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Photodegradation of microplastics
Fotodegradación de microplásticos

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Abstract: The environmental degradation processes that plastics suffer in the environment are described, thus generating minor fragments known as microplastics. The various chemical mechanisms by which these microplastics can be decomposed by the effect of light and environmental oxygen (photo-oxidation of polymers) will be described. Emphasis is placed on the role of photochemistry in the degradation processes of microplastics until they become compounds that are harmless to the environment, that is, until they are mineralized (HCO_3, CO_2, etc.). Some advances in the development of heterogeneous photocatalysts based on transition metals used in the degradation of microplastics are also presented, including a particular and interesting automated microrobot photocatalyst system based on $BiVO_4/Fe_3O_4$, which has proven to be effective. in the degradation of polylactic acid (PLA), polycaprolactone (PCL), polyethylene terephthalate (PET) and polypropylene (PP) microplastics on a laboratory scale.
Key words: Photodegradation, microplastics, photochemistry, polymere, photooxidation.

Resumen: Se describen los procesos de degradación ambiental que sufren los plásticos en el medio ambiente generando así fragmentos de menor tamaño, conocidos como microplásticos. Se describirán los diversos mecanismos químicos mediante los cuales éstos microplásticos se pueden descomponer por efecto de la luz y el oxígeno ambiental (fotooxidación de polímeros). Se hace énfasis en el rol de la fotoquímica en los procesos de degradación de los microplásticos hasta transtornarlos en compuestos inofensivos para el ambiente, es decir, hasta llevarlos a su mineralización (HCO_3, CO_2, etc.). Se presentan además algunos avances en el desarrollo de fotocatalizadores heterogéneos basados en metales de transición, empleados en la degradación de los microplásticos, incluyendo un particular e interesante sistema de fotocatalizador microrobot autómata basado en $BiVO_4/Fe_3O_4$, el cual ha demostrado ser efectivo en la degradación de microplásticos de poliácido láctico (PLA), policaprolactona (PCL), ereftalato de polietileno t (PET) y polipropileno (PP) a escala de laboratorio.
Palabras claves: Fotodegradación, microplásticos, fotoquímica, polímeros, fotooxidación.

1. Introduction

Today, plastics are one of the most versatile materials used by humans, their two main components being a polymer matrix (macromolecules) and a certain number of additives (UV protectants, plasticizers, colorants, other polymers, etc.). The first fully synthetic polymer was obtained in the early 20th century by Leo Baekeland, however, the real beginning of the industrial production of polymers occurred in the early 1950s, since then the manufacture of polymers has grown exponentially reaching 380 metric tons per year (2015) [1]. Most of the polymers produced in the world are of the thermoplastic type, these types of materials are low cost, their raw materials are from non-renewable sources (petroleum) and they are commonly identified simply as "plastics". Among these plastics we have polyethylene (PE), polyethylene terephthalate (PET), high, low and linear-low density polyethylene (HDPE, LDPE and LLDPE), polyvinyl chloride (PVC), polypropylene (PP), polycarbonate (PC), polystyrene (PS), etc. [2-5].

Plastics have enabled the development and evolution of several technological areas, for example, automotive, electronics, food, medicine, aerospace, shipping, clothing, footwear, construction, etc. Most used plastics are very durable due to their chemical and biological inertness, which is the result of their high molecular mass, hydrophobicity and absence of functional chemical groups susceptible to attack by microbes, enzymes, light, water, etc. [6, 7]. The high durability, inertness and impermeability of plastics make them ideal materials for food packaging, sterile medical devices, the construction sector, among others, however, these characteristics also make plastics particularly long-lived when discarded after their useful life. Certain additives incorporated into plastics, such as antioxidants and stabilizers, increase the shelf life of these materials by reducing the rate of degradation in natural environments [6-9].

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materials by reducing their degradation rate in natural environments [6-9].

According to the Organization for Economic Co-operation and Development (OECD) [10], currently, more than 100,000 different chemical substances and compounds are marketed worldwide, including various types of plastics. Many of these plastics, after their use or useful life, end up deposited in natural systems (land, water and air), where they slowly begin to biodegrade through diverse and complex chemical and biological processes that in many cases are initiated or activated by the participation of solar energy. To understand how these processes of photo-degradation of plastics occur, photochemistry provides the basic concepts that adequately describe them, and more specifically the photo-oxidation reactions of polymers allow plausible explanations of these photo-degradation processes [5, 11, 12].

Post-consumer plastics can be degraded by the following pathways: (1) photo-oxidation, (2) thermal, (3) ozone-induced, (4) mechano-chemical, (5) catalytic and (6) biodegradation. In turn, the degradation rate of plastics depends on their chemical composition, molecular mass, hydrophobic character, presence of functional groups, additives, types of bonds present in the main polymer chain, method of polymer synthesis, polymer morphology, environmental conditions where the plastic is placed, size and shape of the plastic part [13].

During the degradation of plastics, these materials undergo fragmentation and consequently a reduction in their dimensions, reaching micro (0.1-5000 µm) and nanometric (1-100 nm) sizes [12]. Nowadays, several studies have found micro/nanoplastics in seas, rivers, oceans, even on mountain tops, and even in the internal organs of many living organisms, surprisingly there is evidence of the presence of micro/nanoplastics in human placenta [14]. Micro/nanoplastics present in seas and oceans can be ingested by organisms as small as zooplankton and transferred to larger animal species, such as fish, when these zooplankton are ingested by them. Various toxic substances present in the environment can adhere to the surface of micro/nanoplastics and are then ingested and transported by living organisms.

The use of photocatalysts to accelerate the degradation of plastics is shown to be an efficient way to reduce the amount of these environmental pollutants. Photocatalysis uses a renewable and inexhaustible energy source such as sunlight. Additionally, the degradation of plastics, induced by photo-catalysts, can generate intermediate products of lower molecular mass that in some cases can be used as raw material for the chemical industry, organic synthesis and in the production of new chemical products and even new plastics [15].

This chapter provides an overview of the various photo-degradation processes of plastics in the presence of oxygen, their reaction mechanisms, the factors governing their reaction rates and some photo-catalytic systems currently being investigated for the degradation of micro/nanoplastics present in the environment.

Plastics and their impact on the environment

Plastics are materials based on polymeric matrices homogeneously mixed with various types of additives such as: colorants, antioxidants, plasticizers, silica, carbon black, calcium sulfate, calcium carbonate, talc, etc. The use of plastics dates to the 19th century with the discovery of the vulcanization reaction of natural rubber by Charles Goodyear [4, 16]. Polymers can be of natural or synthetic origin; the latter being manufactured from chemical compounds of low molecular mass and of fossil origin (petroleum) called monomers. In a synthetic polymer, these monomers are joined together by covalent bonds forming long macromolecular chains of very diverse shapes and chemical compositions. The first synthetic polymers were developed during the 19th century, while the 20th century saw the development of a great diversity of polymeric materials, see Table 1:

Table 1. Timeline of plastics development [4].

The first synthetic polymer was synthesized in 1907: Bakelite, followed by the industrial development of polyvinyl chloride or PVC in 1926, followed by polyurethane (PUR) (1937), polystyrene (1938), high-density polyethylene (HDPE) and polypropylene (PP) (1951). Recent technological advances have led to the development of polymers from bacterial fermentation of sugars and lipids. These materials obtained from natural sources are called biopolymers and include polyhydroxyalkanoates (PHA), poly (lactic acid) (PLA), aliphatic polyesters and polysaccharides [4]. Polymers of natural origin, such as poly(isoprene) (natural rubber), are used for the manufacture of vulcanized rubber used in the manufacture of tires; another biopolymer, poly (lactic acid), is used as a material for food packaging, blister packs or sutures in the medical and pharmaceutical sectors, in 3D printing, etc. [17]. In general, synthetic or natural polymers can be classified into: (i) thermoplastics: materials that can be molded into virtually any desired shape through thermal processes such as rotational molding, injection molding, extrusion, compression molding, blow molding or thermoforming. (ii) elastomers: are materials that have macromolecular chains linked together by bridges and crosslinking points randomly located, this particular macromolecular structure allows elastomers can be deformed without breaking under external forces, and then when this effort ceases the material returns to its original size and shape, these elastomeric materials are commonly referred to as rubbers or rubbers, (iii) thermosets: are materials whose macromolecules are joined together by multiple molecular bridges whose chemical composition may or may not be different from that of the main macromolecular chain, these materials are mostly rigid solids very resistant to heat, once formed thermosetting polymers can not be melted again [9, 18, 19].

As of 2015, global demand for polymers was 388 million tons of which 99.5% were petroleum-based polymers and only the remaining 0.5% were biopolymers [20]. Polypropylene (PP) accounted for 16% of global demand, while low-density polyethylene (LDPE) accounted for 12%, poly (vinyl chloride) (PVC) for 11%, high-density polyethylene (HDPE) for 10%, polyethylene terephthalate (PET) for 5%, polystyrene (PS) for 5%, other thermoplastics for 3%, non-pneumatic elastomers for 2% and thermosetting polymers for 9% [20]. The uses of plastics are very diverse; Table 2 summarizes some of the applications of the main commercial polymers.

Table 2. Applications of the most popular commercial polymers [4].

Once plastics have completed their useful life, they are discarded by companies, commercial establishments, hospitals, homes and other places. Plastic waste can become a major environmental problem due to the absence of policies and/or strategies for the collection, sorting and reuse of plastic waste. Significant amounts of plastic waste can end up in municipal landfills, in the sea or on the ground where it remains indefinitely. Another way in which post-consumer plastics are introduced into the environment is through mechanical erosion. This process generates fine plastic particles that can be transported long distances by air or water; examples of this form of plastic particle generation are the wear and tear of tires during vehicle rolling, or the turning of plastic parts, among others. The way in which plastics are transported and deposited in the environment will depend on the geographic location of the source, the type of activity that generates plastic waste and the existence or absence of adequate infrastructure to collect and process these materials. For example, municipal landfills that lack adequate urban sanitary infrastructure are identified as a major source of plastic waste generation into the environment. An example of plastic pollutants intentionally placed in urban drains is the microscopic PE beads contained in facial scrubs; these plastic particles are probably present more frequently in developed countries where these types of products are massively used. In general, obtaining accurate data on the sources of plastic wastes present in different ecosystems is hampered by the difficulty in determining the length of time that these wastes have remained in bodies of water (oceans, seas, rivers, etc.) and on land [11, 16, 18, 21].

Meteorization of plastics in natural environments

Plastic waste is considered dangerous for the environment due to its capacity to remain for a long time in large bodies of water (rivers, seas, oceans), these wastes can fragment into small pieces and be ingested by living organisms causing their suffocation and/or intoxication. The presence of this plastic waste represents a global environmental threat with harmful consequences for ecosystems and living beings. Potentially, the chemical decomposition of plastics can generate toxic compounds, such as polychlorinated biphenyls, bisphenol A, flame retardants, perfluorinated, phthalates, bisphenols, nonylphenols, among others, Figure 1 [15].

After post-consumer plastics are discarded, part of them are discharged into the environment, these plastics undergo physical, chemical and biological weathering processes which involves a slow decomposition of the large plastic pieces obtaining microplastics and nanoplastics in the process [11, 22-24]. Microplastics can be classified into primary and secondary.

Primary microplastics are those microscopic plastics manufactured for industrial or domestic use, for example, microparticles of polyethylene terephthalate (PET), polyethylene (PE) or polymethyl methacrylate (PMMA) are dispersed in cosmetic products such as toothpastes, body creams, shampoos, scrubs, sunburn creams, makeup and hygiene products, to increase the abrasive effect and improve their performance. Other products such as baby wipes, make-up removers, among others, use polyester (PES), polyethylene (PE) and polypropylene (PP) microparticles. Once these industrial and domestic products are used, the plastic microparticles contained in them are released into the wash water, becoming an environmental liability. In addition, large quantities of primary microplastics are generated by the abrasion of car tires during driving, as well as during the washing of synthetic textiles [25]. Microplastics have become a global problem, since 2010 microplastics have been detected in more than 200 species of edible animal species (164 marine fish, 23 mollusks, 7 crustaceans, 2 birds, 2 freshwater fish, 2 turtles, chicken), some food products (canned sardines, salt, sugar and honey), as well as in beer and water [15, 26].

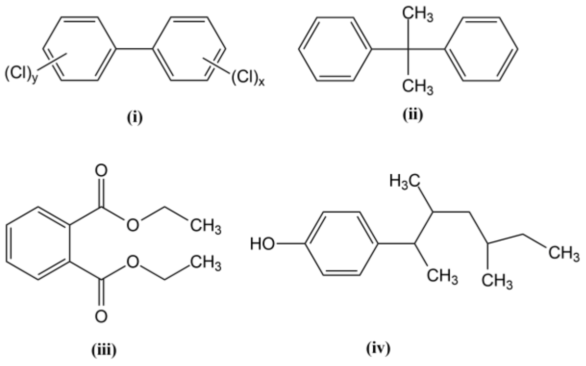

Figure 1. Some toxic compounds generated by chemical decomposition of plastics, (i) polychlorinated biphenyls, (ii) biphenol A, (iii) phthalates and (iv) nonylphenol.

Primary microparticles loose in the environment can undergo degradation processes causing their fragmentation and generating secondary microplastics. These are more reactive and hazardous to marine fauna and living beings than primary microplastics. Secondary microplastics are generated from the wear and tear of fishing nets, industrial resin granules, household items and other types of plastic waste. Various environmental and chemical factors control the levels of fragmentation (degradation) of plastics, therefore, depending on the degradation mechanism that these materials undergo, we can classify these degradation processes into:
(i) biodegradation (action of living organisms), (ii) photo-degradation (light radiation), (iii) thermo-oxidative degradation (slow oxidative decomposition at moderate temperature), (iv) thermal degradation (high temperature), (v) hydrolysis (reaction with water) [15, 26, 27].

Regardless of the degradation process that the plastics undergo, the degradation products that are generated are incorporated into the environment (water, soil, air), thus increasing the concentration and variety of dissolved organic species. This varied chemical environment in turn creates the right conditions for new degradation processes to take place until the polymer macromolecules reach their mineralization (formation of inorganic species in CO2, H2O, N2, H2, CH4, HCO3- salts and minerals).

Upon reaching seas and oceans, microplastics are distributed according to their buoyancy, which is determined by their density and surface interaction (wettability). Today there is an enormous amount of post-consumer plastic in the sea, and the formation of plastic islands up to 3 km in length and areas of the seabed with high concentrations of submerged plastic of up to 1.9 million pieces/m^2 have been reported. As the size of the plastic particle decreases, they can be ingested by microalgae or marine invertebrates, causing their intoxication and even their death, which is why microplastics have been identified as agents that increase the ecotoxicity of the environment and affect the food chain [11]. Plastic weathering occurs due to many different processes and causes alterations in the chemical properties of the contaminants generated by the plastic [22].

The effects of weathering of plastics on the environment include the accelerated release of plasticizers and toxic additives. Weathering and its consequences on plastics are: (1) fragmentation of larger plastic debris thereby increasing the specific surface area; (2) modulation of polymer properties (e.g., crystallinity); (3) oxygen-containing functional groups change the surface properties of microplastics by decreasing their hydrophobicity; and (4) biofilms attached on microplastics increase their toxin adsorption capacity [15].

Photochemical degradation of plastics

Photochemical reactions basically occur as a result of the activation of a molecule from its fundamental state (S0) to an electronically excited state called singlet (S*) and/or triplet (T*), this electronic transition occurs due to the absorption of a photon (light). If this energetic transition occurs without a change of electronic spin in the molecule, the excited electronic state that is reached is called singlet (S1), in the case that the molecule absorbs higher energies at the appropriate frequencies, then higher singlet excited states can be reached (S2, S3, .., Si) [31]. When the electronic transition, caused by the absorption of a photon, produces a change of the electronic spin in the molecule (unpaired of two electronic spins), the excited state obtained is called triplet (T1), moreover, if the absorbed energy is high enough, higher triplet energy states (T2, T3, ..., Ti) can be reached.

When the degradation reaction of a polymer takes place in a radiation-free environment (hv), under an inert atmosphere (vacuum, nitrogen or argon) and without the intervention of other mechanisms such as mechanical or biological, the only changes in the microstructure of the material that occur are chain breaking and cross-linking. On the other hand, when the degradation process of a polymer takes place in the presence of light and under an oxidizing environment (air, oxygen), photo-oxidative degradation of the material occurs. In the photo-oxidative degradation of almost all polymers, the following steps can be considered [9, 19]:

Photoinitiation

Polymers (PH) may contain intramolecular impurities such as certain chromophore groups (light absorbing functional groups), such as: C=O, C=C, ROOH and/or external light absorbing (RR') impurities (intermolecular impurities), such as: traces of catalyst, solvent, additives, atmospheric pollutants, metal particles, etc. These impurities can generate polymeric radicals (P) and hydroperoxide (HO_2 .-) in the presence of air (oxygen) and under the effects of UV/VIS (visible) radiation, the general reaction scheme for the formation of these radicals is shown below. [19]:

$$RR' \xrightarrow{hv} R\cdot + R'\cdot$$

(Radical of external impurity)

$$PH + R\cdot (o\ R'\cdot) \longrightarrow P\cdot + RH\ (o\ R'H)$$

(Polymeric radical)

When light acts on the intramolecular impurities in the polymer described above, chain fragmentation and the formation of radicals of various sizes (R: methyl, ethyl, etc.)

occur, the extent of this type of reaction will depend on other factors associated with the properties of the material.

$$Polymer \xrightarrow{hv} P\cdot + P\cdot\,(y/o\; P\cdot \; + \; R\cdot)$$
(Polymer radical formation)

A very common contaminant found in polymers is catalyst residues, which can generate radicals that initiate polymer degradation reactions. Many commercial polymers contain residues of metallic compounds and certain amounts of additives that are deliberately incorporated into the material, including the presence of particles and metallic traces may be due to mechanical wear suffered by the different production systems of these polymers (reactor walls, blades, pipes, etc.). Catalysts based on transition metals such as titanium or zirconium are widely used in the synthesis of PE and PP. After polymer synthesis, residues of these transition metals can remain occluded in the material in concentrations of around 2-100 ppm. These metal residues are associated with thermal stability and photo-degradation problems in plastics.

$$TiCl_4 \xrightarrow{hv} TiCl_3 + \; Cl\cdot$$

The generation of photosensitizing agents is initiated by the absorption of a photon of light (*hv*) by TiO_2 and the promotion of an electron of the transition metal from its valence band (BV) to its conduction band (BC), thus forming a positive hole-electron pair.

The relative proportion of reactive species formed in photosensitization will depend on the presence of water and oxygen in the reaction system, therefore, TiO_2 will not promote photosensitization without the presence of oxygen and water. Table 3 below shows some photo-initiating compounds for polymer photo-degradation reactions:

Table 3. Various photo-initiators to accelerate the degradation of different polymers.

In turn, photon radiation can catalyze the formation of charge transfer complexes (CTC) between ambient oxygen and the polymer ($PH\cdot\cdot O_2$), these types of complexes are very unstable and generally decompose easily generating polymer radicals and hydroperoxides:

$$PH \;+\; O_2 \xrightarrow{hv} PH \cdot\cdot O_2 \xrightarrow{hv} P\cdot + HOO\cdot$$

Chain propagation.
Chain propagation is the reaction where a peroxide radical group (POO·) is inserted into the main polymer chain, starting from a polymer radical and atmospheric oxygen:

$$P\cdot + O_2 \longrightarrow POO\cdot$$
(Formation of peroxide polymeric radical)

This reaction is very fast and leads to the formation of polymer hydroperoxides (POOH) and radicals (P·) from hydrogen abstraction from a polymer chain (PH):

$$POO\cdot + PH \rightarrow P\cdot + POOH$$
(Hydroperoxide polymer formation)

The abstraction of hydrogen atoms from polymer chains, promoted by peroxide radicals (POO.), occurs preferentially on the tertiary carbons of the chain, however, it has been reported that this abstraction of hydrogens can also occur on secondary carbons [19].

The abstraction of hydrogen atoms during chain extension can also occur intramolecularly, for which there must be a favorable stereochemical arrangement between the peroxide group (POO.) and the hydrogen atom to be abstracted.

In addition to promoting the formation of polymer radicals (P.), radical peroxides (POO) participate in the termination reactions, which compete with chain propagation, forming in the process polymer peroxides (POOP), polymer ethers (POP) and release in the process of molecular oxygen [31].

Norrish Type I and II Reactions
Polymers containing oxygenated groups of the ketone type can undergo two types of photochemical reactions:
a) Norrish type I (radical) reaction, also known as □-scission reaction, generates radicals (P.) and carbon monoxide (CO), Figure 2.

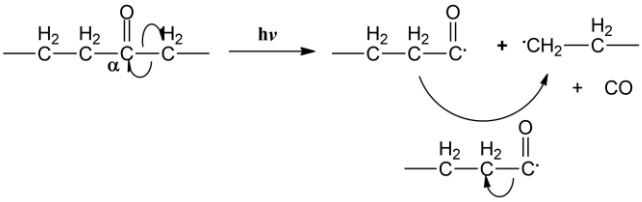

Figure 2. Norrish type I reaction

b) Type II Norrish reaction (non-radical), this type of chain cleavage involves the abstraction of intermolecular hydrogen by a six-membered cyclic intermediate which undergoes a rearrangement resulting in a ketone group on the polymer chain and a short chain olefin, Figure 3.

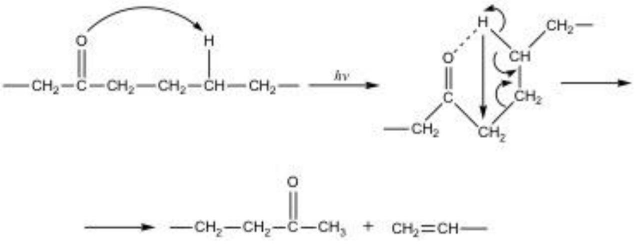

Figure 3. Norrish type II reaction

Type I and II Norrish reactions depend on the structure of the polymer, for example, the type I Norris chain-breaking reaction in ethylene and carbon monoxide polymers occurs in very low yield, since this type of polymers possesses a strong cage effect (solvent protection) and high reactivity of the primary radicals produced in the reaction. On the other hand, the Norrish type II reaction in ethylene-carbon monoxide copolymers do not occur due to the absence of □-hydrogens.

Due to the rapid diffusion of the small acetyl radical (CH_3-$\dot{C}$=O), away from the newly formed radical (P·), this situation increases the effectiveness of Norrish type I photolysis. The Norrish type II reaction depends on the lifetime of the triplet excited state, furthermore this excited species must be stable enough to allow cyclic rearrangement of the chain, which can be a six- or seven-membered intermediate. Six-membered cyclic intermediates are formed in phenyl vinyl ketone polymers (PPVK), while seven-membered cyclic intermediates are produced in methyl methacrylate-methyl vinyl ketone copolymers (MVK-MMA).

The development of Norrish type II photoscission of macromolecules differs significantly from the photoscission of small molecules. The diffusion of small molecules partially controls the energy transfer process, whereas in a polymeric medium the migration of excitation energy depends entirely on the viscosity of the macromolecule. In macromolecules, the development of type I and type II Norrish reactions is very limited when performed below the glass transition temperature of the polymer (Tg), since at this temperature there is no significant molecular motion, while above Tg, the quantum yields of Norrish reactions in polymers are almost identical to the reactions performed in solution at the same temperature (increased molecular mobility) [19].

Photo-degradation of chlorinated polymers.

Dehydrochlorination is the most characteristic reaction of chlorinated polymers such as PVC during UV radiation, this reaction leads to the formation of unsaturated chain sections (-CH=CH-)n in the polymer, n can vary from 2 to 13. These dehydrochlorination reactions are responsible for the appearance of a yellow-red coloration in PVC. In addition to the dehydrochlorination reactions, PVC, when subjected to UV irradiation (hv) in the presence of water and humidity, can undergo typical photooxidation reactions with the formation of carbonyl groups, carboxylic acids, hydroxides and hydroperoxides, as already described in previous sections. In the specific case of chlorinated polyvinyl chloride (CPVC), its photo-dehydrochlorination induces the formation of chlorinated polyene sequences. Polymers obtained from CPVC dehydrochlorination can be completely dehydrochlorinated when laser radiation is used, thus generating graphene structures.

Photo-degradation of polymers induced by dyes or dyestuffs.

Virtually all commercial plastic materials contain dyes or colorants in their composition. Dye-induced photo-degradation is a phenomenon commonly found in various industrial sectors, such as land, air and sea transportation, construction, electronics, and many others.

A dye molecule (D) is able to absorb light and become energetically activated until it reaches a singlet (1D) and/or triplet (3D) excited state (we will denote both excited states as D*).

$$D \xrightarrow{hv} D*$$

The photoactivated dye molecule (D*) can then abstract a hydrogen atom from the polymer (PH) and produce a radical (P·) together with a hydrogenated dye radical (DH·). In the presence of water (moisture) and molecular oxygen, or in the case of the use of wet dyes, the photoactivated dye molecules can generate hydroxyl radicals (HO.) and hydroperoxides (HOO.) and a hydrogenated radical species of the initial dye itself (DH.).

$$D* + H_2O \longrightarrow DH\cdot + HO\cdot$$
$$DH\cdot + O_2 \longrightarrow D + HO_2\cdot$$

The hydroxyl (HO·) and hydroperoxide (HO_2·) radicals are very reactive and rapidly abstract hydrogen atoms from the polymer (PH) thus generating radicals (P·) that can subsequently undergo photooxidation reactions, as described in the previous section.
Inactivation of this photoactive dye molecule (D*) can generate a semi-oxidized radical cation ($D\cdot^{+}$) or a semi-reduced radical anion ($D\cdot^{-}$).

$$D* \longrightarrow D\cdot^{+} + e^{-}$$
$$D* + e^{-} \longrightarrow D\cdot^{-}$$
$$D* + OH^{-} \longrightarrow D\cdot^{-} + HO\cdot$$

The disproportionation reaction of the two dye ions ($D\cdot^{-}$ y $D\cdot^{+}$), leads to the regeneration of two dye molecules:

$$D\cdot^{+} + D\cdot^{-} \longrightarrow 2D$$

Both dye radicals can also participate in the following reactions:

$$D\cdot^{+} + DH\cdot \longrightarrow 2D + H^{+}$$
$$D\cdot^{+} + OH^{-} \longrightarrow D + HO\cdot$$

The radical anion of the dye ($D\cdot^-$) often has a strong tendency to take a proton from the environment and/or establish chemical equilibrium with it.

$$D^-\cdot \ + H^+ \longleftrightarrow DH\cdot$$

Both D.- and DH. species represent semi-reduced forms of the dye molecule in the ground state (S0), the dye radical DH. is a very reactive species and generates a colorless product (DH_2) known as the leucoform of the dye derived from its disproportionation reaction:

$$DH\cdot \ + \ DH\cdot \longrightarrow D \ + DH_2$$

This leucoform can also be formed from the abstraction of a hydrogen atom from the polymer:

$$DH\cdot \ + \ PH \longrightarrow P\cdot \ + DH_2$$

In an oxygenated medium the dye radical DH. produces an oxygen radical ion. (O2.-).

$$DH\cdot \ + \ O_2 \longrightarrow D \ + \ H^+ \ + \ O_2\cdot^-$$

In the presence of water, an electron (e-) can be solvated generating a species (eac-) that can react with the surrounding molecular oxygen and water.

$$e^- \xrightarrow{H_2O} e^-_{ac}$$

Electron solvation

$$e^-_{ac} \ + \ O_2 \xrightarrow{H_2O} O_2\cdot^-$$

Oxygen radical ion formation

$$O_2\cdot^- \ + \ H_2O \longrightarrow HO_2\cdot \ + HO^-$$

Hydroperoxide radical and hydroxide anion

$$2\,HO_2\cdot \longrightarrow H_2O_2 \ + \ O_2$$

Hydrogen peroxide

$$HO_2\cdot \ + e^-_{ac} \longrightarrow HO_2\cdot^-$$

Hydroperoxide radical anion

$$HO_2\cdot \ + H_2O \longrightarrow H_2O_2 \ + \ OH^-$$

Hydrogen peroxide and hydroxide anion

$$2\,O_2\cdot^- + \ 2H^+ \longrightarrow H_2O_2 \ + \ O_2$$

Hydrogen peroxide formation

Another reaction that can occur is the transfer of energy between the excited dye molecule and molecular oxygen, thus forming singlet oxygen (1O2):

D* (T1) + O_2 ------- D (S0) + $^1O_2$
Singlet oxygen formation

Table 4 below shows various types of dyes commonly used in the plastics industry that produce singlet oxygen ($^1O_2$) by energy transfer, the energies of their triplet states (ET) are in the range of 30-56 kcal mol-1.

Table 4. Dyes that promote photodegradation of plastics [31]

All of these dye photoinitiation reactions can cause discoloration of dyes contained in plastics. The mechanisms of dye discoloration are complex and often depend on the structure of the dye and the chemical and/or physical nature of the polymer. Dye photosensitization deterioration of plastics occurs when a dye accelerates the breakdown of the molecular structure of a polymer, all in the presence of molecular oxygen and water. The degree of photo-degradation of plastics due to dyes can be decreased by the addition of stabilizers [33].

Photocatalytic degradation of plastics

Photocatalytic degradation of plastic can be described as the whole set of reactions that polymer chains undergo, promoted by a photosensitizing catalyst, resulting in the decomposition or degradation of the polymer together with the generation of gases, minerals, monomers, oligomers and other different chemicals [34]. The diffusion of reactive species through the polymer matrix increases its macromolecular degradation, among the reactions that occur are oxidation, chain breaking and crosslinking reactions.

Plastics are difficult to degrade due to their poor water solubility, high structural stability and non-biodegradable character. Photocatalysis has proven to be an effective method for plastic degradation. Photosensitization is the process in which a chemical species absorbs a photon of light in the presence of water and/or oxygen, and forms reactive species in the process, such as hydroxyl radical (HO.) and superoxide (HOO.), these species initiate the degradation of the plastic through chain breaking reactions, branching, crosslinking and finally the mineralization of the polymer in the form of H_2O, CO_2 and other compounds. Some studies of photocatalytic degradation of plastics are shown in Table 5 below [35].

For a catalyst to be active in the photo-degradation of plastics, it must consist of a semiconducting metal that absorbs radiant energy or light (hv), thus becoming a photosensitizing species that accelerates the rate of plastic degradation. An ideal photocatalyst should absorb light at room temperature, be highly stable to photo-corrosion and at the same time be non-toxic to the environment and living beings. The effectiveness of a photocatalyst depends on its oxidation-reduction potential. In this sense, the oxidation-reduction potentials of various compounds used as photocatalysts in the degradation of plastics are shown below. The values of the normal oxidation potential are referenced to the normal oxidation potential of hydrogen [36].

If a photocatalyst (semiconductor) has a valence band maximum (VBM) more positive than 1.23 eV (of O_2/H_2O), it means that its oxidation capacity is sufficient to promote water oxidation, therefore, as the VBM value of a given photocatalyst is more positive it means that the oxidation capacity of that photocatalyst will be higher. An order in oxidation capacity of some studied photocatalysts follows the following trend: ZnS > ZnO - TiO_2 > WO_3 > CdS.

On the contrary, if the semiconductor exhibits a minimum conduction band more negative than the normal hydrogen reduction potential, it means that the photocatalyst will then be able to promote the reduction of water, and the higher the value of that conduction band, the higher the reduction capacity of the photocatalyst. (ZnS - CdS - CdSe > ZnO > TiO_2 - Si) [36].

One of the most widely used photocatalysts in the degradation reaction of plastics is TiO_2, which has a high oxidation-reduction potential, high chemical and thermal stability, low cost and is environmentally friendly (non-toxic). On the other hand, zinc oxide (ZnO) has a band gap similar to TiO_2 and is often used as an alternative to TiO_2. Other semiconductors used as photocatalysts in the degradation of plastics are: iron oxide (Fe2O3), cadmium sulfide (CdS), zinc sulfide (ZnS), tungsten oxide (WO_3), tin oxide (SnO), bismuth vanadate ($BiVO_4$), and non-metallic carbon nitrides (N_3C_4) [36]. Table 5 below shows a summary of the different heterogeneous photocatalytic systems that have been studied in the degradation of various types of plastics.

Tabla 6. Photocatalytic degradation studies of various types of plastics [35].

Autonomous photocatalytic microbots for microplastics degradation

One of the important characteristics that a photocatalyst must possess is a large surface area, however, classical synthesis methods of heterogeneous photocatalysts involve physical deposition processes under constant agitation, these types of synthesis methods are expensive and do not generate particles small enough to achieve a large surface area per gram of material. Additionally, most photocatalysts are toxic and cannot be reused after their use in the plastic photo-degradation reaction.

In 2021, Pumera et al., [37] reported the synthesis of novel automaton photocatalytic systems called by their creators as microrobots based on bismuth vanadate (BiVO4), these heterogeneous photocatalysts are able to move through aquatic environments in an automaton way, use low energy and interact with microplastics in the environment to subsequently photo-degrade them inside their structure. These swimming microrobots can be driven by magnetic fields, electric fields, ultrasound and ambient light, in addition, these microrobots contain iron oxide (Fe3O4) which allows the recovery of the microrobots from the reaction medium by using a magnet. The highlights of this particular photocatalytic system are as follows:

I. Adequate potential bandgap.
II. A low recombination speed of the load torque.
III. An asymmetric physical shape.
IV. Easy interaction with visible light.
V. Photoreaction with the water in the medium generates disproportionately shaped products, which promotes their movement (automaton).

The BiVO4/Fe3O4 microrobots were housed in the host tunnel along with a certain amount of microplastics, initially the microrobots were not in contact with the microplastics, subsequently the experiment is initiated by allowing the microrobots to move along the host tunnel while sunlight is applied to the system. The light promotes photoreactions in the microrobots allowing the microrobots to move until they absorb onto the surface of the microplastics. To confirm the adhesion strength of the microrobots on the microplastics, a magnetic field (magnet) is applied to the system to separate the microplastics with attached microrobots from the microplastics without attached microrobots [37]. The adhesion of microrobots on the surface of microplastics is attributed to adsorption/precipitation mechanisms previously observed in the anchoring of heavy metals and organic pollutants on oceanic microplastics.

The microrobots use H_2O_2 as fuel to asymmetrically generate products such as H+ and O_2, the formation of these products drives the microrobots in aqueous media causing them to contact the microplastics thus initiating microplastic degradation reactions. The photodegradation reactions of microplastics involve the formation of free radicals, breaking of C-C and/or N-C and C-O bonds, among other reactions that occur simultaneously.

This study succeeded in demonstrating that the photocatalytic automaton microrobots are able to efficiently degrade different types of microplastics, in particular polylactic acid (PLA), polycaprolactone (PCL), due to their automaton movement capability which allows an effective interaction between the microplastics and the photocatalyst without the need of using external mechanical stirrers. These photocatalytic automaton microrobots have demonstrated for the first time that it is possible to efficiently photo-degrade plastic microparticles in complex confined spaces, which can significantly boost research on environmental microplastic treatments in order to reduce the amount of these pollutants in the environment.

Conclusions

In the last 20 years, the detection of microplastics in aquatic and terrestrial environments and in the air has set off alarm bells in the scientific and industrial sectors; the harmful effects of these micrometric materials on the health of living beings have been scientifically corroborated. Therefore, important projects have been initiated around the world to study this artificial phenomenon in order to minimize its effects on the planet's ecosystems and living beings. Photochemistry provides the conceptual tools necessary to understand and develop technological strategies by which it would be possible to break down microplastics to the extent of harmless mineral compounds. The photo-degradation reactions of plastics depend mostly on the presence of water, sunlight, imperfections and/or contaminants in the plastic and also on the chemical composition of the polymer to be degraded.

The times of photo-degradation reactions of plastics are very long, so the use of heterogeneous photocatalysts to accelerate these photo-degradation processes constitutes a technology strategy with great potential for success to be considered in the future. Great advances have been made in the development of photocatalysts for the degradation of microplastics, it is estimated that within a few decades we will be in the presence of the emergence of important technologies for environmental decontamination of microplastics, and photocatalysis will undoubtedly play a leading role in the purification of seas, rivers and even the air and land of our planet.

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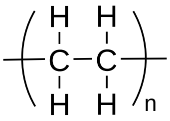
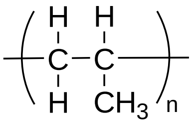
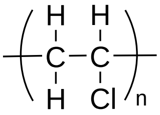
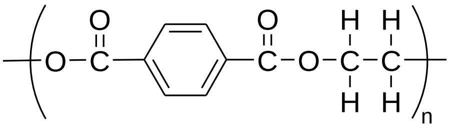
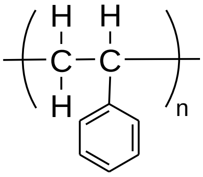
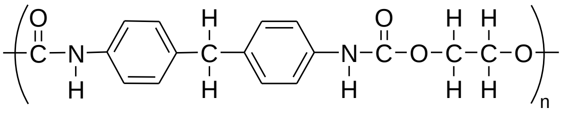
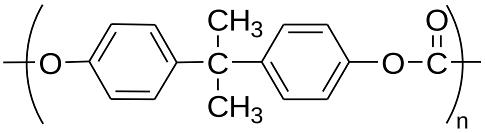
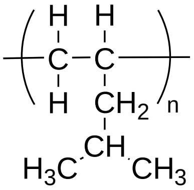
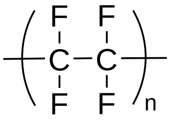
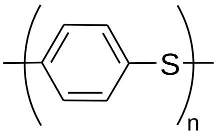
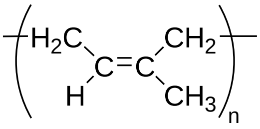
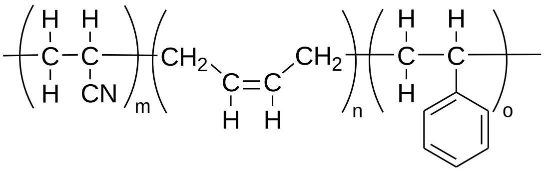
Table 1. Timeline of plastics development [4].

XIX Century		**XX Century**	
Year/Polymer	**Developer**	**Year/Polymer**	**Developer**
1839/ Natural Rubber Latex	Charles Goodyear	1909/Bakelite	Leo Hendrik Baekeland
1839/ Polystyrene	Edward Simon	1926/Plasticized PVC	Walter Semon
1862/Parkesina	Alexander Parkes	1933/ Poly (vinylidene chloride)	Ralph Wiley
1865/ Cellulose Acetate	Paul Schützanberger	1935/Low density polyethylene	Reginald Gibson and Eric Fawcett
1869/Celluloid	Jhon Wesley Hyatt	1936/Poli (metil metacrilato)	Reginald Gibson and Eric Fawcett
1872/ Poly(vinyl chloride)	Eugen Baumann	1937/Polyurethanes	Otto Bayer
1894/ Viscous rayon	Charles Frederick Cross	1938/Polystyrene	Commercially made
		1938/Polyethylene Terephthalate	John Whinfield and James Dickson
		1942/Unsaturated Polyester	John Whinfield and James Dickson
		1951/Polypropylene	Paul Hogan and Robert Banks
		1953/Polycarbonate	Hermann Schnell
		1954/Polystyrene foam	Ray McIntire
		1960/Poly (lactic acid)	Patrick Gruber
		1978/Linear low density polyethylene	DuPont

Table 2. Applications of the most popular commercial polymers [4].

Polymer Type	**Uses and applications**
Polyethylene (PE) 	*Low-density PE:* compressible bottles, toys, carrier bags, electrical insulation, chemical tank liners, heavy-duty sacks, general packaging, gas and water pipes. *High-density PE:* chemical drums, toys, picnic items, household and kitchen items, cable insulation, carrier bags and food wrapping material.
Polypropylene (PP) 	Food packaging, microwave food trays and in the automotive industry.
Poly (vinyl chloride) (PVC) 	Construction, transportation, packaging, electrical/electronic and sanitary applications.
Polyethylene Terephthalate (PET) 	Beverage bottles, cable liner for baking trays.

Polystyrene (PS) 	Food packaging, take-out boxes, beverage cups, plastic cutlery, protective packaging and CD cases.
Polyurethane (PU) 	Printing rollers, solid tires, wheels, shoe heels, automotive bumpers, as foams in mattresses and car seats, and in biomedical applications.
Polycarbonate (PC) 	Bottles, utensils, containers, foils, electrical items and medical applications.
Poly(methylpentene) (PMP) 	Medical articles, syringes, lamp covers (good heat resistance), radar applications, encapsulation and microwave food packaging.
Polytetrafluoroethylene (PTFE) 	Anti-stick coating, gaskets, bearings, high and low temperature medical and electrical applications, laboratory equipment, pump parts and thread sealing tape.
Poli(Sulfuro de fenileno) (PPS) 	Sterilizable electrical, automotive, kitchen, medical, dental and laboratory equipment, hair dryer racks and components.
Polyisoprene (NR) 	Gloves, tires, rubber boots, rubber bands, pencil erasers, hoses, belts, flooring and medical applications.
Acrylonitrile-butadiene-styrene (ABS) 	Piping, musical instruments, golf club heads, automobiles, medical devices for blood access, electrical devices, protective helmets, whitewater canoes, small kitchen appliances and toys.

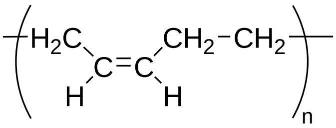
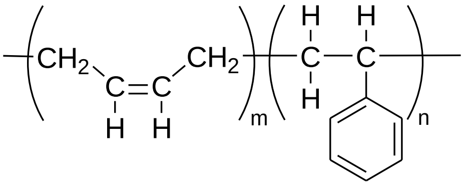
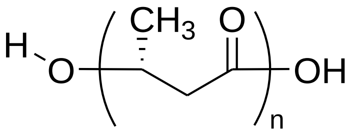
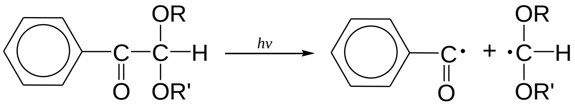
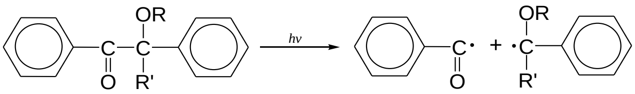
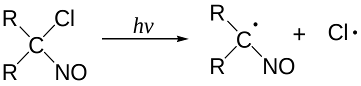
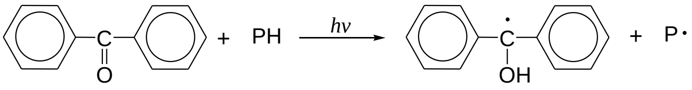
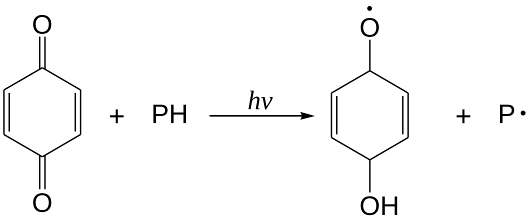
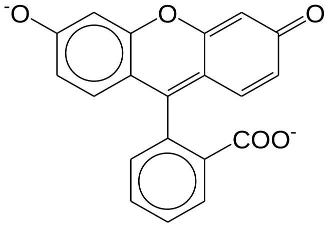
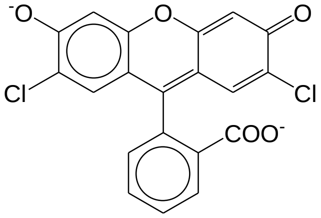
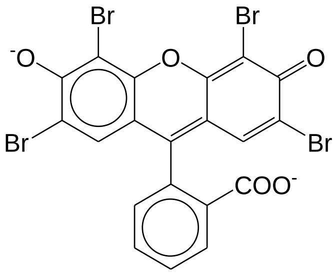
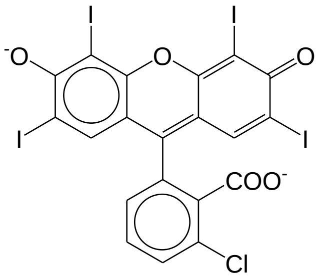
Polybutadiene 	Tires, golf balls and inner tubes.
Styrene-Butadiene (SBR) 	Tires, footwear, construction and paper coating applications
Poly(hydroxyalkanoate) (PHA) 	Medical devices, such as cardiovascular patches, orthopedic pins, adhesion barriers, stents, guided tissue repair/regeneration devices, articular cartilage repair devices, bone implant material, drug delivery system, tissue engineering scaffolding, loading and filling agents.

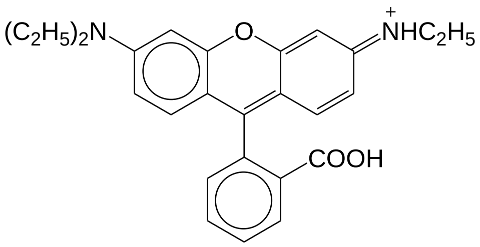
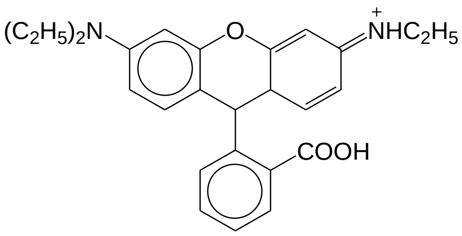
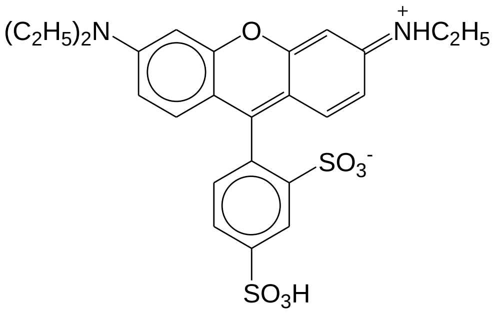
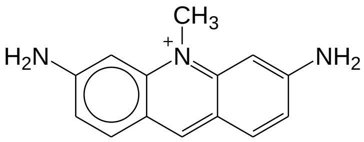
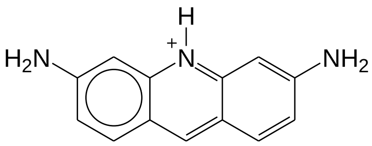
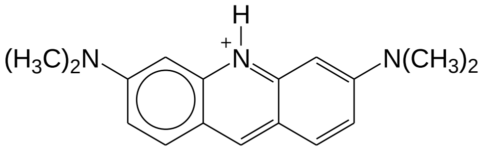
Table 3. Various photo-initiators to accelerate the degradation of different polymers

Photo-initiator	Fragmentation reaction	Polymer
Acetophenone derivative		PE, EPDM B
Benzoin derivatives		PE, PMMA, PVC, PS
Chloronitroso compounds		PI
Benzophenone		PE, PP, PS, PEP, PVAP, PEG, CA PAMS, PBD, EPDM B, PNR,
Quinones		PE, PP, PVC, PS, PA, Cellulose

Note: EPDM B: ethylene-propylene-diene rubber type B, PE: polyethylene, PMMA: polymethylmethacrylate, PVC: polyvinyl chloride, PS: polystyrene, PI: poly(isoprene), PEP: Poly(ethylene-co-propylene), PVAP: poly(vinyl acetophenone), PEG: poly(ethylene glycol), PAMS: poly(-methylstyrene), PBD: polybutadiene, PNR: polynorbornene, CA: cellulose, PA: polyamide.

Table 4. Dyes that promote photo degradation of plastics [31]

Dye	Triplet energy (E_T) (kcal mol^{-1})
 Fluorescein	47,2
 2,7- Dichlorofluorescein	46,0
 Eosin Y	45,5
 Rose Bengal	42,0

 Rhodamine B	43,0
 Rhodamine 6G	42,0
 Sulforhodamine B	41,8
 Acriflavin	51,1
 Proflavine	51,1
 Acridine Orange	

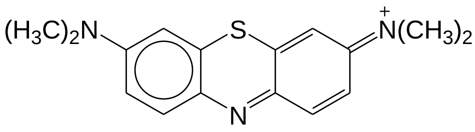
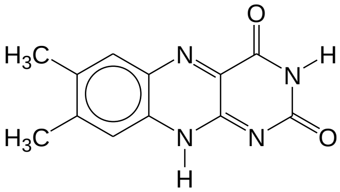
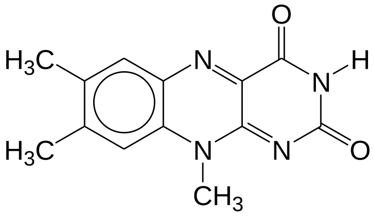
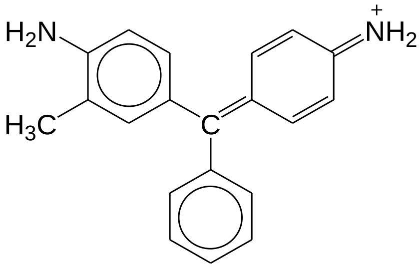
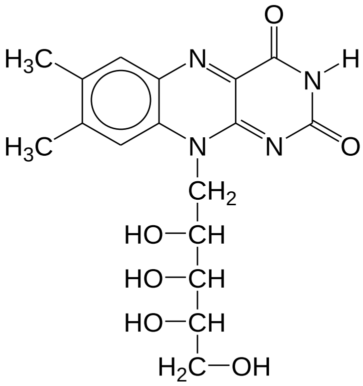
 Methylene blue	32,0
 Lumichrome	55,4
 Lumiflavin	50,5
 Crystal violet	42,0
 Riboflavin	50,0

Table 5. Photocatalytic degradation studies of various types of plastics. [35].

Polymer / Photocatalyst	Experimental details	Experimental results
LDPE/ZnO microplastic wastes	A 50 W dichroic halogen lamp in air was used as a visible light source (≈ 60–70 klux); 175 hours of illumination; 1 x 1 cm size films of LDPE and 20 mM ZnO	The carbonyl index (CI) and vinyl index (VI) showed an increase of 30%; new functional groups such as hydroperoxide carbonyl and unsaturated groups were formed during photodegradation, cracks and stains were observed on the LDPE film after photodegradation.
Micro plastic of LDPE / Pt/ZnO	A 50 W dichroic halogen lamp in air generated visible light (≈60–70 klux); 175 hours of illumination; a commercial PELD film with a thickness of 50 microns and dimensions of 2.5 x 0.75 cm was evaluated; ZnO-Pt substrates with an average diameter and length of 960 μm were used as photocatalyst.	VI and IC increased by 15% and 13%, respectively; various cracks, wrinkles and cavities of different sizes were detected in all photodegraded films, and volatile organic compounds and oxygenated groups were formed.
Micro plastic HDPE / C, N-TiO_2	200 mg of microplastics and 200 mg of the photocatalyst were added to 50 ml of a buffer solution for 50 h of continuous stirring at 300 rpm; a 50 W LED lamp was employed as a visible light source.	Low temperature and pH have a combined effect on microplastic degradation. At pH = 3 and 0°C, the mass loss after 50 h of irradiation was 71%; the degradation rate constant, k = 0.0237
HDPE micro plastic / N-TiO_2	A 27W fluorescent lamp was used as a constant light source in the visible light spectrum for 20 hours at room temperature.	The first order kinetic constant was 12.2×10^{-4} h^{-1} (solid medium) and 38.2 h^{-1} (aqueous medium).
PE micro plastic / hydroxide-rich BiOCl ultra thin film	A water circulation system under a 250 W Xe lamp; 1 $g.L^{-1}$ micrometer grade plastic (PE-S) or 10 $g.L$-^{1} of millimeter grade plastic were dispersed in 100 mL of an aqueous solution; 1 $g.L^{-1}$ of photocatalyst was added.	PE microplastics photo-degraded by BiOCl-1 showed a mass loss of 5.38%, which was 134 and 24 times higher than the degradation obtained with light alone (0.04%) and BiOCl/light (0.22%).
PE and PP / ZrO_2, TiO_2	Degradation was evaluated under a sun simulator and under real sunlight for 20 hours; PE and PP films of size 1.5 x 1.5 cm; ZrO_2, TiO_2 photocatalyst at 10 000 ppm.	The CIs of the original PE and PP were 0.0090 and 0.0072, respectively. The average CIs of PE and PP treated with ZrO_2, under a sun simulator and under real sunlight, were 0.0244, 0.0382, 0.0149 and 0.0190, respectively. Under real sunlight were 0.0244, 0.0382, 0.0149 and 0.0190, respectively. The average CIs of PE and PP treated with TiO_2, under sun simulator and under real sunlight were 0.0226, 0.0260, 0.0112 and 0.0124 respectively. ZrO_2 cause higher photocatalytic effect on the polymers.
PLA, PET and PUR / CdS/CdO_x	CdS of 0.5 μM irradiated for 4 h at 25°C with simulated sunlight (AM 1.5 G, 100 mW cm^{-2}); solution volume was 2 ml of 10M NaOH in a sealed photo-reactor (internal volume of 7.91 mL) under anaerobic conditions; 50 mg mL^{-1} PLA, 25 mg mL^{-1} PET, 25 mg mL^{-1} PUR.	Photo-reforming of PUR, PET and PLA generated H_2 with activities of 0.85, 3.42 and 64.3 mmol H_2 $g.CdS^{-1}$ h^{-1}, respectively. PLA in NaOH(ac) hydrolyzed to sodium lactate, which was oxidized forming an alkaline-induced pyruvate-based compound. PET was hydrolyzed to terephthalate, ethylene glycol and isophthalate, while its photooxidation produced formate, glycolate, ethanol, acetate and lactate. PUR first hydrolyzed to aliphatic and aromatic components, where the aromatic component remained intact during photo-reforming, while the aliphatic component was photo-oxidized to pyruvate, acetate, formate and lactate.
PE and PVC / Pt/TiO_2	500 W Xe lamp, 10 h of irradiation; 300 mg Pt/TiO_2; 150 mg PE and PVC, 30 ml of deionized water	Photo-reforming of PE and PVC generated H_2 with activities of 0.015 and 0.031 mmol H2 $g.cat^{-1}$ h^{-1} in 5 M NaOH.
PET /MoS_2/$Cd_xZn_{1-x}S$	10 mg of MoS_2/$Cd_xZn_{1-x}S$; 60 mL of PET substrate solution; a 300 W Xe lamp with AM 1.5G was used as light source; under anaerobic conditions.	4.3 wt.% de MoS_2 in MoS_2/$Cd_xZn_{1-x}S$ exhibited the best H^2 evolution rate of 15.90 $mmol.g^{-1}.h^{-1}$. PET was finally oxidized to small molecule organic compounds, such as methanol, formate, ethanol and acetate.

PP, PEBD/ $NiAl_2O_4$	A 350 W metal halide lamp; a PP film of size 3 x 3 cm; 30 mg NiAl2O4; DMSO as solvent (20 mL); a 3x3 cm PP film; 30 mg $NiAl_2O_4$; DMSO as solvent (20 mL).	The weight loss of PP, LDPE was 12.5% and 10% respectively with NiAl2O4 (prepared via hydrothermal synthesis) and $NiAl_2O_4$ (prepared via co-precipitation) respectively.
PE and PLA / CN_x/Ni_2P	2 wt% (3.2 mg) ultrasonicated CN_x/Ni_2P, 50 mg polymer, KOH(ac) (1M or 10M, 2 mL), sealed photo-reactor (internal volume 7.91 mL); anaerobic conditions, simulated sunlight (AM 1.5G, 100 mW cm^{-2}, 25°C).	H_2 conversion reached 6.7% for PLA and 24.5% for PET at higher pH (KOH, 10 M). (KOH, 10 M); the results showed that H_2 was generated continuously for 6 consecutive days, the photocatalytic activity reached 4.13 mmol H_2 $g.CdS^{-1}$ h^{-1}, the conversion was 5.15% and the external quantum yield was 2.17% in the degradation of real-world PET water bottles. The PET hydrolyzed to its monomers (ethylene glycol and terephthalate) or soluble oligomer fragments. PLA hydrolyzed to lactate during pretreatment, and then oxidized mainly to CO_3^{-2} and small amounts of acetate, formate and other unidentified products.