POLYMERS RECYCLING: UPCYCLING TECHNIQUES. AN OVERVIEW

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ABSTRACT

Since 1950 plastics became the materials of greatest world production. Thus, in recent years the increase in the use of different types of plastics has been a matter of global concern due to the depletion of fossil fuels and the accumulation of waste in the different environmental matrices, affecting the ecosystem. By 2015, 4.9 million metric tons of plastic waste were recorded in landfills, because more than 40% of the plastics produced are designed for single use. The mass amount of plastic is estimated to exceed 450 million tonnes per year and will double by 2045.

Due to the great problem of plastics and their threats to the ecosystem, the researchers worked on a large number of technologies to mitigate the effect of plastics on the different environmental matrices. Therefore, the main goal of this manuscript is summarizes on the plastics more used as well as the most common techniques to reduce their presence at the environment.

Keywords: Plastics, contamination, recycling, environment.

1. INTRODUCTION

The vast majority of polymers correspond to long chains of molecules composed of many units (monomers) linked together by covalent bonds. These compounds have good properties for use in areas such as medicine and tissue engineering (1, 2), engineering and energy (3, 4), agriculture (5, 6), mining (7), among others, however, being in the presence of high temperatures their structure becomes highly viscous due to the entanglement of the molecules (8, 9). Due to the large number of existing polymers we can find different classifications:

1. *Polymers based on source of availability:*

   a. Natural polymers: naturally present in the ecosystem, such as in plants and animals (10).
   b. Semi-synthetic or artificial polymers: derived from natural ones. Have some type of chemical modification (11).
   c. Synthetic polymers (12).

2. *Polymers based on chain structure:*

   a. Linear polymers: have long, straight chains (13).
   b. Branched chain polymers: their main chain is long, presenting ramifications in it.
   c. Cross-linked polymers: polymers with stronger bonds, generally composed of bifunctional and trifunctional monomers.

3. *Polymers based on their polymerization reactions:*

   a. Addition Polymers.
   b. Condensation Polymers.

4. *Polymers based on their structure and molecular forces:*

   a. Elastomers.
   b. Fibers.
   c. Thermoplastics.
   d. Thermostable Polymers.

Figure 1 exemplifies the different types of polymers according to the classifications already mentioned. This allows us to understand that polymers have been (and are) active participants in the functioning of society as we know it today, since in their structural applications as "plastics" they are used in most activities of daily life since they combine their profitability in production, ease of processing, different beneficial properties in their different varieties and their long degradation times (14).

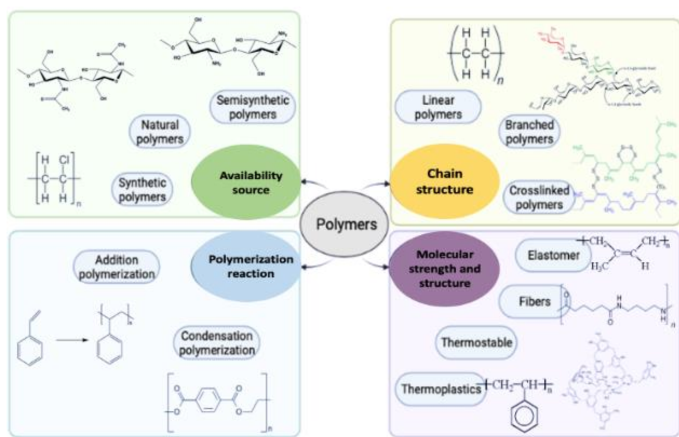

Figure 1. General classification of polymers according to resource availability, chain structure, polymerization reactions and molecular strength and structure.

Thus, since 1950 plastics became the materials of greatest world production (15) thus, in recent years the increase in the use of different types of plastics has been a matter of global concern due to the depletion of fossil fuels (16) and the accumulation of waste in the different environmental matrices, affecting the ecosystem (17). By 2015, 4.9 million metric tons of plastic waste were recorded in landfills, because more than 40% of the plastics produced are designed for single use (18). The mass amount of plastic is estimated to exceed 450 million tonnes per year and will double by 2045 (19). These plastics have been found throughout the water matrix such as beaches, wetlands, rivers (20), coastal regions, ice and ocean (21) including sewage (22) and drinking water.

However, single-use plastics cannot be completely eliminated, since they allow protection against pathogens, better preserve food thus allowing better and greater durability and food safety (23, 24). This characteristic is what makes it highly persistent against degradation being practically indestructible to certain environmental conditions such as those prevailing in the oceans (25, 26).

The great durability due to their chemical structure of polymers such as poly(ethylene) (PE), poly(propylene) (PP), poly(vinyl chloride) (PVC), poly(ethylene terephthalate) (PET), polyurethane (PU), and poly(styrene) (PS) make them the most used plastics (see Table 1), being 90% of plastics produced worldwide.

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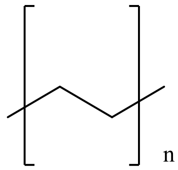
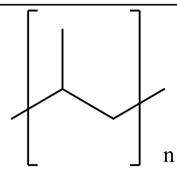
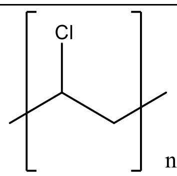
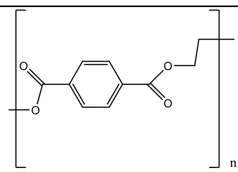
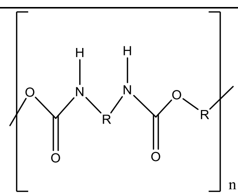
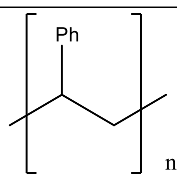
Table 1. Polymers as the most commonly used plastic products, their structure and common uses.

Polymer		Structure	Common uses
PE	Poly(ethylene)		Soap bottles Detergent containers Garbage bags Adhesives
PP	Poly(propylene)		Food containers Bottle caps Children's toys
PVC	Poly(vinylchloride)		Pipes Cables Coatings
PET	Poly(ethyleneterefthalate)		Bottles of drinks, sauces, dressings. Bottles of medicines
PU	Polyuretane		Insulating materials Construction adhesives Waterproofing
PS	Poly(styrene)		Kitchen utensils Packaging materials Food trays

Initially the scientific attention and concern studies based on pollution due to plastic increasingly (see Figure 2) and currently have focused on the study of mesoplastic waste or macro plastics (> 5mm), since its visible presence in oceans and rivers became a symbol of environmental pollution. However, today the study of small particles in aqueous media due to the fragmentation of plastics called microplastics (< 5mm) has added to the topics of study and concern about their possible environmental impact and the latent possibility of being included in the food chain for human consumption (27-29), since low-density microplastics have been found in all aquatic environments, being present throughout the water column and sediments, being potential hazards, involving biological transport and toxicological effects. Although the deposition behavior of microplastics is not known, an idea can be obtained based on the physicochemical properties since the density, shape and size greatly influence their deposition and settlement in the environment. At the same time, biofouling can alter the properties of microplastics and generate an increase in density affecting the vertical flow of different plastics. For example, algae can trap particles of microplastics, helping them to diffuse to deeper layers being part of marine snow.

In this way, the large amount of plastic used has been increasing exponentially and with it the poor management of waste that is expected to persist in the environment being dispersed by winds and water currents (30). Due to the great problem of plastics and their threats to the ecosystem, they have worked on a large number of technologies to mitigate the effect of plastics on the different environmental matrices.

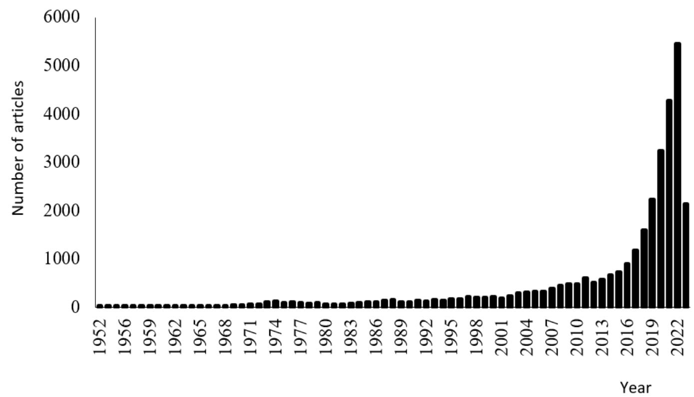


Figure 2. Annual report of pollution by plastics and microplastics between the years1952 to 2023. Data extracted from Scopus. April 22, 2023.

However, since 2020, as a result of the COVID-19 pandemic, environmental pollution has worsened due to the explosive increase in personal protective products, estimated according to the WHO at more than 89 million medical masks, 1.6 million protective glasses and more than 76 million examination gloves (31). With these figures, it has been estimated that masks discarded in 2020 alone would be carrying more than 1370 trillion microplastics into the marine environment, which would correspond to a release rate of 396 billion microplastics per day (32, 33).

In this way, the COVID-19 pandemic has greatly complicated the contamination by plastic products being a trigger in the production and that of these materials (34). At the same time, as a result of this plastic crisis, a large number of new decisions have been opened that will allow the degree of urgency and capacity to respond to this crisis (35), so that both businessmen and politicians decide to opt for the reduction of plastic consumption (36, 37).

As a result of the causes mentioned above and the adverse effects, different techniques for managing this type of waste have been sought, as well as new efficient and sustainable technologies to reverse and treat contaminated systems (38). In this sense, natural and man-made polymers are a viable route for reducing plastic pollution (39, 40). Product of the causes mentioned above and the adverse effects is that different techniques of management of this type of waste have been sought, as well as new efficient and sustainable technologies to be able to reverse and treat contaminated systems. In this sense, natural and artificial polymers are a viable route for the reduction of plastic pollution, since the flow of material produced by natural sources is eliminated or reaches landfills after use and the nutrients obtained in the degradation processes return to the environment fulfilling their natural cycle.

Different biodegradable plastics contain a series of chemical bonds (41) that give them some susceptibility to abiotic reactions, such as hydrolytic, photolytic or oxidative reactions, and biotic reactions such as enzymatic reactions, which allow the reduction of polymers to smaller molecules or smaller polymer fragments (42), allowing it to be completely degraded or metabolized (17).

The enormous success that the use of polymers has had in various areas has led to significant negative effects as a result of their uncontrollable degradation times and the components they release into the environment, this added to the poor management of waste that contaminates the different environmental matrices makes new forms of management and control of plastics are needed where the term sustainable circular economy is increasingly important and attracts the attention of researchers around the world, as it promotes the use of plastic waste through the revaluation of waste materials, by transforming this waste into useful raw material by using different recycling techniques or methods thus closing the cycle of the circular economy (43, 44).

So the field of chemistry carries out the study of new recycled, biodegradable and biologically based materials in order to replace the production of plastics (more than 98%) that use fossil compounds as raw material. In the same way, the sustainability of these new products allows them to be partially or completely biodegradable or to have economic and sustainable collection and recycling techniques. So that the field of chemistry carries out the study of new recycled, biodegradable and biologically based materials in order to replace the production of plastics (more than 98%) that use fossil compounds as raw material. In the same way, the sustainability of these new products so that they are completely biodegradable or that they have economic and sustainable collection and recycling techniques (14).

The IUPAC for 2009 identified the recycling of plastic waste as one of the main emerging technologies in the field of chemistry with great importance for the promotion of the circular economy and to begin to solve the pollution problems that this type of waste has caused (45, 46).

Figure 3. Classification of recycling methods for plastic waste management.

Normally, for waste management, plastics are taken to landfills to be grouped in a certain location (45). However, this is a temporary solution since it does not eliminate these wastes in addition, in these places leaching processes of harmful substances can occur, which leads to induce other environmental problems, such as groundwater contamination (47), so there are currently different methods of primary, secondary, tertiary and quaternary recycling (see Figure 3). Techniques that seek to eliminate waste through reuse, reprocessing or energy recovery (46).

Primary recycling, also known as closed-loop mechanical recycling, is used for the management of uncontaminated or post-industrial plastics as raw material, to produce more of the same product without loss of properties, a typical example of this type of recycling is the production of PET bottles from recycled PET (48). Secondary recycling refers to mechanical methods in which the chemical structure of the polymer does not change, but it undergoes chemical reprocessing to finally obtain products with properties inferior to the starting material. For both primary and secondary recycling, stability problems have been detected as the polymeric material process occurs, since it degrades altering its mechanical properties (47).

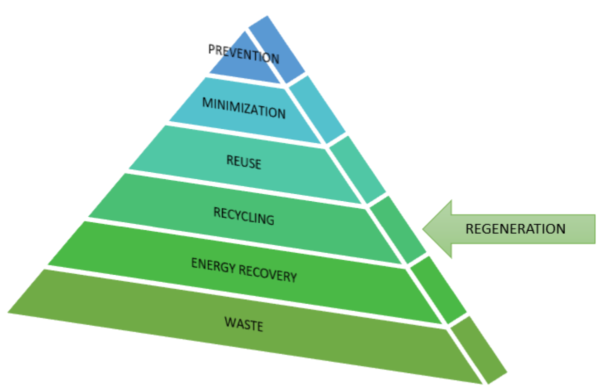


Figure 4. Waste management hierarchy.

Since, the order of actions or hierarchy for waste management (see Figure 4) associates terms with reuse and recycling with the deterioration of material properties which in turn leads to the decrease in economic value, after each cycle. Therefore, it has been necessary to include terms such as regeneration and reuse as an important part of recycling, since these concepts consider that the transformation of the material gives the waste material an added value and in turn manages to restore its functional properties (44).

In this sense, another of the classifications of recycling methods such as chemical or tertiary recycling, a method that is based on the recovery of chemical products from plastics using chemical processes such as glycolysis and pyrolysis to decompose the polymer into value-added products that are used as raw material for the production of fuels and new polymers, it takes on great importance (47).

However, this waste management method consumes a lot of energy in the process and results in complex mixtures that need to be further processed (47). So today has gained strength the "Upcycling" a method of plastic refinery based on chemical recycling and revaluation of waste materials, has the potential to produce products with better characteristics than the original by using catalytic techniques with less energy requirements and using recycled materials, using depolymerization processes of the most common plastics. Hydrogenolysis, photoreforming, and microwaves (46), this new emerging approach is exploited by industry as a fine chemical and value-added functional material with properties equal to structural characteristics as the original material (26, 47, 48).

Another process for waste management is incineration or quaternary recycling and is based on the recovery of energy from plastic waste where toxic gases are released into the atmosphere such as dioxins, furans and greenhouse gases, as well as ashes with microplastics, compounds that reach the soil and water further aggravating pollution problems, in addition to presenting extra costs for remediation and collection of hazardous wastes (47, 49).

Among these recycling methods, chemical recycling is gaining increasing attention from researchers as it uses techniques based on structural characteristics and molecular forces, in which plastics are broken down into original monomers or larger units that can be polymerized, as well as fragments that can be used in industry (49, 50).

As mentioned above, this review explores scientific progress in new chemical recycling techniques used as upcycling and the production of new polymeric materials in search of a sustainable circular economy.

2. CHEMICAL UPCYCLING RECYCLING

The development in different recycling technologies is responding to the growing availability of plastic products, at the end of their useful life and the growing increase in the demand for these products (51, 52), added to the fact that the environmental legislations of many countries are becoming increasingly strict, managing to restrict a series of materials that are disposed of in landfills (53). In this way, the chemical recycling of plastic waste represents a greener alternative to landfilling and incineration (54), and offers a solution to the environmental consequences of the increase in plastic waste (55). The effectiveness of one or another chemical approach to processing originates, among others, from the chemical nature of the plastic. Solvolysis, hydrogenolysis, photoreforming and microwaves are the techniques that Upcycling recognizes for the treatment of plastic waste, techniques that seek to convert plastic waste into "high three" products (high value, high quality, and high performance) (56).

2.1 SOLVOLYSIS (SOL)

The one also known as chemolysis is one of the most studied methods for the depolymerization of polymers in compounds with functional groups with carbonyl, where the plastic chains are depolymerized by solvent molecules (also serve as a reagent) that are presented in excessive quantities through nucleophilic substitutions (47, 57) this process involves the breaking of intramolecular bonds (58), where compounds possessing saturated carbon atoms attached to functional groups with heteroatoms are more sensitive (59). There are reports that only a couple of dozen are mentioned in which polymeric composites are recycled from carbon fiber, and although most of these technologies are based on conventional pyrolysis, the study and development of solvolysis seems to be an alternative (53), because it presents a series of advantages including a lower cost of energy that translates into a lower economic cost and at the same time, generates fewer greenhouse gas emissions (47, 57, 60).

This method is directly related and depends mainly on the type of solvent used, the most common being ethylene glycol (glycolysis), water (hydrolysis), methanol (methanolysis), amines (aminolysis), and ammonia (ammoniolysis) (44).

Thus being the most studied processes for the depolymerization of plastic waste where the synthetic products are chemical compounds of added value, being able to be used for the synthesis of new products of the same or different characteristics than the original such as textiles, plasticizers, adhesives, binders, corrosion inhibitors, all this depending on the solvent used in the process (56), a clear example of this type of recycling is applied to PET waste (see Figure 5).

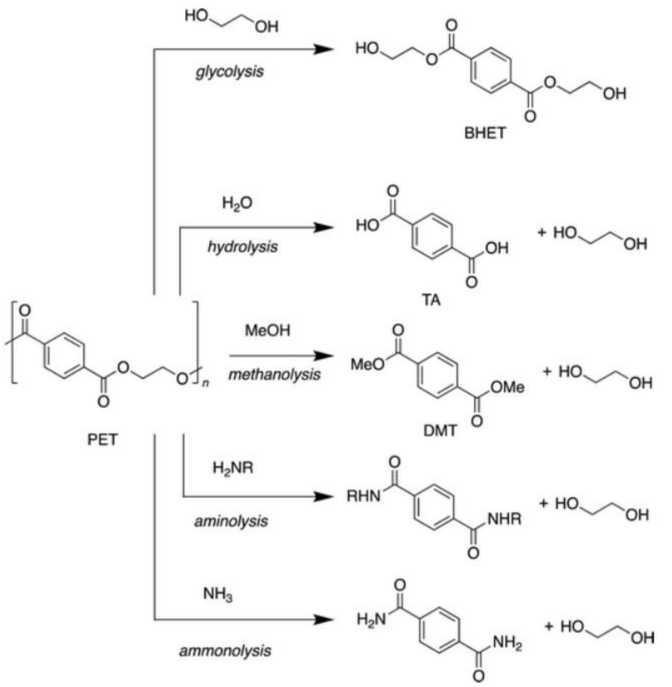


Figure 5. Value-added compounds obtained from PET plastic waste by upcycling by solvolysis (44).

This recycling method can also be used in combination with other methods such as low temperature pyrolysis, Wei, et al. made this combination for the recycling of carbon fiber reinforced polymer waste using low temperature pyrolysis with a solvolysis pretreatment to ensure the highest material utilization and energy efficiency of the process, where it was also shown that the solvolysis process increased the retention of the mechanical properties of the fibers to 90.53% by reducing heat consumption during recycling by 10.21% higher than the percentage of retention obtained in conventional pyrolysis processes, with this we can show that the combination of upcycling with other techniques can offer several advantages (61).

There are methods of solvolysis by supercritical and subcritical fluids such as water or alcohols for the recovery or recycling of waste compounds since this type of fluid has intermediate properties between gas and liquid, as well as good solubility allowing the decomposition of the polymer and its partial oxidation (62).

2.2 HYDROGENOLYSIS (HL)

Hydrogenation or hydrogenolysis is economical, sustainable and eco-friendly for the different transformations of organic compounds since it is a method that does not generate waste because hydrogen can be generated from renewable sources (63, 64). It corresponds to a specific form of depolymerisation and refers to the disruption of chemical bonds, particularly C-C bonds by application of hydrogen (65).

The catalytic hydroconversion of the different plastic wastes is allowing the valuation of these, adding an added value (66). This is generated by a chemical decomposition that is capable of reverting large chains to monomers, oligomers or other products that can be useful in different commercial areas. So far, a number of methods have been investigated that allow the conversion of large polymers to monomers. In this way we find conventional chemical recycling by hydrolysis or trans-esterification of PET (49), hydrogenolysis of PET on C/MoO_2 and catalysts such as ruthenium in the presence of different solvents (67, 68), hydrogenolysis of aromatic compounds on ruthenium / niobium catalysts (Ru / Nb_20_5) (69) allowing to obtain high conversion yields to p-xylene, being used as a probe reaction for the investigation of the cleavage of the C – O bonds.

Another method is the hydrogenolysis of PET using ruthenium catalysts with dimethyl sulfoxide (DMSO) as solvent (64).

In the case of polyolefins, hydrogenolysis is used by rhodium (Rh) catalysts, this due to the vacuum d orbital (70) provides good catalytic activity, stability and useful life (71, 72). However, this method is not only used in petroleum derivatives but also in artificial polymers such as polylactic acid, a polymer obtained by fermentation from lactic acid (73). This material becomes solid waste due to its slow degradation in natural environments and studies are registered where they develop the solvent-free catalytic hydrogenolysis of PLA powder obtaining conversion percentages of 99 and 100% (74) and being able to obtain biofuels with the aim of achieving zero waste.

In this way, hydrogenolysis processes allow the recycling of polymers, giving them an added value of great importance due to the formation of biofuels. The high performance values make it a viable technique in terms of developing this green technology.

2.3 PHOTOREFORMING (FR)

Due to the large amount of plastic that exists, and that these are produced from fossil fuels, if all the plastic produced in a year is recycled, it is estimated that around 3500 million barrels of oil could have been saved, equivalent to more than 176 billion dollars only for the year 2017 (75), considering that after the COVID-19 pandemic these values increased greatly.

At the same time, the implementation of polymer recycling has as a problem the size of the materials since those that are small (microplastics) are difficult to collect and reuse, ending up in drinking water (76), sediments (77), oceans (78) and practically throughout the ecosystem (79). Due to this problem is that the forms of management of plastic waste have been unable to adequately process the wide variety of waste. However, the photoreform system has been presented as an alternative to deal with this problem.

It consists of a simple, low-energy method based on the conversion of plastic waste into H_2 and other by-products such as acetic acid, using in principle sunlight, photocatalyst and water (80).

Photoreforming of plastic waste under mild conditions (room temperature) (55) results in low selectivity and low performance. However, photoreform processes have been achieved for materials such as polylactic acid (PLA), polyethylene terephethalate (PET) and polyurethanes, at room temperature and on an economical CdS/CdOx catalyst in alkaline solution (81), although this is toxic (80). This technique has been given only at small scales because it complicates performance (82).

In general, this method uses (in addition to what has already been mentioned) an organic substrate that acts as an electron donor and is oxidized by the photocatalyst. The photogenerated electrons are transferred from the photocatalyst to a cocatalyst and reduce the water to H_2 which corresponds to a valuable product used in the chemical (83), pharmaceutical (84), agricultural (85), and renewable energy areas (86).

Du et al., (87) establish the implementation of photoreforming of PLA, PET and PE under ambient conditions using a CdS photocatalyst (MoS_2/CdS) with MoS_2 tip, this process allows integration of light (CdS) and electron collector (MoS_2), allowing a migration of fast charge.

While Gong et al., (88) developed a hybrid of carbon nanotube nitride with carbon nitride and NiMo through a NiMo-assisted catalysis pathway, thus having an efficient and stable photocalizer (89) because NiMo nanoparticles have a high durability (90-92). They explain that due to π-π interactions between nanotubes and carbon nitride they promote electron transfer, increasing carrier lifetime and enhancing photocatalytic activity.

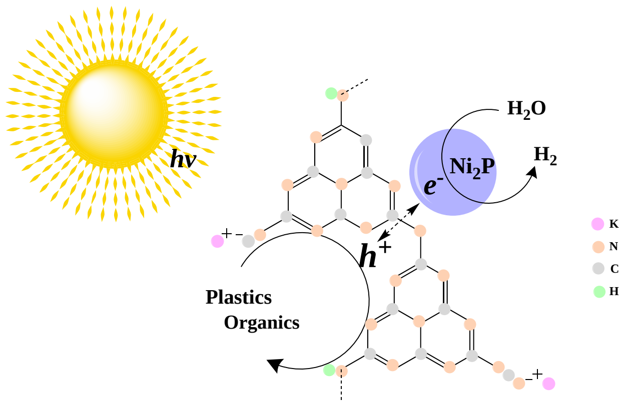


Figure 6. Diagram of polymer photoreforming using CNx| Ni_2P. Image adapted from Uekert et al., (82) and redesigned with ChemDraw 16.0.

Studies suggest the use of noble metal-free and Cd-free catalysts for the disposal of plastic waste and the synthesis of renewable fuels from PET and PLA using carbon nitride catalyst with a nickel cocatalytic, CNx| Ni_2P (see Figure 6) (82). The advantage of this catalyst is that it is a non-toxic and economical photocatalyst (93).

2.4 MICROWAVES (MW)

Conventional pyrolysis recycling processes are designed to produce hydrogen-rich gases, in addition to carrying out the process must have a significant energy input so they emit large volumes of CO_2, as well as produce low value-added compounds such as oil and synthetic gases. Therefore, upcycling to convert single-use plastic waste into higher value-added chemicals with high energy efficiency is a better alternative (94). In this sense, microwave heating has different advantages over conventional pyrolysis, such as non-contact, selective, fast and high-efficiency heating (95).

Initially, microwaves were only used for communication purposes (96), however in 1946 it was demonstrated that surfaces could be heated by using microwaves (97-99), and the curing of elastomers began between 1970 and 1980 (100). Today, the microwave technique is still used, but this time, in a more developed way (101).

Radiation, microwave energy is delivered directly to the absorbing component through molecular interactions in the presence of electromagnetic fields (102) orthogonal to each other (95), within a wavelength range of 1 to 300 mm and frequencies of 300 MHz – 300 GHz, while in terms of energy, they are weaker than other forms of electromagnetic waves (103, 104) and heat is generated instantaneously. The heat required to initiate catalytic depolymerization of plastic polymers, plus the selectivity of microwave irradiation, as MW interact almost exclusively with absorbent catalyst particles while the plastic substrate remains cold (49).

In recent years, microwave pyrolysis has gained increasing attention and has been considered a promising technology for solid waste valorization due to its advantages over conventional pyrolysis, reporting that heavy hydrocarbons are easier to break into light fractions under microwave irradiation (105). This process is based on heating polymeric materials without the use of air to break down macromolecular structures into smaller units (106).

There are a number of advantages and disadvantages to the industrial applications of using microwaves for polymer recycling (see Table 2). However, despite the disadvantages, it has been successfully applied for the pyrolysis of PVC and ABS, where the presence of carbon as an absorber allows complete depolymerization (107).

Table 2. Advantages and disadvantages of using microwaves for polymer degradation.

Advantages	Desventajas
Reduction of time and energy used	Accelerated thermal runaway
Precise temperature control	Low heating in low-absorption materials
Selective heating	Warm up self-limiting
Rapid heating of thermal insulators	Inefficient microwave energy transfer
Uniform heating	
Short processing times	
Reduction of emmisions	
Synthesis of new materials	

3. RECYCLING OF THE MOST USED POLYMERS TODAY

3.1 POLY(ETHYLENE) (PE)

PE is included in the most widely used plastics category, with a production capacity of 80 million tons per year. It is typically formed by polymerization by addition of ethylene molecules in the presence of initiators and catalysts. PEs are manufactured under different conditions to produce various grades depending on the branching and density of the chain. The most commonly used PEs are high-density PE (HD) which has an almost linear structure and higher crystallinity, and low-density PE (LD) which has higher chain branching and lower crystallinity. Several other varieties of PE are also in use, for example, linear LDPE (LLDPE), medium density PE (MD) and other copolymers with vinyl alcohol, vinyl acetate and others. Usually, the higher the crystallinity, the higher the density, as the nearby packing structure and branching mostly reduce crystallinity, resulting in lower density. According to the American Society for Testing and Materials (ASTM), PEs with a density greater than 0.941 g cm^{-3} are called HDPE, densities between 0.926–0.940 g cm^{-3} are called MDPE, 0.919 to 0.925 g cm^{-3} are called LLDPE, and range from 0.910–0.925 g cm^{-3} are called LDPE. Due to the low crystallinity and high amorphous content, LDPE polymers are capable of producing very clear films that make them suitable for food packaging applications. Other uses of LDPE include containers, toys, and bags. HDPE, on the other hand, produces dense plastic with less clarity due to high crystallinity and is therefore used as packaging bottles for shampoo and detergents, gas pipes, water pipes, fuel tanks, and industrial wrapping films. HDPE pipes are a comparatively safer option than PVC and pose no direct threats to the environment (such as the high chlorine content in PVC), except for the degradability problem (44).

3.2 POLY(PROPYLENE) (PP)

Chemically it is a derivative of the olefinic monomer propylene, generated through the process of polymerization by addition, where heat, high-energy radiation and a reaction initiator are added to obtain the polymer (108).

This polymer is found in three stereospecific configurations: isotactic, where methyl groups are on one side of the chain. Sindiotactic, methyl groups are alternated on both sides of the chain. Atactic, the methyl groups are in an irregular/disordered arrangement. Another of its characteristics is its melting point that varies according to this arrangement (108, 109).

Poly(propylene) is one of the most used plastics (110) and versatile due to its high crystallinity-to-weight ratio, which guarantees good properties such as rigidity and good tensile strength, useful in different applications being food packaging the main utility (111), so it can also be easily processed (112), is chemically inert, resists moisture and has good temperature resistance (113).

However, the properties of polypropylene vary according to process conditions, copolymer components, molecular weight and their distribution (114).

It is important to consider that about 90% of the demand for plastics corresponds to poly(propylene), poly(ethylene), poly(vinyl chloride), poly(styrene), and poly(ethylene terephthalate) (115). In 2015 alone, around 55 million tonnes of PP (18) were produced. There are reports of dissolution and precipitation of PP present in face masks used during the COVID-19 pandemic (116), using p-cimene instead of xylene, which is the common solvent for this process (117).

Other studies refer to the formation of fluorescent carbon dots (118), these carbon spots are zero-dimensional materials with unique physical and chemical properties as they have good biocompatibility, low toxicity and have easy-to-functionalize surfaces (119). These carbon points are useful for biological imaging (120), different types of chemical analysis (121), administration of specific drugs, environmental monitoring (122), for the diagnosis and therapy of diseases (123) and also for anti-counterfeiting applications (124).

At the same time, to reduce the costs of recycling plastics such as PP, a number of other alternatives have been suggested; An example is the compatibility process, which involves the addition of a substance (compatibilizer), which adapts to an immiscible mixture of plastics or materials in order to increase their compatibility (125) and stability (75). The objective of this procedure is to be able to use PP and mixtures with PP to give it an equal or greater value (125).

Thus, Burak, et al developed compounds from recycled PP using upcycling techniques of microwave to 400W from disposable masks, obtaining products with high impact resistance (126), or in turn Cui et, by obtaining liquid oil using this same technique of recycling waste at 800W, reporting yields of 79.3% by weight with a large presence of cyclans, alkenes, and alkanes (see Figure 7), thus a high quality value-added product, demonstrating that this technique increases the selectivity of small molecular products that can be obtained from PP (127).

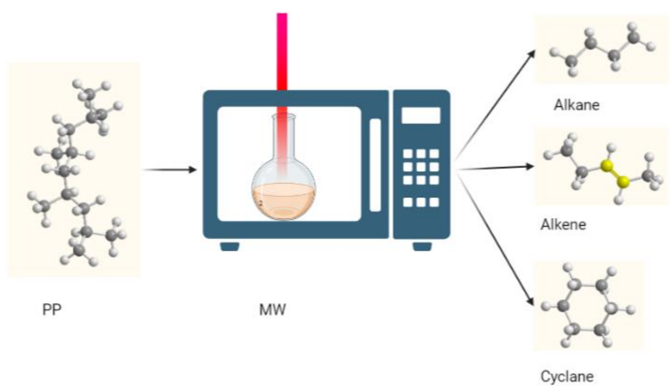


Figure 7. Polypropylene plastic microwave-assisted pyrolysis scheme for liquid oil production, based on Cui et, al. (127), redesigned ChemDraw 16.

Another technique for recycling PP consists of photoreform, which allows the conversion of the material into renewable synthesis gas through the use of solar energy, without gas and in ambient conditions, this through nano sheets of Co – Ga_2O_3. The advantage of this method is that it is not only effective with large plastic materials, but also allows the photo degradation of powders from commercial plastic bags, however it must also be taken into account that this method can also generate other types of microplastics (128).

3.3 POLY(VINYL CHLORIDE) (PVC)

It corresponds to one of the most used plastics in constructions such as pipes, profiles for windows, floor coverings, sheets for roofs, among others (129), however this material generates an important environmental impact since there are more than 45 million tons of PVC that does not degrade in soils or aquatic environments (130), where finally at the end of its useful life a large amount of scrap is produced.

The complexity of contamination and recycling of this type of material is that it is often found mixed with other plastics such as poly(ethylene) (PE), polycarbonate (PC) and/or acrylonitrile-butadiene-styrene (ABS) (131, 132) and are more difficult to separate by common processes due to the physical and chemical similarities they present (132).

The removal of PVC by conventional methods such as incineration produces large amounts of toxic gases and the formation of toxic dioxins and furans that pollute the environment (50, 133). Thus, hydrogenolysis on Ru / Al_2O_3, allows the conversion of plastics containing PVC with a higher efficiency in the use of Cl of more than 80%, due to the Al_2O_3 present for the activation of the C-O bond and the metal Ru for the activation of the C – Cl and H_2 dissociation bond (133-135).

Diethylhexyl phthalate (DEHP) is the most widely used plasticizer (40 – 50%) in PVC due to good molecule compatibility. However, this is a product of great toxicity, so the control of risks to the environment and human health are of interest for study, so techniques have been proposed for its elimination or degradation such as ozonation or microbial degradation, however the application by solvolysis with supercritical fluids in water-alcohol reaction systems has helped to produce new chemical substances due to reactivity of alcohol, with a significant influence on the behavior of DEHP and chlorine in subcritical water treatment (136).

3.4 POLY(ETHYLENE THEREFTALATE (PET)

Poly(ethylene terephthalate) (PET) is a synthetic polymer derived from petroleum is generated from ethylene glycol and terephthalactic acid and is one of the most commonly used polymers recycled worldwide, where its production has increased dramatically in recent years, reaching 30 million tons per year (137), and with a growth rate in the market of 4% (138) being a threat to the ecosystem (139, 140). A number of studies have shown that biological degradation of PET is possible, which differentiates it from other plastics. This is possible due to the ester bond present in the molecule that is broken with some hydrolases such as PETase (141), cutinase (142), lipase (143) and stereoase (144) achieving a rupture of the molecule (145).

Global PET production exceeded 30 million tons in 2017, accounting for about 13% of total global plastic production. PET is one of the most widely used entry-grade thermoplastics, with applications ranging from food packaging to single-use beverage bottles. This polymer can also be depolymerized by chemical oxidation, leading to chain fragmentation and the formation of smaller oxygenated chains that are soluble (146), at the same time, this method allows the depolymerization of polymer mixtures. However, despite seeming an attractive technique, the high cost of catalysts and with it the generation of products, is that there are few studies in which reference is made to chemical oxidation.

Solvolysis, especially glycolysis, is the most common method for PET depolymerization. Depending on the choice of nucleophiles (e.g. ethylene glycol, water, and methanol), the resulting products could be bis (hydroxyethyl) terephthalate (BHET), terephthalic acid (TA) and dimethyl terephthalate (DMT). In addition to oxygen-focused nucleophiles, many nitrogen-containing nucleophiles, such as amines and anilines, are also applicable to solvolysis (46). At the same time, hydrogenolysis processes have been of great help for the recycling of this material, since when applying the technique in the presence of certain catalysts, good results and high conversion yields have been obtained (see Figure 8).

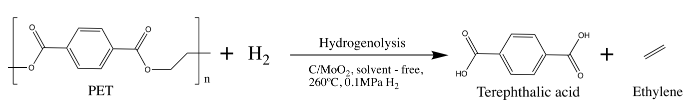


Figure 8. PET hydrogenolysis process.

3.5 POLY(URETANE) (PU)

Plastics from PU represent an important class of polymers whose mechanical, chemical and thermal properties are adapted by the reaction of various polyols and polyisocyanates, used to ensure lightness in cars or aircraft, for their insulation capacity in construction and for their biocompatibility as in food packaging and biomedical devices (147). Most of these plastics are cross-linked and are not considered thermoset due to their physicochemical characteristics, so they can be recycled by different mechanical, chemical or energy methods.

However, chemolysis or solvolysis processes are currently the most used for this type of waste (147, 148).

The solvolysis of PU using water (hydrolysis) as solvent, carried out under temperature conditions greater than 160 °C, with a reaction time of 15 min, a process that favors the formation of polyesters and polyamides compounds of added value that can be used for the manufacture of protection panels, in the same way when using glycols as solvents originates processes of transesterification of carbonate groups. A process that is carried out with lower economic cost and whose by-products can be used for the formation of hard foam (50, 149).

On the other hand, the glycolysis of PU has advantages such as mild reaction conditions, low volatility of solvents and their products, the product can be easily recovered and then mixed with virgin raw materials, in addition new catalysts such as metal hydroxide, alkoxides, acetates and octoates, have been studied to obtain flexible foams (150). For example, solvolysis has been used as an upcycling method to recover β-methyl-δ-valerolactone with excellent purity and performance under mild conditions from PU for use in the production of adhesives (147, 150, 151).

3.6 POLY(STYRENRE) (PS)

Poly(styrene) is one of the most versatile polymers that exists, being used in the manufacture of rigid and foamed materials (152), for insulation and packaging. However, like the other polymer materials exposed, the elimination of PS is generating serious environmental problems due to the long time of natural degradation (153) and its poor management in final disposal issues. In this way, there are different ways in which poly(styrene) can be recycled, such as mechanical, chemical and physical methods (154).

At the same time, expanded polystyrene is used as a substrate for obtaining polyelectrolyte (155), recycled polystyrene is used to manufacture a material with properties similar to wood in terms of density, physical appearance, and structural characteristics, that material corresponds to extruded polystyrene (XPS) and is used for the construction of windows, houses, floors, etc. (155). However, like the other polymer materials exposed, the elimination of PS is generating serious environmental problems due to the long time of natural degradation (153) and its poor management in final disposal issues. Because most recycled polystyrene is converted into products such as garden furniture or pots (156), it has been recommended to explore and exploit new ways of recycling the material generating value-added products (157).

One of the methods used for recycling PS corresponds to recycling by solvolysis, and although there is a large number of solvents that allow its dissolution, such as toluene (158), xylene (159), benzene (160), chloroform, acetone, cyclohexane, butyl acetate, among others (161). However, as these solvents are toxic, other types of solvents more friendly to the environment have begun to be used, such as p-cymene and other substances related to tree leaf oils (162), (R)-Limonene and its structural isomers have a high dissolving power for PS (163).

Other recycling processes involve an anaerobic, organicalytic and photochemical recycling process from polystyrene to benzoic acid, using anthroquinone as a photocatalyst, obtaining yields ranging from 25 to 58% (164). Catalytic hydrogenolysis of polystyrene has also been reported in many papers. This process consists of the cleavage of a C-C or C-X bond (carbon heteroatom) by molecular hydrogen, allowing small molecular hydrocarbons to be obtained. This type of reactions occurr at high temperatures and pressures with limited selectivity, catalysts are generally used obtaining varied results in yield issues, with the use of catalysts such as Rh/C (164), Pd/$CaCO_3$ (165), Ni/Kieselgur, among others (166).

Like hydrogenolysis, microwave pyrolysis processes to recycle polystyrene have been reported in a number of works, being an incipient technique in the treatment of plastic waste to generate biofuels (167). This method allows energy recovery with mixed waste streams of PP and PS, completely decomposing these waste materials and generating bio petroleum consisting of gasoline grade hydrocarbons (168), they can also be copirolized with KOH as a catalyst (169), also the use of $NiFe_2O_4$ allows to generate carbon nanotubes with better structures and higher relative purity than with other catalysts such as Al_2O_3 and Fe_2O_3 (167, 170).

CONCLUSIONS

With upcycling, plastic waste can be transformed into substances with high added value, so it is considered a promising method to achieve the recycling and reuse of plastic waste. Within this type of recycling we can find different techniques such as solvolysis, a technique closely related to the type of solvent to be used for processing, and which can also be combined with conventional treatment techniques improving the characteristics of the products obtained. Hydrogenolysis is an economical, sustainable and eco-friendly technique for the different transformations of organic compounds since it is a method that does not generate waste because hydrogen can be generated from renewable sources. Photoreform a simple, energy-efficient technique based on the conversion of plastic waste into H_2 and other by-products such as acetic acid, using sunlight, photocatalyst and water in principle. Microwave, a non-contact, selective, fast and high-efficiency heating technique, which has displaced conventional treatment techniques such as pyrolysis when obtained with these products with greater added value and energy efficiency. Due to the scarcity of petroleum resources and social awareness for the protection of the environment, the development of these new techniques to achieve recycling and use of resources increasingly attracts the attention of researchers, so these techniques have been applied for the recycling of the different types of polymers considered the most used today, obtaining good results as in issues of performance and revaluation of plastic waste. Taking into account the applicability of recycled plastics, it is possible to work effectively on better waste management in order to generate value-added by-products and mitigate the effects of plastic pollution.

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