actinobacteria, yeast and filamentous fungi [32]. Two types of microbial degradation are defined: *i*) Depolymerization by free radicals produced by extracellular enzymes in which the size of the polymer is reduced to lower molecular weight intermediates [33]. Due to the size of the intermediates, depolymerization processes are extracellular processes. *ii*) Mineralization, which is the degradation process in which microorganisms use low molecular weight intermediates from depolymerization for their metabolism, thus producing residual bio-products (CO_2 , H_2O , CH_4 and/or biomass) depending on the aerobic or anaerobic conditions [34].

Additionally, microorganisms develop several complementary mechanisms that favour degradation in microbial degradation under natural conditions or *in vitro*. They can adsorb and adhere to different types of polymers through different mechanisms. One of them is adsorption to the surface of the material, which is an independent process of the metabolism and is mediated by the interaction of certain functional groups (carboxyl, amino, hydrogen sulfide, among others) present in the cell wall with some functional groups of the polymer (carbonyl). This union can be irreversible and is influenced by pH, chemical characteristics of the surface of the material (hydrophobic or hydrophilic), temperature, presence of dissolved ions, among others [35]. Once the adsorption process occurs, microorganisms can adhere to the material, which involves the production of substances such as exopolysaccharides and the formation of biofilms. Different microbial communities are present in these biofilms which through highly specialized structures (flagella, fimbriae and pili) and surface proteins bind to the surface of the polymer and communicate with each other to interact synergistically or in proto-cooperation to increase the degradation of the material [36]. The biodegradation ratio of a certain material depends fundamentally on environmental conditions such as temperature and humidity and the class of microorganisms present in it [37].

Once the adsorption and adhesion processes to the surface of the material occurs, the microorganisms can continue to colonize it through the growth of the biofilm (bacteria, yeast, filamentous fungi or actinobacteria) or by the extension of the mycelium in filamentous fungi. In addition to the colonization capacity of the mycelium, the fungi produce hydrophobic type proteins that form hydrophobic or hydrophilic interfaces that facilitate the penetration of hyphae and the growth of the mycelial network on the PE [38]. As the colonization process continues, microorganisms produce different classes of enzymes. The enzymes that catalyse oxidation processes are oxidative enzymes such as manganese peroxidases (E.C.1.11.1.13) [39], lignin peroxidases (E.C.1.11.1.14) [40], oxygenases (E.C.1.1.1.13 or E.C.1.1.1.14) [41] and polyphenol oxidases (E.C.1.10.3.1) [42]. The enzymes present in each cell define its metabolic processes and, in particular, the polymers (artificial or bio-based) can be degraded by the action of enzymes secreted by certain microorganisms. This type of degradation is often referred to as enzyme-mediated degradation or enzymatic degradation. For example, PE and polyurethane can be oxidized by peroxidase, catalase (E.C.1.11.1.6) and other oxidases. Under the appropriate composting conditions and polymer molecular weight, the appropriate microorganism(s), a certain plastic compound can be completely mineralized by aerobic oxidation processes [43-48].

In enzyme-mediated degradation, the substrate is required to enter the active centre of the enzymes for the catalytic reaction to occur, representing a problem in the degradation of polymers since they have a high molecular weight and cannot enter into the active centre. An alternative to this inconvenience is the use of redox mediators, which have been broadly studied in ligninolytic fungi, producers of laccase, which substantially improve the degradation of different types of polymers.

A mediator is a molecule with low molecular weight and high redox potential (585 mV) which is first oxidized by the laccase, giving place to form benzyl radicals that react with O₂, presenting the dissociation of hydrogen due to the breakdown of the C_α – C_β bond [49]. This requires a high oxidation potential of the mediator and, in addition, a stable laccase enzyme that is not inactivated by the free form of the mediator [50]. Thanks to this mechanism, the redox mediator can carry out the oxidation of polymer compounds away from the influence of hyphae, since it can diffuse over the material [38].

At last, some microorganisms, such as ligninolytic fungi, have an additional mechanism to favour the degradation of polymers called biological Fenton based on the production of hydrogen peroxide from the metabolism of organic compounds such as cellulose, hemicellulose, cellobiose, glucose, among others. This hydrogen peroxide, under adequate acidity conditions, reacts with iron salts, forming reactive oxygen species that, in turn, oxidize the aliphatic portion of the LDPE, generating oxidative transformation by breaking C–C bonds [51].

2.4. Oxo-biodegradation

It is the degradation that results from the aerobic oxidative process (photo-oxidation and thermo-oxidation) and abiotic oxidative process (enzymatic oxidation) that can occur simultaneously or successively [52]. It is very important to mention that one of the main differences between aerobic processes and anaerobic processes is that in the former, CO₂ is produced as a residual product and, in the latter, CH₄ (methane) is produced, which is another one of the named greenhouse gases.

2.5. Abiotic and aerobic oxidation

Given, on the one hand, that in general artificial plastic compounds are not biodegradable (in the sense that there is some microorganism that attacks the material and transforms it into CO₂, H₂O and biomass) and, on the other hand, that the photo-degradation processes transform the material into micro-plastics, currently, the trend is to achieve a successful synergy between the two processes. Nowadays, for plastic to be considered environmentally degradable, it must meet the following conditions: *i*) Its exposure to the environment or its disposal in a landfill should create microscopic hydrophilic fragments of low weight molecular. *ii*) The micro-fragments obtained must be capable of being transformed by a biological attack into CO₂, H₂O and biomass without the presence of toxic by-products. These two conditions are often called abiotic oxidation and aerobic oxidation respectively, [53]. These concepts indicate that one of the most important processes, particularly in plastics, is the process of oxidation. The Ziegler-Natta and Phillips polymerization processes, the single-site catalyst method and the cocatalyst method involve oxidation processes produced by peroxide radicals on the hydrogen atoms of the polymer. During the thermoforming process, free radicals are also generated in the polymer structure so that hydrogen atoms of the polymer chain are replaced by peroxide radicals. To initiate this type of reaction, it is required that, in some way, the breaking of the C–C and C–H bonds of the polymer chain is induced. While the role of stabilizing additives is to include atoms or molecules in the polymer chain, so that the activation energy required to break the C–C bonds is higher; the typical way to induce the breaking of the C–C and C–H bonds is by introducing energy to the system through temperature (thermo-oxidation) or by inducing electromagnetic radiation, mainly ultraviolet radiation (photo-oxidation) in the presence of oxygen molecules and, generally, transition metals. The effect of the oxidation processes in the plastic compounds is to break the polymer chains, reducing the molecular weight, losing elastic properties and fragmenting the material, mainly in the amorphous regions of the material. From this point of view, additives can be used to inhibit (stabilizers) or, on the contrary, to promote the production of free radicals

(pro-degradants). Both uses can also produce temporarily controlled oxidation effects. In both cases, of course, there are by-products (hydroperoxides, metal complexes, alcohols, carboxylic acids, etc.) that eventually can be toxic.

3. Plastics and the environment

Since the development of the Goodyear vulcanization process in 1839, polymers have played a fundamental role in the technological development of humanity, displacing the use of natural materials such as metals, glass, wood, rubber, and paper. In its initial stage, the development of polymer compounds was controlled exclusively by the producing companies that patented and offered highly designed products with improved properties, high cost and environmentally friendly. In 1972, the National Academy of Sciences and the United States Academy of Chemistry supported the first event in which the participation of different associations in the scientific study of plastic compounds and their environmental impact was raised [54]. It was only up to this point that society had asked the question about the benefits and drawbacks of polymer technology and its negative environmental impact was recognized. Society recognized plastic compounds as potentially toxic and incompatible with the environment. One of the first results of this event was the forecast, made in 1972, of the production of plastics in the United States. Until now, the prediction of an annual increase of 6 % has been fulfilled, with a production of around 150×10^9 kg per year, far exceeding the production, in volume, of other types of materials such as steel, placing us in a very accelerated process known as the era or age of plastic [55]. Furthermore, the prediction that 20 % of the total production would be used for packaging applications of different types of products has been fulfilled and of these, 2 % would become waste. Another historically important event was the appearance of the Green Report [56], in which various practices are suggested, in particular, for the fabrication of plastic compounds. Among the practices with the greatest environmental relevance are: *i*) Environmental demands must be universal and proven with scientific evidence, and *ii*) Product specifications must include possible effects on the environment during each of the stages that define its life cycle, including the materials used during its production, contamination from natural sources, the energy consumed in its fabrication, the appropriate processes for its recycling (residues) and the waste control process. The energy required to create a renewable PE container is 30 times less than for a similar glass or aluminium container, which, of course, also has a direct implication in the efficient use of energy [57].

3.1. Bio-based Plastics

Historically, different points of view have been presented, both of the environmental impact of plastics as well as the different strategies to mitigate the problem. A common point of view on the problem focused on the idea that, due to the complex chemical structure of the plastic compounds, no biological organisms have been developed that are capable of assimilating it into the environment. This inability to assimilate plastics by biological organisms implies an excessive accumulation of this material, to such an extent that it is predicted that in a very short time the earth's surface will be covered by a 3-meter thick plastic layer [58]. In response to this supposed inability of the natural microorganisms to assimilate polymer compounds, the design and fabrication of bio-based plastics has been proposed. Bio-based plastics are thermoplastics (PE, polyester, polystyrene) synthesized from renewable or living natural substances through a fermentation process of mainly wheat, grains, cellulose, biomass or starch. However, it is well known that various naturally occurring microorganisms (bacteria, fungi, algae, etc.) are capable of assimilating different kind of plastic compounds under specific conditions [59].

Since its initial approach, bio-based plastics encountered, beyond various political and economic interests, three arguments that strongly impeded their implementation. The first is that the use of renewable sources to replace some synthetic polymers requires the use of large tracts of land dedicated to monocultives, which makes this approach environmentally non-viable [60]. For example, different local studies [56] have shown the non-viability of replacing PE with wood, in the sense that it would not be possible to cover the current demand of PE with the total production of timber trees, which would also lead to serious problems with the physicochemical and biological balance of the soil. The second argument is that the cost of production from materials increases considerably, which ends up being economically unattractive. In particular, the use of renewable materials implies an increase in the energy cost of fabrication or reprocessing. Finally, due to high prices and the lack of essential properties required for main applications, the third argument refers to the fact that the bio-based materials with improved properties have yet to be developed [15]. For example, the mechanical integrity of a paper bag could not replace that of a plastic bag, limiting its applications. In addition, the fact is that the production of paper has much more implications in terms of air and water pollution, compared to the fabrication of PE [59]. On the other hand, taking into account that plastic bag weighs one-tenth that of a paper bag, there would also be problems in terms of waste management [54].

Generally, it is assumed that bio-based plastics are, by definition, environmentally friendly or sustainable, that they meet these characteristics, specifically, the property of not presenting “unacceptable” effects in terms of depletion of natural resources and environmental pollution. Within the framework of the concept of Life Cycle Assessment (LCA) the term “unacceptable” implies the relative comparison between bio-plastics and plastic compounds from a green economy point of view [61]. The LCA assumes that the production of bioplastics does not use fossil sources because the synthesis and degradation of this type of material fulfil the carbon cycle through biological processes [56]. Unfortunately, this type of approximations, primarily referring to the energy used and the environmental pollution generated in the fabrication process, has led to a series of inconsistencies and lack of traceability that even generate contradictions in the carbon footprint model. Not only energy and environmental pollution must be taken into account in the fabrication process, but also the ability of polymers to re-integrate the energy consumed during the fabrication process.

At last, it is important to clarify that, although the general definition of bio-based plastics, commonly called bioplastics, indicates that they are based on renewable or living materials, this does not imply that they are necessarily biodegradable. Biodegradability does not depend on the origin of the material but exclusively on its chemical structure. In particular, bioplastic is biodegradable only if it is susceptible to degradation by enzymes, otherwise, if another degradation procedure takes place it cannot be considered biodegradable. For this reason, it is not appropriate to assume in advance that bio-based plastics are environmentally friendly [62]. Of course, not all the biodegradable plastic is a bioplastic.

3.2. Plastic garbage and litter

A basic relationship between production, garbage and litter is stated within the concept of “sustainable growth”, [54]. Garbage is the part of the total production that a community takes care of and obtains added value through the collection, incineration, recycling or dumping [18]. On the other hand, litter is the part of the production total that escapes from solid garbage management systems so that, eventually, they end up contaminating different ecological systems, especially rivers, seas and oceans [63]. In general terms, litter definition states as synthetic objects that are where they should not be [18].

From the point of view of the so-called “green design” [3], the specific action plans regarding garbage and litter (which can include a wide range of materials such as polymer compounds used in construction, electronics, food packaging, automotive and pharmaceutical industries, etc.) comprise the following fundamental aspects [64]: *i*) restrictions on the generation of garbage through the reduction in production, *ii*) stimulation of the reuse of materials, *iii*) stimulation and development of suitable materials for recycling, and *iv*) end-of-life garbage disposal systems.

Garbage management is, in terms of final disposal systems, considered principally defined by recycling (re-processing), incineration, composting and landfill technology [65]. All of them have advantages and disadvantages from an environmental and economic point of view. On the other hand, the success of these processes depends mainly on *i*) very specific environmental conditions (oxygen, heat, UV radiation, microorganisms), *ii*) the type of plastic (plastic compound, or bioplastic) that is intended to be treated, and *iii*) an adequate collection system that guarantees a low generation of litter [66]. It is important to mention that, in the case of recycling, a mechanical process [64], both plastic compounds and bioplastics, leads to problems in the performance of recycled products. This is because the quality of plastics strongly depends on their origin and history. Therefore, recycling processes can produce changes in the molecular structure of the polymer chains, inducing a deterioration in the physicochemical properties of the material.

3.3. Degradation of plastics

Perhaps one of the most important definitions on which consensus must be reached is the concept of degradation. Until very recently, polymer degradation processes focused on avoiding material malfunctions caused by its transformation, i.e., the work focused on avoiding the degradation of the defined materials, so as any change in the physicochemical properties of the material. For this reason, a significant development can be observed in the concept of degradation. ASTM-standard defines degradation as a change in the chemical structure, physical properties or appearance of the plastic, while the ISO-standard establishes that it is an irreversible process characterized by a significant change in the structure of the material (typically characterized by a change in its properties such as integrity, molecular mass, structure, viscoelastic properties), and/or by fragmentation. The degradation is affected by environmental conditions that act in a time interval and can comprise one or more steps. From these points of view, absolutely all matter found on the face of the earth is degradable and, above all, there is a risk that in the degradation process more toxic and dangerous by-products are obtained than the original material. The E-CO case is an example of this situation. From the point of view of materials science, the above-described definitions are called transformation and degradation definition states as the degradation of the material into water, carbon dioxide and, eventually, biomass. In many contexts, this definition is known as mineralization and the definition states as the essential process to close the (bio-geo-chem) carbon cycle. Currently, plastics must have a very stable pre-defined life cycle in which their physicochemical properties should not suffer significant changes. After this time the material must start a rapid degradation process.

3.4. Biodegradability and Biodegradation

These concepts are usually synonyms. The former refers to the potentiality that is the possibility of plastic compounds for degradation by a certain biological agent. The latter refers to the biodegradation process (measurable by some defined method) of a plastic compound that occurs under certain conditions, in a certain interval of time. The biodegradability of a plastic compound is determined from the study of its biodegradation and material is considered biodegradable when, at least, 90 % of its mass has been transformed, in at least, six months. Initially, it was considered

obvious that there should exist, at least, one enzyme in the biosphere that would be capable of attacking the chemical bonds of a specific polymer chain. Currently, it has been shown that polymeric chains present a strong resistance to be attacked by microorganisms due to low surface area, high hydrophobicity and high molecular weight. Microorganisms tend to attack the ends of polymer chains so that, taking into account that the number of said ends is inversely proportional to molecular weight, polymeric chains are not biodegradable. The biodegradability of a plastic compound depends mainly on the hydrophilicity, the oxidation degree of the polymeric chains that compose it and the molecular weight. Other physicochemical properties of the material such as crystallinity, orientation, tensile properties, surface area and the film thickness can affect the degradation rate [67]. The biodegradation rate is a function of the surface area of the sample in such a way that, in general, the material should be first fragmented into small particles through abiotic processes that transforms the material into nanometric pieces with a high surface area and a low molecular weight [68]. Biodegradable plastic compounds (biobased or fuel based) can be hydro-biodegradable or oxo-biodegradable. In both cases, the microplastic is assimilated by enzymatic processes generated by microorganisms in the environment until, ideally, complete the mineralization of the material.

In its initial stage, biodegradation results from the use of polymer chains as a nutrient (carbon source) for microorganisms, so that, in the biodegradation process, the formation of a biofilm on the surface of the plastic compound is necessary, which is strongly dependent on the hydrophilicity of the surface, taking into account that the surface of plastic compounds is highly hydrophobic [69]. From the litter point of view, it is very important to generate complete mineralization processes in a very short time, whilst from the garbage point of view, this is not a desirable effect.

According to ASTM-standards, biodegradable plastic is a degradable material in which degradation results from the action of microorganisms present in the environment such as bacteria, fungi and algae. Conversely, the ISO-standard defines it as the degradation produced by biological activity, especially by enzymatic activity, producing a significant change in the chemical structure of the material. This standard directly relates biodegradation to the composting of plastic garbage. In addition, there are definitions found in the literature such as *i)* A process produced by the exposure of the material to biotic environment (soil or compost), and *ii)* A process in which microbial growth is evidenced on the surface of the material. Nowadays, it is relatively well established that the only way to measure the biodegradation of material is in terms of CO₂ production (mineralization) when it is exposed to a specific biotic environment (soil or compost) for a determined period. The CEN/TR 15351 standard defines biodegradable plastics as plastic capable of undergoing physical or biological decomposition, so that, ultimately, it decomposes into CO₂, H₂O and biomass and that, according to European standards on the packaging, is recovered through composting and anaerobic digestion.

Although without being an established definition by a regulatory entity, biodegradation is currently defined as a process by which a material disintegrates and is decomposed by microorganisms into elements that are found in nature, such as CO₂, H₂O and biomass. Additionally, biodegradation can occur in oxygen-rich environments (aerobic biodegradation) or oxygen-poor environments (anaerobic biodegradation). Despite its inherent importance, historically, the concept of biodegradability has been characterized by the absence of precise and traceable technical standards. For example, only recently there was a suitable method proposed to evaluate the biodegradability of different types of plastics in aqueous media (marine environments) by quantifying the CO₂ produced by a specific type of bacteria [70]. It has been established recently that to determine the biodegradability of a given material in different environments (particularly in marine environments), current regulations and measurement methods are insufficient and present little

traceability [71] and that, in general, the determination of the composition and taxonomy in the so-called Plasticsphere (surface of the material in contact with the marine environment) is not enough to justify the enzymatic oxidation of the material. Currently, the work should focus on the development of models that adequately identify the degradation mechanisms, mainly in marine environments [43].

3.5. The origin of micro-plastics

The biodegradable plastics technology has shown significant advantages in terms of litter management. One of the most successful cases of biodegradable plastics was the development of the Hi-ConeTM. This plastic complies, in principle, with the properties of an ideal material from the sustainable growth perspective [54]. Specifically, Hi-ConeTM has a low weight, requires a low demand of non-renewable resources, and exhibits physicochemical properties that make it a candidate to replace plastic compounds and paper used for packaging. Additionally, this material diminishes the risk of contamination in natural environments and presents a minimalist design that demonstrates the triumph of the concept of under packaging. Initially, it was defined as a photo-degradable compound with very little waste production that protects wildlife in forests and oceans. Subsequently, some modifications of this new biodegradable plastic led to the development of the photo-degradable polymer compound ethylene-carbon monoxide (E-CO). The federal laws in the United States demanded that, in the 1990s, all six-pack carrier type products should be produced with photodegradable E-CO compounds (US Public Law 100-556).

At present, it is known that the E-CO polymer compound does not comply with the basic postulates of sustainable development since they are the main source of environmental contamination by micro-plastics [72]. This unfortunate example shows what has been the main problem in the recent development of degradable plastics: the lack of incorporation of scientific concepts, precise definitions and technical standards that regulate technological developments in this important human activity. As bacteria can biodegrade compounds with molecular weight up to 1500 Da [73, 74] which corresponds, in the case of LDPE with a density of 0.94 g cm^{-3} , to fragments with a volume of the order of 4.0 nm^3 . There is evidence, thus, of the need for a redefinition of the concept of degradation that adapts more adequately to the concepts of garbage, litter and recycling of all types of plastics. The fragmentation of polymer compounds, including photo-degrading additives, is part of the process of degradation of materials, therefore they can be considered as a by-product of such process i.e., the fragmentation process implies the production of micro and nano plastics [75].

3.6. Composting

Furthermore, composting is currently one of the most used methods in the management of solid garbage, and consists of transforming compostable plastic into biomass, through a controlled oxidation process, under conditions, also controlled, of forced aeration, temperature and humidity in a given time. In other words, compostable polymers must degrade without generating by-products such as heavy metals, toxins or micro (nano) plastics. The ASTM 6400-19 standard establishes that plastic is compostable if it degrades by the effect of biological processes during composting until it is reduced to CO_2 , H_2O , inorganic compounds and biomass at a consistent degradation rate with other compostable materials, without leaving visible, distinguishable or toxic residues. The EN 13432 standard specifies requirements and procedures to determine the compostability and anaerobic treatability of packaging and packaging materials. It addresses characteristics of

biodegradability, disintegration during biological treatment, effect on the biological treatment process and effect on the quality of the resulting compost. Plastics certified according to EN 13432 can be labelled by the “Seedling” logo.

Composting, ultimately, is a biodegradation process forced by external conditions that define the biological activity inside (aeration and natural heat production). The result is a material that contains beneficial nutrients for the soil. For a material to be compostable, it must meet: *i*) Disintegration during composting until the plastic waste is not visually distinguishable ($< 2 \text{ mm}^2$) from other organic materials in a period of no longer than 12 weeks. *ii*) Composting material must contain at least 50 % organic matter and must not exceed the limits of toxic elements. *iii*) The products must biodegrade or mineralize for at least 90 % in a period of fewer than 6 months under controlled composting conditions. *iv*) It should not hurt plant growth in the compost product compared to composting material produced by biowaste.

Typical examples of compostable plastics are cellulose-based films, starch-based copolymers, polylactic acid (PLA) and polybutylene adipate terephthalate (PBAT). Legislative acts in different countries establish that the commercialization, distribution and delivery of single-use plastics (disposables) are permissible only if they are compostable plastics [76] encouraging, in this way, the use of bio-based plastics.

3.7. Oxo-degradation vs oxo-biodegradation

The terminological guide in the field of degradable and biodegradable plastics and polymers of the European Commission for Standardization (CEN) CEN/TR 15351 establishes that oxo-degradation is the degradation process that results from the oxidative breakdown of macromolecules and that oxo-biodegradation is the degradation produced by oxidation phenomena and by the action of cells that can occur successively or simultaneously. On its part, the ISO 472: 2013 standard defines oxidatively degradable plastic as degradable plastic in which degradation results from oxidation processes. On the other hand, the Directive (EU) 2019/904 establishes that an oxo-degradable plastic definition states as “plastic materials that include additives which, through oxidation, lead to the fragmentation of the plastic material into micro-fragments or to chemical decomposition”. From these documents, it is observed that the different directives and recommendations must be very clear and careful to not use the terms oxo-degradable and oxo-biodegradable as synonyms.

4. Oxo-biodegradable plastics technology

Recently a new technology has been developed in which it is proposed to use pro-oxidant (pro-degradant) additives to control the degradation of different types of plastics. This technology is intended to control the life cycle of polymers so that, depending on the specific application required, the stability of the product can be guaranteed and, once the product is discarded, sunlight and temperature initiate (accelerate) the aerobic oxo-degradation process. The result of this oxidation is to fragment the material so that micrometric pieces of the material are produced with low molecular weight, hydrophobic and, therefore, suitable for enzymatic oxidation processes. Oxo-biodegradable additives (based on molecules of cobalt, nickel, manganese, iron compound) are typically incorporated at the end of the synthesis process of plastics (PE, PP, polystyrene and others) at a defined concentration according to the use (storage time and degradation time) of the final product. An important advantage of this technology is that it does not substantially alter the manufacturing process of the material, which has a direct effect on the cost of production.

Although it is a technology designed for waste management, the fact of it being a process activated by both sunlight and heat allows the oxidation process to take place even when the material does not directly receive radiation in the garbage management and composting processes.

Oxo-biodegradable plastics are defined, according to the Oxo-degradable Plastics Association, as plastic materials to which a pro-oxidant additive has been added that promote the degradation of different types of polymers such as PE and PP through the catalysis of the naturally oxidative polymer chains, producing a decrease in molecular weight and oxidative degradation. This oxidation causes loss of mechanical properties and, as a further matter, the oxygen consumption increases hydrophilicity and reduces molecular weight, producing a material that is no longer plastic and can be assimilated into the environment by microorganisms commonly present in the soil and the oceans. It is also said that the so-called oxo-plastics or oxo-degradable plastics are conventional plastic compounds to which additives are added, accelerating their fragmentation into very small pieces. The fragmentation process is induced by UV radiation and heat. The fragmentation process terminates in the production of micro (nano) plastics with adequate properties so that a process of microbiological attack begins, inducing, in this way, their enzymatic biodegradation. At present, the possibility arises that pro-degradative additives not only induce the breaking of polymer chains but also act as a catalyst in the formation of intermediate biodegradable molecules activated, the catalyst, by UV radiation. In this sense, it has been shown that radiation-induced oxidative degradation caused by oxo-biodegradable additives in PE continues even in dark conditions during a subsequent thermo-oxidation process [77].

Taking into account the benefits in economic terms of the technology of plastics with pro-oxidant additives (production costs between 10 % and 20 % lower than the production cost of traditional biopolymers) different studies, recently, have been developed aimed at demonstrating the abiotic oxidation and aerobic mineralization of different types of biodegradable oxo-plastics, using the standards methodology: ASTM D6954 "Standard Guide for Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation", British Standard 8472 "Packaging – Method for determining the degradability, oxo-biodegradability and phytotoxicity of plastics", French Accord T51-808 "Plastics Assessment of oxo-biodegradability of polyolefinic materials in the form of films", Swedish Standard SPCR 141 "Polymer waste degradable by abiotic and subsequent biological degradation – Requirements and test methods", UAE Standard 5009:2009 "Standard & Specification for Oxo-biodegradation of Plastic bags and other disposable Plastic objects", Saudi Standard "Technical Regulation for Degradable Plastic Products", ISO 17556 Plastics "Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved". Although very common, it is important not to confuse the term oxo-biodegradation with oxo-degradable, photo-/thermo-degradable, or oxo-fragmentable.

The technology of oxo-biodegradable plastics has been proposed, in principle, as a viable alternative in the management of plastic waste because, in composting systems, solar radiation does not directly affect the material. However, the benefits that this technology can have in plastic garbage management and recycling processes, as well as packing and landfill, are raised. It has been suggested that mechanical recycling (direct re-processing of plastic garbage) is the most effective method, economical and viable in the treatment of plastic garbage [78].

However, it should be taken into account that significant amounts of stabilizers and anti-oxidants are generally used for proper garbage management (during the synthesis process and in the recycling process) which are intended to increase the lifetime of plastics. A synergistic balance

can then be achieved between adequate amounts of anti-oxidant and pro-oxidant additives that result in oxo-biodegradable plastics, having a certain lifetime depending on the desired application and the final disposal method.

This technology is not alien to the traditional methodology of plastic compounds in the sense that each manufacturer registers and patents different pro-oxidant molecules at different concentrations, making it difficult to predict the behavior of the final product and, unfortunately, it is necessary to rely on extrapolation models. In the process of developing the pro-oxidant additive technology and to validate it as a real environmental alternative, the ASTM recently implemented the D6954-18 standard by which a methodology is established to compare and classify, at the laboratory level, the loss degree of physical properties and, more importantly, the mineralization ratio in a given period, as well as the ecological impact in specific applications and different environments of disposal after aerobic and biotic degradation of different types of plastics. This is an empirical standard in which the impact of final products (micro-plastics, toxicity and composting) on the environment of plastics with and without oxo-degradable additives is comparatively analyzed.

4.1. Regulations regarding oxo-biodegradable plastics

The following are illustrations of the general legislation in force and an overview of oxo-biodegradable plastics; based on several concrete cases.

4.1.1. Assessing the Environmental Impacts of Oxo-degradable Plastics Across Their Life Cycle, A research report completed for the Department for Environment, Food and Rural Affairs, Loughborough University (UK), January 2010

This report focuses on the environmental impact in terms of establishing the rate and time of biodegradation of litter and garbage of oxo-degradable plastics. The general conclusion of this report is that oxo-biodegradable plastics do not perform better concerning their environmental impact and that, on the contrary, they can potentially produce certain negative effects on the environment.

This conclusion is based on the following findings: *i)* The rate and time of degradation of oxo-biodegradable plastics cannot be exactly pre-determined because this process depends on the specific environmental conditions of each region. For example, it is reported that in the UK oxo-biodegradable plastics under disposed of conditions break into small fragments within 2 to 5 years. *ii)* Oxo-biodegradable plastics are not compostable according to EN13432 and ASTM 6400 standards, because persistent plastic fragments could affect the quality of the compost after the degradation process. *iii)* Labelling oxo-biodegradable plastics as biodegradable can lead to confusion, in the way that this type of waste can be assumed to be compostable, causing serious contamination in composting plants. *iv)* Biodegradation of oxo-biodegradable plastics can occur only after they have been fragmented and at a slower rate than compostable plastics. The fact that the rate of degradation is generally not a fundamental part of the definition of biodegradability, means that the concept is meaningless unless both the rate and specific conditions of degradation are specified, preferably concerning a defined standard. *v)* The fate of the plastic litter fragments is uncertain and no evidence was found, one way or another, of the effect of this litter on the environment. *vi)* No evidence of a toxicological impact was found, which means that the concentration of pre-existing metals in the soil is higher than what can be induced by oxo-biodegradable plastics. *vii)* The fact that they are degradable limits their application in reusable systems and make their use in recycling systems more complicated. *viii)* It is found that the best approach to the garbage management of oxo-biodegradable plastics is incineration and,

as a second option, dumping. *ix*) Each product needs to be labelled according to the best waste model of management. *x*) Oxo-biodegradable plastics are not suitable for garbage management because, under certain defined environmental conditions, within 2 and 5 years there are still visible fragments that have not started a biodegradation process.

In this report, the following recommendations are made: *i*) The current definition of the term biodegradable does not include the concepts of degradation rate and time, that means it should not be included in the labelling of products, so it is recommended, on the one hand, to explicitly label products with these two concepts and, on the other hand, not to use the term biodegradable to label the products but to give precise instructions for their final disposal. *ii*) Since the final destination of the plastic fragments is not clear, studies should be carried out aimed at determining both the degradation rate in terms of the time in which said fragments are transformed into CO₂ and H₂O and, if this time is very long, determine their impact on different ecosystems. *iii*) The absolute uncertainty of mixing oxo-biodegradable plastics with recyclable plastic compounds indicates that the safest solution is to keep oxo-biodegradable plastics away from recycling plants.

4.1.2. The Impact of the Use of "Oxo-degradable" Plastic on the Environment for the European Commission DG Environment. The project was conducted under Framework Contract No ENV.A.2/FRA/2015/0008. Eunomia Research & Consulting. 2016

This report establishes that there has been an intense debate regarding whether oxo-biodegradable plastics, defined in the way that producers of this type of material do, damage the environment and/or if they produce adverse effects in recycling processes in such a way that, in November 2014, members of the European Parliament proposed a total ban on oxo-degradable plastics in the European Union. However, this measure was repealed and, through an amendment to the "Packaging and Packaging Waste" directive in May 2015, a commission was put in charge to examine the environmental impact of the use of plastic bags made with oxo-biodegradable materials in the environment. This report is the result of the general conclusions of said commission and compiles different types of information available regarding the environmental impact of the material to form an adequate opinion in decision-making.

The methodology of this report is proposed in terms of collecting information, both scientific and non-scientific, regarding 13 hypotheses raised both by the producers of the material and by common beliefs disseminated in society. The general result on the validity of these hypotheses is *i*) Pro-oxidant additives can accelerate the fragmentation of plastic compounds in open environments: Evidence is found. *ii*) Oxo-biodegradable plastics can be considered non-compostable: Evidence is found. *iii*) Oxo-degradable plastics, after fragmentation, are biodegraded in open environments: Partial evidence is found. *iv*) Oxo-biodegradable plastics do not degrade in landfills: Evidence is found. *v*) Oxo-biodegradable plastics are biodegradable in marine environments: No information available. *vi*) Partially degraded plastic fragments and their additives have negative effects on the soil or ecosystems: Partial evidence is found. *vii*) The use of oxo-biodegradable plastics promotes the attitude of using and disposing of: No information available. *viii*) Oxo-biodegradable plastics are a possible solution to reduce the problem of plastic litter in marine environments compared to conventional plastics: No information is available. *ix*) Oxo-biodegradable plastics can be identified and separated into collection systems: Claim disproved. *x*) Oxo-biodegradable plastics can be identified and separated in recycling systems: Claim disproved. *xi*) The quality of recycled plastic compounds is not adversely affected by the presence of oxo-biodegradable plastics in recycling systems: Claim disproved. *xii*) The presence of oxo-degradable plastics in recycling systems does not affect recycling costs or commerce: Claim disproved. *xiii*) The

presence of oxo-biodegradable plastics in recycling systems does not affect the ability of producers to guarantee specific requirements (physical-chemical properties) of the final products: Depends on the market.

Based on these findings, the final recommendations of this report are: *i)* The debate on the biodegradability of oxo-degradable plastics is not over, however, it can be affirmed that they simply fragment, so it must be confirmed if the biodegradation rate is high enough to be acceptable from an environmental point of view and if this biodegradation takes place in natural environments. *ii)* The wide variety of formulations about oxo-degradable plastics, most of which have intellectual property registration and are therefore confidential, and the lack of regulation on this type of additives implies that there are no guarantees about adequate performance of oxo-degradable plastics, as much as in its commercialization and its litter. *iii)* No type of certification allows producers to affirm that oxo-degradable plastics are biodegradable under specific environmental conditions. It is considered that the existing certifications in France (AFNOR AC T51-808) and in the United Arab Emirates (UAE-standard 5009-2009 in which only the commercialization of oxo-degradable plastics is allowed) are not valid. *iv)* To be able to commercialize oxo-degradable plastics it is necessary to develop adequate European standards. *v)* One of the most notorious obstacles that both producers and legislators have to overcome in matters related to oxo-biodegradable plastics is the lack of unification of related standards. *vi)* There is a large number of producers of oxo-degradable plastics, each developing a new additive from which they claim to obtain complete biodegradation. This fact makes it very difficult to obtain conclusive evidence that allows defining whether oxo-degradable plastics technology, as a whole, hurts the environment. *vii)* While both standardization methods and adequate technical norms are being developed, the sale of oxo-degradable plastics should be prevented under specific conditions where their disadvantage has been proven, i.e., in composting and anaerobic degradation systems. *viii)* There is no clear evidence that oxo-degradable plastics are the solution, as claimed by producers, to the problem of plastic pollution in marine environments. Advertising of the product in this regard should not be allowed, in particular in separately sold products. *ix)* All oxo-degradable plastics should present toxicity tests. *x)* It must be shown that litter does not have a negative toxic effect on the environment. In addition, the technical (European) regulations regarding this effect must be included. *xi)* Litter management behaviour should be established for all biodegradable or compostable products.

Lastly, this report encourages producers to work towards the development of appropriate standards that allow scientific tests to be carried out to verify the claims they make regarding the properties of their products, as well as to standardize the nomenclature regarding biodegradable products in relevant environments.

4.1.3. Report from the commission to the European Parliament and the council on the impact of the use of oxo-degradable plastic, including oxo-degradable plastic carrier bags, on the environment. 2018

The main objective of this report is to influence the reduction of the consumption of low-weight plastic bags and, therefore, the reduction of the generation of litter and accumulation in the environment (mainly marine) produced by the use of this type of product. In particular, the commission examined the impact of oxo-degradable plastics on the environment on three main fronts: *i)* biodegradability of oxo-degradable plastics in various environments, *ii)* environmental impact in terms of the generation of litter and *iii)* recycling.

In general terms, this report conclude (wrongly) that, although there is a certain consensus among the scientific and industrial communities that, in open environments, pro-oxidant additives can accelerate the fragmentation of the material, there is no scientific documentation on its complete biodegradation in any of these environments. It is recommended to design and carry out tests in short periods to demonstrate complete degradation of molecular weight measurements. Furthermore, since there is no evidence available, tests should be done in real environments.

The report establishes that oxo-degradable plastics are not suitable in composting or anaerobic degradation systems while in the outer layers of landfills (high oxygen availability) they are. There is no evidence of the biodegradation of this type of material in marine environments in reasonable periods and in addition, it is established that oxo-degradable plastics should be identified and separated from other plastic products in recycling systems because they can affect the recycled product quality.

On the one hand, there are no standard methods to date that allow obtaining certifications on the oxo-biodegradability of these materials, in particular on negative effects on the environment in terms of toxicity in real environments and, on the other hand, certification tests must be done for each product given a large number of products of this type with different classes of additives and concentrations.

4.1.4. Directive (EU) 2019/904 of the European Parliament and of the council on reducing the impact of certain plastic products on the environment, June 5, 2019

This directive is contextualized within the parameters of the "European Union Action Plan for the Circular Economy" in which a circular economy is proposed in which the design and production of plastics and plastic products fully respect the needs of reuse, repair and recycling, and in which more sustainable materials are developed and promoted.

Although the main objectives of this directive are: *i*) prevent and reduce the impact of certain plastic products on the environment, in particular the aquatic environment, and on human health and *ii*) foment the transition to a circular economy with innovative and sustainable business models, products and materials since it applies, in particular, to products made with oxo-degradable plastic, in Article 5 it establishes "The Member States shall prohibit the introduction on the market of products made of oxo-degradable plastic".

This directive is supported by the statement: Oxo-degradable plastics do not biodegrade properly and therefore contribute to the contamination of the environment with microplastics, it is not compostable, it negatively affects the recycling of conventional plastic and it does not offer proven environmental benefits.

As mentioned, from the apparent contradictions and the lack of clarity both in the definitions and in the standards of measurement processes and protocols related to the (bio) degradation of plastics, there is currently great confusion regarding the convenience, in terms of environmental pollution and the generation of microplastics, the massive use of pro-oxidant additives or, in general terms, oxo-biodegradable plastics.

The producers of oxo-biodegradable plastics propose this technology as the "solution to environmental pollution produced by plastics" because it *i*) induces biodegradation of LDPE and HDPE in open and marine environments without causing any toxicity, *ii*) is compatible with existing composting technologies (UV radiation activates thermal oxidation processes, which continue even in dark conditions) and recycling (the programmed degradation, controlled by the

concentration of pro-oxidant additives, does not alter the properties of the final product), *iii*) the micro-plastics produced during the abiotic process are easily biodegraded in a reasonable time during the biotic process, guaranteeing that this type of waste does not contaminate the land nor bodies of water. *iv*) The main source of confusion arises from confusing the concepts of oxo-degradation and oxo-biodegradation.

Moreover, environmental movements and some government reports suggest that *i*) oxo-biodegradable plastics contribute significantly to the problem of environmental pollution, mainly in marine environments. *ii*) The colossal use of oxo-biodegradable plastics can impact the behaviour of the population regarding their commitment to the management of plastic waste. *iii*) pro-oxidant additives may not be compatible with recycling processes. *iv*) Abiotic oxidation processes are not activated in recycling, composting or dumping systems. *v*) The oxo-biodegradation process, in litter management processes, is strongly dependent on environmental conditions.

4.2. Technical reports on oxo-biodegradable plastics

The information and contradictory concepts issued by previous reports and directives are addressed within the context of the previous sections in which, based on technical studies, on the one hand, the massive use of pro-oxidant additives is recommended and, on the other hand, its prohibition is recommended. Specifically, over time, there have been several reports on the impact of oxo-biodegradable plastics on the environment, where different institutions have raised the advantages and disadvantages of this technology from different points of view. These reports and directives explicitly show the tendency to confuse between the established definitions and the real impacts on the environment under different degradation conditions and, in addition, clearly show the evolution of this type of study.

4.3. Are oxo-biodegradable plastics biodegradable in the marine environment, composting, recycling, litter and landfills?

Given this situation, this work proposes, based on an adequate bibliographic revision, to answer the question: Are oxo-biodegradable plastics biodegradable in the marine environment, composting, recycling, litter and landfills? The following definitions are assumed:

4.3.1. Biodegradation

Process in which a polymer is transformed by the action of microorganisms into natural chemical elements, such as CO₂, H₂O and biomass. The biodegradation can occur in an oxygen-rich atmosphere (abiotic biodegradation) or an oxygen-poor atmosphere (anaerobic biodegradation).

4.3.2. Oxo-biodegradation

Biodegradation process in which the polymer is transformed into CO₂, H₂O and biomass through the simultaneous or successive action of photo-oxidation (exposure to UV radiation), thermo-oxidation (heat) and enzymatic oxidation (microorganisms). The oxo-biodegradation of conventional plastics, especially LDPE, is induced through the incorporation of pro-oxidant additives in the polymer chains.

4.4. Literature review of the Incidence of oxo-biodegradable plastics in the environment

To determine the incidence of oxo-biodegradable plastics in the environment from the analysis of the production collected and analyzed in a state of the art, i.e., bibliographic research, it was possible to collect and systematize the scientific production (peer-review) regarding the measurement of the biodegradation ratio of this type of materials. In the first place, in the introduction, a literature review was made on the historical development of this important class of materials and the different transformation/degradation mechanisms of plastic compounds were defined (heuristic phase). In the second part of the work (hermeneutic phase), the results of the selected publications are classified and interpreted. The analysis was performed as described below: Scientific literature was screened, limiting a time window for analysis between 2010 and 2021, limiting the search to 100 articles, in the databases of Scopus and WoS using the following keywords: Oxo-biodegradation, degradable polyolefins, biodegradable polyolefins, pro-degradants.

The literature analysis presented in this work focuses specifically on studies that explicitly state the use of oxo-biodegradable material, pro-oxidant, or pro-degradative additives, discarding those that work with oxo-degradable, photo-degrading, or thermo-degrading plastics. In general, reports of various types of polymeric matrices (plastic compounds), to which pro-oxidant additives are added at different relative concentrations, were found in the selected literature. LDPE, HDPE and LLDPE were predominantly found as the most used types of plastic, and the transition metal ions of Co, Fe and Mn, added in the form of organic complex (stearates), as the commonly used pro-oxidant additives. The use of Zn and Zr stearates is also reported. In some cases, the analysis of commercial materials such as d2w, Bionelle, Ecobag, EcoPure, PDQ-H, P-Life, TDPA and AddiFlex is reported. Due to the great diversity of manufacturing processes and types of materials reported in the oxo-biodegradable plastics literature, it is impractical to perform an analysis based on these criteria. Alternatively, in the present work we focus on analyzing: *i*) the degradation process of the material, defining it as a universal degradation process, classifying it as biotic, abiotic and mixed, and *ii*) the characterization methods reported to study the toxicity of these materials, which play a definitive role in the standardization of regulations for the manufacture and use of oxo-biodegradable plastics.

In terms of material degradation, most studies use as an operational definition of the degree of abiotic transformation the carbonyl (Carbonyl Index, CI) and hydroxyl (Hydroxyl Index, HI) defined from measurements using infrared spectroscopy (Fourier Transform Infrared, FTIR). Alternatively, and although it is not a direct measurement of the degree of transformation, the technical standard ASTM 882–85 establishes as a measurement method of transformation of the material the change in its mechanical properties through tests of tensile strength and elongation break, mainly. Other commonly reported methods for the analysis of the transformation of the material include, *i*) analysis of the surface topography of the film using Scanning Electron Microscopy (SEM) or Atomic Force Microscopy (AFM), *ii*) determination of the crystallinity of the material using X-Ray Diffraction (XRD), and *iii*) characterization of optical properties (colour) employing Optical Density (OD). On the other hand, within the methods for analyzing the degree of biotic degradation, the following are reported: *i*) mineralization under biotic conditions from the measurement of carbon dioxide (CO₂) production and defined oxygen (O₂) consumption in the ASTM D5988-18 standard, and *ii*) the use of calorimetric techniques such as, for example, Differential scanning calorimetry (DSC) and Thermogravimetry (TGA). At last, different analytical techniques have recently been proposed as tools to quantify the degradation ratio under abiotic or biotic conditions, for example, different types of chromatography or mass spectroscopy.

Concerning the evaluation of toxicity, several reports seek to analyze the degree of toxicity of plastic bags manufactured mainly with oxo-biodegradable materials. Generally, these studies report the use of X-ray fluorescence (XRF) and Spectrometric atomic absorption to determine primarily the presence of metals, such as Al, Pb, Fe, Cu, Cr, Mn.

5. Abiotic treatments of oxo-biodegradable plastics

In the analyzed literature, several works were found that aim to verify the adequate abiotic transformation of oxo-biodegradable plastics. Based on the conditions in which the transformation occurs, the studies were classified into *i*) real environmental and laboratory conditions and *ii*) packaging and recycling conditions. **Table 1** summarizes the materials, additives, transformation conditions (photo-degradation and/or thermo-degradation), analytical characterization techniques, and the main conclusions of the studies focused on abiotic transformation under accelerated conditions (laboratory) and in real environments. Table 1 also shows that depending on the type of plastic and the additive incorporated, as well as the analysis technique used, the results of the abiotic treatment can change; changes related to the time required for structural changes are appreciated in the material. Pro-oxidant additives accelerate oxidative degradation which manifests itself in as loss of tensile properties, chemical specifications and visible signs of degradation. However, the energy consumption in this type of treatment is crucial, as the presence of pro-oxidant compounds can slightly speed up the transformation process. In this respect, Table 1 shows in the results column some important implications taken into account by the authors of the articles reported.

In general, it can be concluded that the pro-oxidant additives do induce the loss of tensile properties, the creation of fractures and voids and, finally, the material's fragmentation under suitable radiation and temperature conditions. However, important differences have found both between the times required to obtain a certain transformation ratio and between accelerated and environmental processes, which represent a challenge from the point of view of standardization in abiotic transformation processes.

In particular, an important difference is identified between ASTM D5272-08 (Outdoor Exposure) and D5208 (Fluorescent UV Exposure) regarding the presence of UVB and UVC radiation emitted by fluorescent lamps, which are not observed within the solar radiation (Figure 1). It was also found that the oxo-transformation ratio depends, additionally, on the relative concentration and the chemical nature of the pro-oxidant additives on other types of additives present and, even, on mixtures with organic material in the oxo-biodegradable material. Finally, a strong synergistic relationship or correlation is found between photo-oxidation and thermo-oxidation in soil and composting environments.

Table 1. Studies of Abiotic treatments (Accelerated/Environmental)

Ref	Material	Additive	Condition	Analytical techniques	Results
[79]	LDPE	Starch, PLA, Oxo (different concentrations)	Left in the atmosphere. Buried under the ground. Buried under the ground with a regular daily irrigation of the ground. 6 months for all the experiment	TGA, FTIR, SEM, XRD, DSC, Tensile strength (ASTMD638-ISO1184), Impact resistance (256ASTM-D)	Highest change of mechanical properties when using combined additives. Chemical specifications of the films were not remarkably changed, when adding oxo-material and PLA.
[80]	LDPE, LLDPE	PDQ-H Pro oxidant (Willow Ridge Plastic)	Accelerated thermal degradation (ASTM D5510-94) Environmental conditions (ASTM D5272-08) 260 days for both experiments	Trouser tear tests (Tensile strength)	Abiotic oxo-degradation leads to similar trends between accelerated and environmental conditions. Time at which the change in properties occurs which are extremely different.
Continued					

Continuation of Table 1

Ref	Material	Additive	Condition	Analytical techniques	Results
[81]	PE	Transparent commercial grade plastic bags claimed to be of oxo-biodegradable nature	Accelerated (ageing) weathering tests (ASTM D 4329) Exposure cycles for 8 hours of UV exposure at 60 °C, followed by 4 h of condensation at 50 °C.	FTIR, XRF, DSC, SEM/EDS, Tensile strength (ASTM D 882), light transmittance (ASTM D1003-13), Color (ASTM D 2244-11)	Commercial PE bag claiming to be oxo-biodegradable started to show signs of degradation after accelerated weathering. However, biodegradation of such polymers is still relatively limited. There is still a requirement for substantial energy input to the degradation to initiate, and it is uncertain whether these polymers are biodegraded or whether they disintegrate into smaller pieces
[82]	LDPE	Stearates of Mn, Fe and Co.	Accelerated photodegradation (ISO 4892-2:1994) Thermo-oxidative degradation (70 °C)	Tensile strength, elongation at break (ASTM 882-85), FTIR, TGA, DTA, DSC, Flow index (ASTM D1238)	Strong photo-oxidant nature of all three stearates. A thermo oxidative degradation occurs in the presence of pro-oxidant to follow the order: cobalt > manganese > iron.
Continued					

Continuation of Table 1

Ref	Material	Additive	Condition	Analytical techniques	Results
[83]	LDPE, HDPE, PE-BIO, and PE-OXO bags samples were obtained in supermarkets Mexico	Oxodegradable polyethylene	Accelerated photodegradation (UV-B lamps: 280 nm to 320 nm).	IR-ATR	PE-BIO and PE-OXO, respectively, increase their photo-oxidation degree. UV-B radiation induces the increase of crystallinity and the orientation of the chains. LDPE and HDPE pretreated with the correct dose of UVB radiation before its commercial uses or after its final disposition may be an option of biodegradable material without the need to add organic or pro-oxidant agents. The final dispositions of PE-BIO and PE-OXO films must be done according to plastic manufacturers recommendations to these polymers to degrade, which otherwise would not suffer any degradation and would be accumulated in landfills
[84]	PP	d2w	Accelerated photodegradation (ASTM D4329-13)	FTIR, DSC	The oxo-additive induces the oxidative degradation of PP (3 % w/w)
Continued					

Continuation of Table 1

Ref	Material	Additive	Condition	Analytical techniques	Results
[85]	HDPE	HES-W oxo-biodegradable additive	Photo-Oxidation (ASTM D6954-04), 6 weeks	XRD, DSC, FTIR, SEM	Maximum oxo-biodegradability of the samples occurs at 3wt%. Although UV irradiation increased the crystallinity of samples, which can hinder the decomposition of them, low molecular weight polar chains can enhance the oxo-biodegradation since they provide more favorable conditions to microorganisms activity.
[86]	HDPE	cobalt stearate (0.075 % w/w)	Accelerated thermal degradation (vacuum oven 25 °C and 75 °C for 10 days)	TGA, SEM, tensile tester.	Thermal degradation accelerates the degradation rate. Thermal degradation at 75 °C reduces the HDPE weight by 75.99 %.
[73]	LDPE	TDPA	thermal-oxidative degradative treatment in an oven at temperature comparable to those occurring in a full-scale composting process	Tensile (ASTM D 882), SEM, FTIR, SEC, Respirometric biodegradation tests	LDPE-TDPA formulations are effective in promoting the oxidation and subsequent biodegradation of PE in soil environments. Low molecular weight oxidized fragments from LDPE are rapidly biodegradable. LDPE-TDPA blown film gave substantial polymer fragmentation, with loss of mechanical properties in 11 days.
Continued					

Continuation of Table 1

Ref	Material	Additive	Condition	Analytical techniques	Results
[87]	HDPE, LLDPE, PP	oxo-degradable d2w additive	Exposure to natural weathering	FTIR, DSC	Oxo-bio-HDPE/LLDPE blend degrade very rapidly in a few months and increase in crystallinity.
[88]	LDPE, LLDPE	Iron stearate or calcium stearate as pro-oxidant additives (at 0.2 % w/w) were prepared by Repsol.	Natural weathering (ASTM D1435-99) Accelerated weathering (Xenon lamp and a solar filter (300 nm to 800 nm, 45 °C)	FTIR, DSC, TGA, Chemiluminescence	The effect of pro-oxidants was clearly significant in PE aged under natural weathering. Different activity of iron and calcium stearates as pro-oxidants in LDPE and LLDPE under natural an artificial exposure.
[89]	LDPE, LLDPE	Oxo biodegradable additive PDQ-H (Willow Ridge Plastic) at 1 % and 2 % w/w)	Accelerated thermal oxidation (ASTM D5510-94) Environmental oxidation (ASTM D5272-08)	GPC, FTIR, DSC, Tensile test (ASTM D638-10)	Pro-oxidant additive used in this work induces oxidation of PE samples. The main difference from the mechanical point of view is the time at which such loss of properties occurs, which is extremely different between accelerated oven degradation and weather exposure
Continued					

Continuation of Table 1

Ref	Material	Additive	Condition	Analytical techniques	Results
[90]	HDPE	Mn and Fe stearates	Abiotic treatment: aged under accelerated laboratory conditions to mimic the abiotic oxidation occurring in natural conditions (wavelength longer than 300 nm, 60 °C, 40 h)	FTIR, Mass spectrometry, NMR spectroscopy.	The oxidation of polymers under natural environment is an important dynamic process to produce a significant amount of degradation products affected by the abiotic conditions.

On the other hand, **Table 2** shows abiotic transformation studies under packaging and recycling conditions. Due to a necessary balance between pro-oxidant additives and anti-oxidant additives in recycling processes, work must be done towards determining the appropriate relative concentrations of different classes of additives for the final product to be suitable for recycling, i.e., do not affect the stability of other types of plastic compounds. In general, oxo-biodegradable plastics are found to be suitable for recycling as long as the concentration of the pro-oxidant additives is low (less than 1 % w/w, approximately). In terms of the use of oxo-biodegradable plastics for packaging purposes, an adequate concentration of pro-oxidant and anti-degradation additives is sought so that the lifetime of the material can be programmed under suitable environmental conditions, which complies with the respective toxicity standards, and as shown in some works.

Table 2. Studies of Abiotic treatments (Recycling/Packing).

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[91]	LDPE	Pro-degradant P-Life (Mn) and Nor-X (Fe)	Accelerate thermo oxidative (heating cabinets with low airflow at 70 °C)	FTIR, DSC, Tensile test (ISO 527-3:1995)	Incorporation of minor fractions of oxo-biodegradable polyolefins materials in the existing recycling streams will not present a severe effect on the stability of the recycles.
[92]	LDPE	Oxo-degradable d2w additive	Controlled photo oxidation (ASTM D5071-06) Neat LDPE with Aged Oxo degradable and LDPE	FTIR, Tensile test (ASTM D882-12), DSC, Crystallinity (ASTM D3418-15), Melt Flow Rates (ASTM D1238-13)	The reduction of the LDPE elasticity, plasticity, and tensile strength was evident due to the chains rupture and crosslinking of the LDPE molecular structure caused by the oxidation of the aged plastic. The use of these formulations (1 %, 5 % and 10 % w/w), as recycling products is not recommended.
[93]	LDPE	Mix of antioxidants and cobalt stearate	Artificial weathering (A340 UV lamp, 63 °C)	FTIR	Transition metal stearates, and especially cobalt stearate, accelerate the photo-degradation of LDPE films. These experimental results suggest that recycled LDPE could be re-stabilized with cobalt stearate as a photo-degradant.
Continued					

Continuation of Table 2

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[94]	LLDPE	Oxo-biodegradable additive (HES-W) mixed with poly(1-hexene)	Photo-oxidation (254 nm, 338 h and 1008 h)	FTIR, TG, DTG, AFM, tensile strength and elongation-at-break (ASTM D638)	Presence of other kind of additives in LLDPE matrix can deteriorate its oxo- biodegradability.
[95]	LDPE	Pro-oxidant additive cobalt (III) stearate (0.3% w/w) (K. K Polycolor India)	Photo oxidation (40-W UVB Lamp, 280 nm to 350 nm, 30 °C, 49 days).	Contact angle and surface energy, SEM, AFM	Formation of larger holes on the surfaces of LDPE films containing oxo-biodegradable additive and the increase in the surface roughness of such films. Mechanical properties of LDPE films with incorporated additive become more fragile after 49 days of UV irradiation. Additives inducing hydrophilicity. The modified polymers were useful in the packaging industry, because they reduce the accumulation of polyethylene in soil, which further facilitates microbial attachment on the polymer surface and aids biodegradation.

5.1. Biotic degradation of oxo-biodegradable plastics

According to the literature, studies that focus on biotic transformations are mainly developed in soil or composting conditions. **Table 3** summarizes works focused on studying the biotic degradation of oxo-biodegradable plastics under soil conditions. In this type of work, an abiotic pre-treatment of the material is not carried out and the aim is to determine the degradation ratio by enzymatic oxidation processes in a soil environment and in the laboratory or real conditions. The mineralization ratio must be measured in terms of CO₂ production and is strongly influenced by the local microbiological content of the soil. A high mineralization ratio of LDPE, HDPE and LLDPE is even demonstrated with specific microbial cultures (microorganism consortium and their enzymes) without the need for previous abiotic treatment. It is also reported that mineralization under soil conditions and without an abiotic pre-treatment of PP, PS, PETE is not adequate.

Table 3. Studies of Abiotic treatments (Soil).

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[96]	LLDPE, HDPE	Pro-degradant oxo-biodegradable additives among other fillers (plastic bags used on the Kuwaiti market)	Aerobic bacteria in contact with soil under controlled conditions (ASTM D5988 – 18) Local soil secured from an arid site within the State of Kuwait mimicking local landfill conditions	TGA, GCMS, ICP-OES.	Level of pro-oxidants used in the pro degradant formulation is responsible for the fragmentation rate. Application of such abiotic conditions test methods that represent local environments. Regulating the content of such heavy metals is essential for a more sustainable practice.
Continued					

Continuation of Table 3

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[97]	PP, PS, PETE	ECM MasterBatch	Biodegradation in soil (ASTM D5988-03).	Rate of carbon conversion to CO ₂ under conditions that mimic a commercial scale industrial composting facility (ASTM D5338-98), pH electrode, SEM	Relative biodegradability of a range of polymeric materials and natural fiber composites carried out under composting, soil incubation and anaerobic digestion conditions. Plastics containing additives did not improve the biodegradability of the polymers. Under anaerobic incubation, some of the bio-based plastics biodegraded to generate methane, a potent greenhouse gas that unless captured may restrain the perceived environmental benefits of using these materials.
[98]	LDPE	pro-oxidant AddiFlex (10 % and 20 %)	The mineralization of the materials occurred in soil columns at an incubation temperature of 60 °C. Active soil was composed of 90 % plant substrate of peat and 10 % mature compost.	Tensile (ASTM D 882/2010), ICP-MS (DIN 54900)	Pro-oxidants do not influence greatly the mechanical properties of the films and the concentrations of heavy metals were below those tolerated by the standard DIN 54900. The obtained degree of mineralization was around 60 % after 200 days of incubation for both studied polymer films.
Continued					

Continuation of Table 3

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[99]	LLDPE, HDPE	Oxo-biodegradable plastic bags (Institute of Chemistry of Vietnam Academy of Science and Technology)	Biodegradation treatment by incubation of a Bacterial strain (<i>Bacillus</i> sp. BCBT21)	SEM, FESEM, weight loss (ASTM D6003-96), FTIR, Tensile strength and elongation at break (ASTM D638), colour parameters (ASTM D2244-89), GC-MS.	Bacteria was capable of degrading oxo-biodegradable plastics from various resources. Hydrolases secreted by <i>Bacillus</i> sp. BCBT21 including chitinase, CM Case, protease, xylanase, and lipase acting in the high temperature might play an important role in plastic degradation. Potential of the microorganism consortium and their enzymes in plastic degradation
[100]	LDPE	Materials marked “Biodegradable” were obtained from various commercial establishments in Philippines	Biodegradation in culture medium: white rot fungus (<i>Phaenarochoete chrysosporium</i>) and bacteria (<i>Cellulomonas flavigena</i> and <i>Arthrobacter luteus</i>). Soil burial	Weight loss, SEM.	In the natural environment, natural soil microflora are the ones involved in the biodegradation of the oxo-biodegradable plastic. SEM analyses of oxo-biodegradable plastic incubated with pure culture of the white rot fungus <i>P. chrysosporium</i> exhibited signs of degradation (holes or pits, cracks, striations, and flakes in the surface) Fungus <i>Phanerochaete chrysosporium</i> could breakdown the oxo-biodegradable plastic in laboratory condition maybe due to its ability to produce enzymes (lignin peroxidases, manganese peroxidases, laccases, amylases and cellulases).

Continued

Continuation of Table 3

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[101]	LDPE	Plastic bags that are commonly used in supermarkets (Spain), with the description D2W or oxo-biodegradable	<i>P. ostreatus</i> after 45 d of incubation in the substrate	SEM, HPLC, FTIR, DRX	<i>P. ostreatus</i> is capable of degrading oxo-biodegradable plastics and producing mushrooms, using the plastic waste without any prior physical treatment.

On the other hand, **Table 4** shows biotic studies under composting conditions. One of the main aspects regarding the standards of compostable plastics, ASTM D6400 - 04 for example, is the required mineralization time. In this study, it is reported that although oxo-biodegradable plastics do not hurt compostable material, the mineralization time does not meet the respective standards. These results have extrapolated to be able to obtain adequate conditions for complete biodegradation in a period of two years.

Table 4. Studies of Biotic treatments (compost).

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[102]	PE	TDPA (EPI)	Municipal composting plant (Wiener Neustadt): An in-vessel, forced aeration “tunnel” process for 1 week followed by an outdoor treatment on a paved area with weekly watering and turning for at least 10 weeks.	Ballast matter as required (ON S 2200), DIN V 54900, EU-CEN prEN 13432, DIN V 54900-3, ON S 2200 and ON S 2023	The batch test did not have any deleterious effect on the composting operation. Adjust the system during the first implementation stage considering the physical conditions of the material. No negative effects on the quality of the resulting compost observed. TDPA technology meets the requirements to be a degradable/compostable plastic and the final product of compost was fully acceptable as land fertilizer.
Continued					

Continuation of Table 4

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[103]	HDPE (TDPA), PP (d2w), and materials certified as compostable (starch, polycaprolactone)	TDPA (EPI)	Industrial composting plant (Czech Republic and Poland)		The samples made of polyethylene with additives cannot be claimed to be compostable as they do not meet requirements of the existing standards and did not decompose within the time stipulated by the norms (had not been decomposed, their colour had not changed and no degradation neither physical change (thickness) had occurred). The experiment used the same samples in laboratory conditions, too. Results of this experiment were similar as the ones obtained in real conditions. However, in contrast to the laboratory conditions, the real conditions are affected by several factors such as air temperature, pH of the environment, water content of the compost pile, precipitation etc. All these factors can significantly affect the rate and degree of decomposition.
Continued					

Continuation of Table 4

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[104]	HDPE	Commercial polyethylene shopping (Poland) bag ECObag (TDPA),	Degradation under industrial composting conditions (Poland). Hydrolytic aging in the abiotic laboratory conditions. ISO 13432 (EN 13432:2000)	Mass loss, GPC, TGA, DSC, FTIR,	Samples exposed to industrial composting (biotic) and to hydrolytic conditions (abiotic) during 70 days experimented only modest changes. Oxo-degradable products offered on the markets degrade very slowly under composting conditions. Even fragmentation is slow

5.2. Mixed biotic degradation and abiotic transformation of oxo-biodegradable plastics

In the literature, there are studies that simultaneously analyze the biotic and abiotic processes of oxo-biodegradable plastics. Specifically, **Table 5** summarizes the studies that report an abiotic pretreatment followed by (or simultaneously with) a biotic treatment. In general, it has been found that a synergistic effect is reported between abiotic oxidation and enzymatic oxidation in both the type and concentration of pro-degrading additives, such as in microorganisms present in the soil and accelerated or extremely specific environmental conditions. This synergy between abiotic transformation and biotic degradation makes it possible to establish oxo-biodegradable plastics as a viable alternative for the development of materials with a programmed lifetime and adequate biodegradation in soil or packaging conditions. Additionally, it is found that with an adequate pre-treatment and under soil conditions, the oxo-biodegradable plastic does undergo significant fragmentation (pieces of fewer than 1 μm) and has adequate hydrophilic properties for enzymatic oxidation.

In contrast, different types of microorganisms that produce an efficient enzymatic degradation on LDPE and LLDPE with pro-oxidant additives based on Fe and Ca stearates are reported. Microorganisms such as *Rhodococcus* sp., *Bacillus* sp. (BCBT21), *P. chrysosporium* and *P. ostreatus* produce enzymes (chitinase, CM-case, protease, xylanase, lipase, peroxidases, manganese peroxidases, laccases, amylases and cellulases) which, in turn, produce high rates of enzymatic oxidation on oxo-biodegradable plastics. Similar results are obtained for composting conditions processes.

Table 5. Studies of abiotic and biotic treatments.

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[105]	LDPE	Cobalt, zinc, and zirconium-based additives.	Pre-oxidized in air at 90 °C for two days, soil (GOST 9.060-75: Method of laboratory tests for microbiological destruction stability)	Mass loss, IR	Pro-oxidant additives that contain cobalt, zinc, and zirconium, which have a good effect on the biodegradation of the material after preliminary oxidation with atmospheric oxygen, are fragmented after a month of exposure. The combination of a natural filler and a pro-oxidant additive in polymer compositions makes it possible to obtain a material with a programmed life and destruction.
[106]	HDPE, LLDPE	Pro-oxidant additive	Simulated soil (ASTM G160-03)	FTIR, SEM Accelerated aging test (ASTM G154-00)	Degradation of pre-oxidized films occurred after exposure in simulated soil, due to combined effect of photo-degradation and pro-oxidant additive, although the biodegradation will be at a slow rate. The addition of pro-oxidant additives, when combined with accelerated aging may be an alternative to propagate the oxidation of polyethylene, but extremely specific conditions were required for the uptake of oxidation byproducts by microorganisms in simulated soil.
Continued					

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[107]	LLDPE	Envirocare AG1000 (Ciba) and Tinuvin (Ciba): light stabilizers and UV absorbers)	Pretreatment: exposed in a high intensity UV accelerated ageing system (50 °C, 800 h) Real soil burial conditions (full-scale watermelon cultivation)	Tensile strength, elongation at break and stress at yield (ASTM D882), DSC, FTIR, SEM	PE mulching films with pro-oxidants that are strongly degraded during their useful lifetime (depending on the aging conditions and the type and ratio of pro-oxidants to UV stabilizers), and buried in the field at the end of the cultivation season, will be gradually transformed at relatively low rates (e.g., in decades), into tiny micro fragments and finally into invisible PE micro-fragments If the PE mulching film with pro-oxidants is not severely degraded under natural conditions (under solar UV radiation), it is likely that the remains of the so degraded LLDPE mulching films with pro-oxidants will not suffer serious fragmentation in the soil within a short period of a few years but will remain and accumulate in the form of large pieces and smaller fragments affecting the physical properties of the soil
Continued					

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[108]	LDPE, LLDPE, HDPE	Stearates of Co, Mn, and Fe .	Accelerated photo ageing (10 h to 40 h, > 300 nm, 60 °C) followed by 60 h in aerated oven (60 °C) Mixed with mature compost (58 °C or fresh forest soil (25 °C). <i>Rhodococcus rhodochrous</i> (ATCC 29672)	FTIR, SEC, NMR spectroscopy, SEM, GC (CO ₂ production and O ₂ consumption), ATP and ADP assays	Whatever the pro-oxidant used, the HDPE matrix is less efficiently oxidized than the LDPE and LLDPE. The nature of the pro-oxidant additive and the relative amounts of metals in the complex are the major factor controlling the biodegradability of LDPE, LLDPE and HDPE films. Cobalt is not toxic at low concentrations and could be use as pro-oxidant in PE films with limited and controlled concentrations. The more oxidized is the PE polymer, the more hydrophilic it becomes, and the highest the interaction with <i>Rhodococcus</i> sp., cells (more dense and compact biofilms on the surface of oxidized LDPE films). Experiments performed in compost and soil (environmental conditions) were consistent with the results obtained under our simplified conditions using one pure strain of <i>Rhodococcus</i> sp., (ATP test).
Continued					

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[109]	LDPE	prooxidant additives based on organometallic complexes (balance the pro-degradant activity phenolic antioxidants were used in the blends)	Accelerated photo ageing chamber (> 300 nm, 60 °C, 120 h) Three different forest soils	Contact angle, Absorbance	Several members of Rhodococcus genus were isolated proving their role in the interaction of pre-oxidized PE with natural bacterial communities. Broader spectrum of isolated taxon showed that the microorganisms capable of adhering to pre-oxidized PE surface and metabolizing some of its oxidation products are not rare in forest soils The microorganisms capable of adhering to pre-oxidized PE surface and metabolizing some of its oxidation products are not rare in forest soils. If the pro-oxidant technology ensures continuation of the PE chain breakdown process after PE waste disposal, one can expect such oxidation products to be biodegraded.
Continued					

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[110]	LDPE, LLDPE	Calcium and iron stearates (0.2 %)	Accelerated photo-degradation (300 nm to 800 nm, 45 °C, 500 h). Bioreactors (aerobic biodegradation by bacteria) 30 °C and 45 °C	GPC, ATR-FTIR, Contact angle, GC-MS, Chemiluminescence.	Bacteria <i>B. cereus</i>, <i>B. megaterium</i>, and <i>B. subtilis</i> form a biofilm in only in the photo-degraded samples buried in soil and cultured in the laboratory (45 °C) after one week of bacterial treatment. More efficient biodegradation of oxo-biodegradable films on the bioassays carried out at higher temperature (45 °C). The percentages of carbonyl index (CI) decrease were higher when the biodegradation occurred at 45 °C and, particularly, on higher photo degraded films containing Ca and Fe stearates. The metabolic action of bacteria at 45 °C reduced the carbonyl index by 75 % to 85 % in the PE films containing Fe stearate and by 31 % to 67 % in the case of Ca stearate. The disappearance of photo-generated low-molecular products with biodegradation were more efficient on the biodegraded films at 45 °C. Photo-degradation increases the rate of biodegradation of the polyethylene films by the bacteria studied in this work. Hence, the use of a pro-oxidant in the polyethylene formulations could be an interesting way to prepare efficient biodegradable materials.

Continued

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[111]	LLDPE	Envirocare AG1000 (Ciba)	Artificial ageing (less than 290 nm to 3000 nm, 50 °C. No humidity, 11 weeks) films buried in the soil (Athens)	Mechanical (ASTM D 882), DSC, FTIR-ATR,	Photodegradable LLDPE films with pro-oxidants under real field cultivation conditions and in the laboratory indicates a rapid degradation that occurs rather abruptly and at much time as compared to conventional LLDPE. Controlled ageing behavior suggests that the pro-oxidants induce an abrupt and controllable photo-chemical oxidation of LLDPE under the action of UV radiation, combined with temperature.
[112]	LDPE	Addiflex and pro-oxidant additives based on Mn and Fe stearates.	Abiotic thermal oxidation Mixed with mature compost.	FTIR, GPC, elongation at break, ICP-MS, SEM	All pre-oxidized materials investigated were significantly biodegraded in both soil and compost environments. Differences between microflora in compost and soil could affect the mineralization
Continued					

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[113]	Selected waste sacks and shopping bags, which were subject to decomposition under the actual conditions of an industrial composting plant (HDPE).	d2w, TDPA	UV radiation Composting plant (Poland).	AAS	Additives used for producing oxo biodegradable plastics contain heavy metals compounds. Only two samples of the ten analyzed were totally degraded during composting. Changes in the composition of plastics depend on the UV irradiation. Some of the metals tested occurred in smaller quantities in the samples subjected to irradiation in the long term. Oxo biodegradable plastic waste can be a source of pollution, released into the environment due to the varied nature of the changes identified
[114]	HDPE	d2w	UV lamp Composting plant in (Poland)	Principal Component Analysis (PCA)	All the studied materials contained heavy metals (copper, zinc, chromium, lead, nickel, and cadmium). No significant effect of UV radiation on the degree of decomposition and on the composition of oxo-biodegradable plastics occurred.
Continued					

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[115]	PELD	Manganese stearate as the pro-degradant	Thermo-oxidative degradation tests (60 °C and 70 °C) Abiotic degradation in a compost environment (ISO 20200) Degradation tests in aqueous solutions (ISO 14852)	SEC, FTIR,	Show clear evidence that moisture has a strong accelerating effect on the rate of thermo-oxidation of polyethylene materials containing a Mn pro-degradant. The rate of degradation in compost was much slower. It demonstrated that some liquid components, such as ammonia and hydrogen peroxide, generated by microorganisms in compost, had a deactivating effect.
[116]	Different degradable plastics available in the Mexican market	d2w	UV chamber (300 nm to 400 nm, 14 days) Home composting	Loss of mechanical properties	Oxodegradable polyethylene degraded only if it had been previously oxidized in a UV chamber.
Continued					

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[117]	LDPE	P-Life (based on a manganese salt)	Thermo-oxidative degradation Simulating the soil Environment Simulating Industrial compost	SEC, tensile testing, molecular weight	It is possible to create LDPE-based materials that will almost completely biodegrade in soil within two years. Oxidized PE is to an overwhelming extent converted to carbon dioxide in the soil mineralization and only to a small extent converted to new biomass
[118]	LDPE	Mn stearate as pro-oxidant	Thermo-oxidation (ASTM D 5510-01) Composting plant (Mexico City).	GPC, shear viscosity, Carbonyl Index. FTIR (ASTM D 5576-06),	Assess the suitability of the degradation methodology, using manganese stearate and other pro-oxidant additives with PE. To establish the best conditions for film production respect to the times for biotic and abiotic degradations, it is required to precisely set additive concentrations and production-control variables to assure a complete biodegradation. Considering the ASTM D 6400 procedure, the Mn-LDPE films with a molecular weight less than 6000 g mol^{-1} are classified as degradable, biodegradable, and compostable.
Continued					

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[119]	PE-LLD	Different proprietary pro-oxidant additives	Abiotic degradation: Exposure to natural sunlight (ASTM D5272). Thermal degradation. Biotic degradation: Screening tests with single fungal strain in agar plates.	FT-IR, DSC, TGA, SEM,	Degradation of oxo biodegradable plastics is enhanced by the synergistic action of both abiotic and biological factors after its initial oxidation by exposure to direct sunlight. The data validate oxo-biodegradable polymers and confirm that PE-LLD films with pro-oxidant additives are environmentally degradable via combination of abiotic and biotic factors
[120]	HDPE, LLDPE	d2w	Abiotic degradation: Exposed to conditions of natural and saturated humidity. Biotic degradation: stabilized compost	SEC, FTIR, DSC, Tensile test	Exposure to natural weathering for a period of 3–4 months decreased the mechanical properties of the material causing disintegration of the material. Saturated humidity increased abiotic oxidative degradation and biodegradation. Fungi belonging to the genera <i>Aspergillus</i> and <i>Penicillium</i> grew on oxo-biodegradable PE films in environments with saturated humidity
Continued					

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[121]	LLDPE	Antioxidants with or without pro-oxidants	Abiotic treatment: UV exposure Biotic treatment: Laboratory-Scale composting	permeation chromatography, Tensile test (ASTM D638), Contact angle,	PE incorporated with 0.1 w/w % of Fe-stearate films lost the tensile properties and molecular weight abruptly with the increase in UV exposure time. The decay of the tensile properties and molecular weight of PE-Fe did not depend significantly on the intensity of the UV irradiation but increasing UV irradiation temperature accelerated the deterioration of the tensile properties and molecular weight of PE-Fe. Previous studies employed PE films containing additives such as heat and photo-stabilizers, while only an extremely small amount of the antioxidant was used during the preparation of the LLDPE films in the present study. This was believed to be mainly responsible for the discrepancy between the photo-degradation rates. <i>C. gleum</i> EY1 isolated from activated sludge soil was active for the degradation of UV-exposed PE-Fe even at moderate temperatures.

Continued

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[122]	PP	AG1000C (Envirocare, TDPA)	Accelerated soil burial test (DIN EN ISO 846:1997). Biotic degradation: biodegradation in soil	DSC, TGA	The pro-oxidant/pro-degradant additive can promote the abiotic oxidation of polypropylene during UV-irradiation. Previous abiotic oxidation is responsible for further extent of degradation of the polypropylene matrix by soil microorganisms. Biodegradation of this polyolefin is a complex process that occurs in different stages. Changes in both the morphological and thermal properties of the polypropylene matrix during soil incubation were found to be proportional to the additive load and the previous photo-oxidation extent. Synergetic effect of abiotic degradation (due to UV exposure) and biotic degradation (due of the metabolic activity of the soil microorganisms) promotes the extent of the whole degradation of the PP samples containing pro-oxidant/pro-degradant additive.
Continued					

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[123]	PE	d2w	Abiotic test: UV radiation, Thermal aging. Laboratory Aerobic biodegradation tests.	Tensile properties (ASTM D-3826), FTIR, cumulative production of CO ₂	The additive promoted degradation by abiotic factors and increased the microbial activity in the early stages of the biodegradation.
[124]	HDPE	Mn and Fe stearates	Abiotic treatment: accelerated photo-ageing ($\lambda \geq 300$ nm, 60 °C, 40 h), thermal oxidation (aerated oven 60 °C, 300 h). Biodegradation experiment: pure bacterial strain (<i>Rhodococcus rhodochrous</i> , ATCC 29672) in aqueous ambient	FTIR, Mass spectrometry, NMR spectroscopy,	Opens new directions of research: Combining different analytical techniques that can be used in the future to analyze the structure of oligomers and to assess their biodegradability. Demonstrates experimentally the relationships between the structures of the oligomers (molecular weight, number of carbons and oxygen atoms, functional groups) and their biodegradability by a strain of <i>R. rhodochrous</i> .

Continued

Continuation of Table 5

Ref	Material	Additive	Condition	Analytical techniques	Conclusion
[125]	LDPE	d2w	Pretreatment: thermally aged for 180 days in an aerated oven at 70 °C Biotic treatment: aquariums (circulating seawater)	AFM, Contact angle, Epifluorescence Microscopy, Flow Cytometry, Bacterial production (BP),	Did not evaluate the biodegradability of the polymers tested during our experiment. Nevertheless, a better understanding of the biofilm forming on plastic in natural conditions is necessary to develop realistic biodegradation tests.

5.3. Toxicity of oxo-biodegradable plastics

Finally, **Table 6** summarizes the studies that aim to determine the toxicity of oxo-biodegradable plastics. In general, these studies take plastic bags from public sources, such as supermarkets, and commercial establishments and analyze them mainly looking for the presence of metals. At this point, it is important to remember that oxo-biodegradable plastics mainly contain Co, Fe and Mn stearates as the basis for their manufacture. The presence of other metals is due to the use of various polymeric matrices and additives incorporated into them (mainly in the form of antioxidants) so that the content of heavy metals varies greatly depending on the commercial product analyzed.

Although the content of toxic elements in different plastic products is regulated by different regional standards: ASTM F963, ASTM D6400–04, ISO 8124-3, EN 71, EN 13432, 94/62/EC, EU No. 10/2011, ABNT NBR 15448-2:2000, in some cases there are commercial products that exceed the values established in the regulations. This is because producers mainly focus on the content of Co, Fe and Mn present in pro-oxidant additives, leaving in the background the contribution of plastic compounds that also intervene in the manufacturing process. In consequence, it is important the final commercial products, which are a combination of various additives and polymer complexes, comply with the regulations.

Table 6. Toxicity studies.

Ref	Material	Additive	Technique	Analyzed metals	Results
[126]	36 Plastic bags were collected from supermarkets in Shanghai (PE, HDPE, LDPE, PVC)	Not specified.	Inductively coupled plasma optical emission spectrometry (ICP-OES)	Pb, Cr, Cd, As, Cu, Zn, Mn, Ba and Se	Some plastic bags samples were found to violate the standard limits of Pb, Cr, Cd and As.
[127]	Different kinds of bags used to collect municipal solid waste. (Compostable vs PE)	Colour	Spectrometric atomic absorption	Fe, Zn, Cu, Ni, Cr, and Pb	Very high variations in heavy metal composition between different types of PE bags. Compostable bags presented much lower values in Fe, Cr and Pb. Manufacturers should limit the pollutants in their product
[128]	33 commercial plastic bags were collected in Mexico City (Single-use plastics): HDPE and LDPE	Advertised as biodegradable and oxo-biodegradable.	FTIR, SEM-EDS, X-ray fluorescence, TGA, TDA	Al, Ti, Fe, Ca, Mg, K, P, S, Cl, Si, As, Cu, Cr, Mo, Pb, Zn, V, Zr, Sr, Sc, Ga, Nb, Y, U, W	The polymer composition did not fulfill the criteria of biodegradable polymers as advertised by marketers. Tested materials (oxo-biodegradable and biodegradable) are exclusively conventional HDPE and LDPE plastics.
Continued					

Continuation of Table 5

Ref	Material	Additive	Technique	Analyzed metals	Results
[129]	Disposable plastic bags of HDPE were sampled in shopping facilities in Brazil	Identified as oxo-biodegradable.	Instrumental Neutron Activation Analysis (INAA), FTIR	As, Br, Ca, Co, Cr, Fe, Hf, K, La, Na, Sb, Sc, Ta and Zn	The oxo-biodegradable plastics studied are not potential pollutants of the environment. The diversity of elements in various mass fractions suggests lack of standardization and contamination during the manufacturing of these materials.
[79]	Transparent commercial grade plastic bags claimed to be of oxobiodegradable nature.	Identified as oxobiodegradable	XRF	Rb, Cr, Mn, Cu, Sr, Zn, Ti, Zr, Fe. K, Ca	Only chromium was present (7 ppm) which means that it adheres to the regulation (94/62/EC).

6. Conclusions

This paper presented a brief review of both the regulations and the current development of the basic concepts involved in the technology of oxo-biodegradable plastics, initially highlighting the important development obtained concerning the concept of degradability of plastics, in general, and biodegradability, in particular. From 1972 to date, increasingly realistic physicochemical and biological models have been developed, allowing to have a clearer idea of the different mechanisms involved in the biodegradation process of different types of polymer compounds and their potential impact on the environment. Along with these scientific developments, both technical standards and legislation have progressively implemented these concepts and models in their general concepts.

For completeness in the analysis, first, the main conclusions on the biodegradation of polymer compounds, in general, are listed and, later, the conclusions regarding the collection of information on the determination of the biodegradability ratio of oxo-biodegradable plastics are established.

Most polymers are manufactured from the Phillips-Nakka processes in which metallic catalysts are used to induce the polymerization process activated by UV radiation. Although at low concentrations, these metals can eventually have a serious impact in terms of toxicity in the environment.

The additives are used, generally, to improve the physicochemical properties of polymers, especially to prevent degradation/oxidation of the material. Practically all the polymers produced today contain some type of additive that, in addition, contain transition metals like Mn and Co.

The existing government legislation is primarily responsible for regulating the use of plastic compounds in specific applications, but not for reviewing the particular degradation properties of the materials involved, as suggested by the Green Report. The main recommendations of the Green Report remain valid: *i)* Need for adequate standardization and *ii)* Need for relevant and unified technical standards.

Despite the typical claims of producers, currently no material meets all the specific properties to be considered biodegradable in different environments (litter, composting, landfill, recycling or marine environment).

The biodegradation of plastic compounds strongly depends on the specific environment in which they are found: litter, composting, landfill, recycling or marine environment. It is fundamental to study the degree of biodegradability of each material in each specific environment. Again, there is currently no plastic compounds that is biodegradable in all final disposal environments and that maintains adequate physical-chemical properties for commercial use.

Presently, it is known that abiotic and aerobic processes must be carried out simultaneously or sequentially in the biodegradation process of a polymer compound. In the first process, microscopic (nanoscopic) fragments are produced with adequate properties (molecular weight and hydrophilicity, mainly) so that they can be attacked by microorganisms, which cause enzymatic degradation, in the second process resulting, finally, in the mineralization of the material into CO₂, H₂O and biomass. Any biodegradation study must contemplate the analysis of abiotic and aerobic processes under natural or accelerated conditions and in specific environments of the final disposal. The mean technical standard that defines the study of biodegradability based on abiotic and aerobic processes is the ASTM D6954-18 standard, which additionally defines residual toxicity studies produced by metals. There are national standards on biodegradability as, for example, "Évaluation expérimentale de l'oxobiodégradabilité de matériaux polyoléfiniques

sous forme de films - AC T51-808”, “Methods for the assessment of the oxo-biodegradation of plastics and of the phyto-toxicity of the residues in controlled laboratory conditions - BS 8472”, “Standard & Specification for Oxo-biodegradation of Plastic bags and other disposable Plastic objects - UAE.S 5009 /2009”, “Certification rules for Classification for treatment of polymeric waste”.

Despite undergoing completely different degradation mechanisms, at present, there is no technical standard that unequivocally differentiates oxo-degradable, photo-degradable, bio-degradable and oxo-biodegradable plastics as well as the concept of pro-oxidants additives. They are frequently assumed as synonyms, causing great confusion to governmental legislative entities.

It is the responsibility of the state to define and monitor efficient collection and final disposal systems that guarantee the least amount of plastic litter like implementing new disposal and recycling technologies following the generation of new materials. It is as well responsible for the metrological certification of the different claims that manufacturers make of the material.

According to the analysis of the report of the different studies regarding the biodegradation of oxo-biodegradable plastics, the following conclusions are reported:

- The biodegradation of oxo-biodegradable plastics is a synergistic process that involves the simultaneous or successive action of abiotic oxidation (radiation and/or temperature) and enzymatic oxidation. To obtain a material that complies with the respective environmental regulations on compostable and recyclable materials, it is necessary to determine both the appropriate variables of the pro-oxidant additives (chemical and concentration variables) such as the variables of radiation, temperature and humidity. The general conclusion of the majority of the studies analyzed is that it is necessary to continue working in this direction and to develop new methodologies that allow a univocal definition of the biodegradation ratio of, in particular, oxo-biodegradable plastics.
- In suitable abiotic conditions of radiation and temperature, oxo-biodegradable plastics undergo an expected transformation (fragmentation, reduction of molecular weight and hydrophilicity) in relatively short periods.
- The enzymatic oxidation of oxo-biodegradable plastics strongly depends on the concentration and nature of the different additives present in the material, as well as the microorganisms present in the composting or soil system.
- The presence of pro-oxidant additives does not affect the properties of the resulting material when different types of plastic compounds are mixed in recycling applications.
- There is a lack of traceability of the results in terms of accelerated experiments or real environments, mainly because there are currently no defined methodologies for real environments.
- Different types of microorganisms that produce enzymatic degradation are found in oxo-biodegradable plastics.
- LDPE, HDPE and LLDPE containing Ca and Fe stearates have a good biodegradation ratio.
- The concentration of toxic elements present in pro-oxidant additives (Fe, Mn, Ca) are within the range allowed by different technical standards.

- There is a lack of research with eco-toxicological tests, The ASTM 6954 standard suggests, in its last stage, to carry out terrestrial and aquatic ecotoxicity tests to “...*obtain evidence on the effects of the product on plant and animal life...*”.

7. Conflict of interest

The authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation as speakers' membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent arrangements), or non (such as personal or professional relationships, affiliations, knowledge, or beliefs) in the subject matter or materials discussed in this manuscript. Potential conflicts of interest related to individual authors' commitments. Potential conflicts of interest related to commitments of editors, journal staff, or reviewers.

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Análisis y revisión crítica de las propiedades, estándares y regulaciones de los plásticos oxo-biodegradables

Resumen: Tomando como base recientes avances científico-técnicos en cuanto a los mecanismos de transformación y biodegradación de los compuestos plásticos, se ha progresado tanto en la conceptualización de definiciones relevantes como en el desarrollo de normas técnicas que permiten determinar de manera más precisa y reproducible la tasa de biodegradabilidad de un material determinado. A partir de estos avances, se han desarrollado, además, los llamados plásticos oxo-biodegradables, en los que se añade aditivos pro-oxidantes al polímero crudo, permitiendo un proceso de transformación abiótica óptimo (oxidación foto/térmica) y produciendo la fragmentación del material en condiciones adecuadas para su degradación biótica simultánea o sucesiva (oxidación enzimática). Aunque actualmente los plásticos oxo-biodegradables se utilizan ampliamente en diferentes aplicaciones, por ejemplo, en la agricultura y como plásticos de un solo uso, hasta hace muy poco tiempo no se había desarrollado una norma técnica que permitiera determinar la tasa relativa de degradación de diferentes tipos de plásticos en condiciones abióticas y bióticas. Este proceso implica que, para que los productores puedan utilizar términos específicos de biodegradación y oxo-biodegradación con fines publicitarios que afirmen ofrecer un producto respetuoso con el medio ambiente, las entidades pertinentes deben llevar a cabo pruebas metrológicas a la luz de las nuevas definiciones y normas técnicas. Además, se ha generado una gran cantidad de literatura especializada que determina la tasa de biodegradación de los plásticos oxo-biodegradables en entornos y condiciones muy específicos. Esta revisión hace un recuento detallado de las diferentes definiciones y conceptos científicos involucrados en la degradación oxo/bio, y muestra cómo estos conceptos han evolucionado con el tiempo. También muestra cómo han evolucionado las normas técnicas, que en general se adaptan a los nuevos avances científicos y técnicos en el campo de los plásticos. Finalmente, un análisis detallado de los resultados reportados en la literatura científica muestra cómo la oxo- biodegradación depende de diferentes parámetros (radiación UV, temperatura, tiempo de exposición, tipo de enzimas), entornos específicos (suelo, compostaje, residuos, reciclaje, etc.), diferentes tipos de plásticos (LDPE, HDPE, LLDPE, aditivos pro-oxidantes) y, finalmente, de las diferentes técnicas analíticas utilizadas (FTIR, DSC, TGA, SEM, prueba de tensión).

Palabras Clave: plásticos oxo-biodegradables; Aditivos pro-degradantes; Mineralización; Termo- oxidación; Foto-oxidación; Oxidación enzimática.

Análise e revisão crítica das propriedades, normas e regulamentações dos plásticos oxo-biodegradáveis

Resumo: Com base nos recentes avanços científico-técnicos em relação aos mecanismos de transformação e biodegradação dos compostos plásticos, tem-se progredido tanto na conceituação de definições relevantes como no desenvolvimento de normas técnicas que permitem determinar de maneira mais precisa e reproduzível a taxa de biodegradabilidade de um material determinado. A partir desses avanços, foram desenvolvidos os chamados plásticos oxo-biodegradáveis, nos quais são adicionados aditivos pró-oxidantes ao polímero bruto, permitindo um processo de transformação abiótica ótimo (oxidação foto/térmica) e produzindo a fragmentação do material em condições adequadas para sua degradação biótica simultânea ou sucessiva (oxidação enzimática). Embora atualmente os plásticos oxo-biodegradáveis sejam amplamente utilizados em diferentes aplicações, por exemplo, na agricultura e como plásticos de uso único, até muito recentemente não havia sido desenvolvida uma norma técnica que permitisse determinar a taxa relativa de degradação de diferentes tipos de plásticos em condições abióticas e bióticas. Este processo implica que antes que os produtores possam utilizar termos específicos de biodegradação e oxo- biodegradação para fins publicitários que afirmem oferecer um produto ecologicamente correto, as entidades relevantes devem realizar testes metrológicos à luz das novas definições e normas técnicas. Além disso, uma grande quantidade de literatura especializada foi gerada, na qual a taxa de biodegradação dos plásticos oxo-biodegradáveis é determinada em ambientes e condições muito específicos. Esta revisão apresenta uma conta detalhada das diferentes definições e conceitos científicos envolvidos na degradação oxo/bio, e mostra como esses conceitos têm evoluído ao longo do tempo. Também mostra a evolução das normas técnicas, que em geral se adaptam aos novos avanços científicos e técnicos no campo dos plásticos. Finalmente, uma análise detalhada dos resultados relatados na literatura científica mostra como a oxo-biodegradação depende de diferentes parâmetros (radiação UV, temperatura, tempo de exposição, tipo de enzimas), ambientes específicos (solo, compostagem, resíduos, reciclagem, etc.), diferentes tipos de plásticos (LDPE, HDPE, LLDPE, aditivos pro-oxidantes) e, finalmente, das diferentes técnicas analíticas utilizadas (FTIR, DSC, TGA, SEM, teste de tração).

Palavras-chave: Plásticos oxo-biodegradáveis; Aditivos pro-degradantes; Mineralização; Termo- oxidação; Foto-oxidação; Oxidação enzimática.

Juan Carlos Salcedo Reyes Full professor at Physics Department, Universidad Javeriana, Bogotá, Colombia. Minciencias Colombia senior researcher. Associate professor at Physics Institute, Universidad de Guanajuato, México (2006). Master of Science (physics) at Universidad Nacional de Colombia (2000), PhD (physics), Center for Research and Advanced Studies of the National Polytechnic Institute (CINVESTAV), México (2005). IEEE/PHOTONICS Senior Member. National Science Award, Alejandro Angel Escobar Foundation, Colombia (2018). Postdoctoral research at University of Texas at Dallas (USA) and Instituto de Ciencia de Materiales de Madrid (ICMM-Spain).

ORCID: 0000-0002-6209-0502

Octavio Alejandro Castañeda Uribe Principal professor at School of Engineering, science and technology, Universidad del Rosario, Bogotá, Colombia. PhD. in engineering with research interests in the field of nanotechnology with biomedical applications. His research has focused on the manufacture and characterization of nanomaterials. Within the manufacturing area, he has studied and developed polymer nanocomposites with electromagnetic blocking properties that present potential applications in the electronics, military, and medical devices industry. In the area of characterization, he has studied and developed new techniques for electrical properties measurements in micro and nano scales, using Atomic Force Microscopy (AFM). The new AFM techniques that have been developed present potential applications in evaluating the quality of commercial products with nanomaterials.

ORCID: 0000-0003-4858-2591

Luis David Gómez Méndez Currently, Professor at Microbiology Department since 2000; MINCIENCIAS Junior researcher from 2020 (Colombia). Degree in Microbiology at “Universidad de Los Andes” (Bogotá, Colombia, 1996). MSc in Microbiology (2002) and PhD in Biological Sciences at “Pontificia Universidad Javeriana” (Bogotá, D.C., Colombia, 2019). Member of Environmental and Industrial Biotechnology Group (GBAI) from 2007. Leader of hotbed of research in the degradation of polluting plastic polymers. His main research interests are related to environmental microbiology, in the search for physicochemical and microbiological strategies for plastic degradation.

ORCID: 0000-0002-9452-4686

Aura Marina Pedroza Rodríguez Full professor at Microbiology Department since 2000; MINCIENCIAS Senior researcher from 2013 (Colombia). Bacteriology at Pontificia Universidad Javeriana (1995), MSc in Microbiology (2000) and PhD at Center for Research and Advanced Studies of the National Polytechnic Institute (CINVESTAV), México (2006). Her main research interests are related to environmental biotechnology, soil microbiology and waste transformation using biological, physical and chemical processes.

ORCID: 0000-0002-1200-0265

Raúl A. Poutou-Piñales Currently, Professor at Microbiology Department since 1995; MIN-CIENCIAS Senior researcher from 2013 (Colombia). Technician in Analytical Chemistry at Chemistry Institute “Mártires de Girón” (1983); and Degree in Biochemistry at “Universidad de la Habana” (Ciudad de La Habana, Cuba, 1992). MSc in Microbiology (1999) and PhD in Biological Sciences at “Pontificia Universidad Javeriana” (Bogotá, D.C., Colombia, 2006). Leader of Environmental and Industrial Biotechnology Group (GBAI) from 1996. His main research interests are related to molecular biology and microbial biotechnology for the expression of recombinant proteins and enzymes and their use in different industries such as food, pharmaceutical, environmental and agrobiological.

ORCID: 0000-0001-8841-2357