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Degradation of Various Plastics in the Environment

By

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4th Stage

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Abstract

Plastics are polymers derived from petrochemicals which are further synthetically made from monomers by some chemical processes to produce these long chain polymers.

It is very important to understand the interaction between plastics and environment in ambient conditions. The plastics degrade because of this interaction and often their surface properties change resulting in the creation of new functional groups. The plastics after this change continue to interact with the environment and biota.

Plastics play an important part in every sector of economy all over the world due to their extensive use in agriculture, building and construction, health and consumer goods. They are the backbone of many industries because they are used in the manufacturing of different products including defense materials, sanitary wares, tiles, plastic bottles, artificial leather and different other household items. Plastics are also used in packaging of food items, pharmaceuticals, detergents, and cosmetics.

Plastic causes pollution and global warming not only because of increase in the problem of waste disposal and land filling but also release CO₂ and dioxins due to burning. They include polyethylene terephthalate (PET), high, low density polyethylene (HDPE, LDPE), polyvinyl chloride (PVC), polypropylene (PP), and polystyrene (PS). The vast majority of plastics produced today, including all of the aforementioned commodity polymers, are made from nonrenewable petrochemicals, so named because they are derived from fossil oil, natural gas, and coal.

Although these plastics are inexpensive, each is a highly engineered material with precise physical properties. In general, the effects of heat, light, air and water are the most significant factors in the degradation of plastic polymers. The major chemical changes are oxidation and chain scission, leading to a reduction in the molecular weight and degree of polymerization of the polymer. Some of the factors that effects on polymer degradation such as chemical composition, molecular weight, hydrophobic character, chemical bonding, effect of stereos and environmental conditions.

Keywords

Plastic, Polymer, Degradation, Polymer degradation, Environmental conditions.

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1. Introduction

1.1 History of Plastic

Plastics have been around for centuries, but the first synthetic polymer created occurred in the 19th century, by Leo Hendrik Baekeland in 1909 who created Bakelite. From this base polymer, many plastics used today have been created. (Wellfair, 2008)

The word plastic comes from the Greek word plastikos, which means 'able to be molded into varied shapes. Plastic is defined as the polymer which become mobile on heating and thus can be cast into moulds. The plastic is made up of carbon, hydrogen, silicon, oxygen, chloride and nitrogen, Plastics are made up of linking of monomers together by chemical bonds. (Kale et al., 2015).



Figure (1): Leo Handrik Beekeland

1.2. Plastic polymer

Plastics are polymers derived from petrochemicals which are further synthetically made from monomers by some chemical processes to produce these long chain polymers. Plastics are light weight, low cost, highly durable and are of high strength. In our daily life the plastics are available in various forms such as nylon, polycarbonate, polyethyleneterephthalate, polyvinylidene chloride, Urea formaldehyde, polyamides,

polyethylene, polypropylene, polystyrene, polytetrafluoro ethylene, polyurethane and polyvinyl chloride. (Raziya fathima et al., 2016).

Plastic is a polymer consists of the elements carbon, hydrogen, silicon, oxygen, chlorine, and nitrogen. Seven major types of synthetic plastic are used around the world. These are polyethylene terephthalate (PET), high density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), and various other plastics that include acrylic, polycarbonates, polylactic acid (PLA), fibers, and nylon..(Ekanayaka et al., 2022).

Synthetic polymers are made by linking together hundreds or thousands of organic subunits (“monomers”) via strong covalent chemical bonds. They can be molded into virtually any desired shape through rotation, injection, extrusion, compression, blowing, or thermoforming. Their material properties are adjusted during and/or after synthesis to achieve the desired strength, permeability, porosity, opacity, and color. (Chamas et al., 2020).

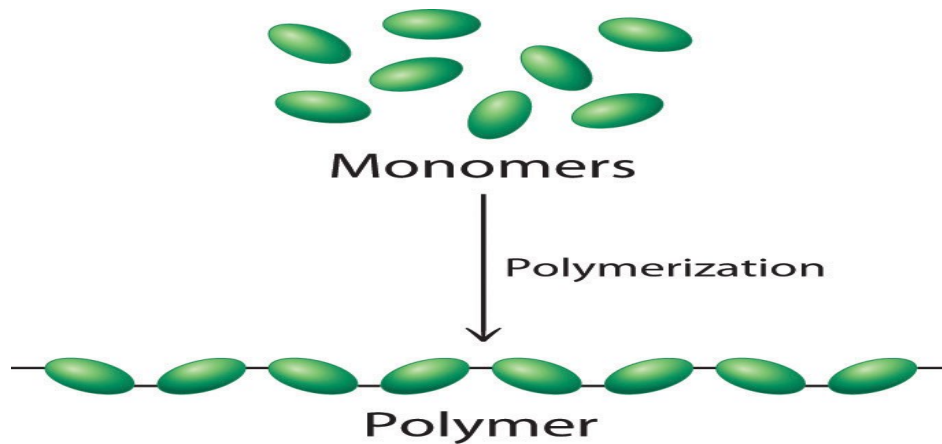


Figure (2): Polymeric solids

Plastics can be differentiated into degradable and non-degradable polymers on the basis of their chemical properties. **1-**These are naturally degradable, as a source of cellulose, starch and algal material, an important component in plants, animals and algae. These polymers are also produced by microorganisms. **2-** Non-degradable plastics, typically known as synthetic plastics, are derived from petrochemicals and are higher in molecular weight due to the repetitions of small monomer units.(Elahi et al., 2021).

1.3. Plastic derivations

Plastic derived from petroleum or fossil fuels is a lightweight, resistant, and used material in crucial sectors such as packaging, agriculture, automotive and electric appliances. However, it needs a long time to degrade (from 20 years of a plastic bag to 500 years of a toothbrush). At the end of its life path, it can be incinerated in a plant, recycled, or placed in landfills, but in some cases, it is dispersed in the environment.

Plastics are one of the most fundamentally used materials worldwide due to their attractive physicochemical properties and characteristics, which include; weathering resistance, levity, and inexpensive transparent material. In addition, it does not require high maintenance. All these valuable properties help in facilitating the implementation of plastics into various activities including agricultural, mercantile, and industrial activities.(Dimassi et al., 2022).

Plastic is a versatile material, It is waterproof, strong, easily shaped and can be made rigid or flexible. Furthermore, it is relatively cheap to manufacture, making it widely available across the world. However, the inherent stability and durability of this material has resulted in widespread accumulation of plastics in both terrestrial and aquatic environments.(Rose et al., 2020).

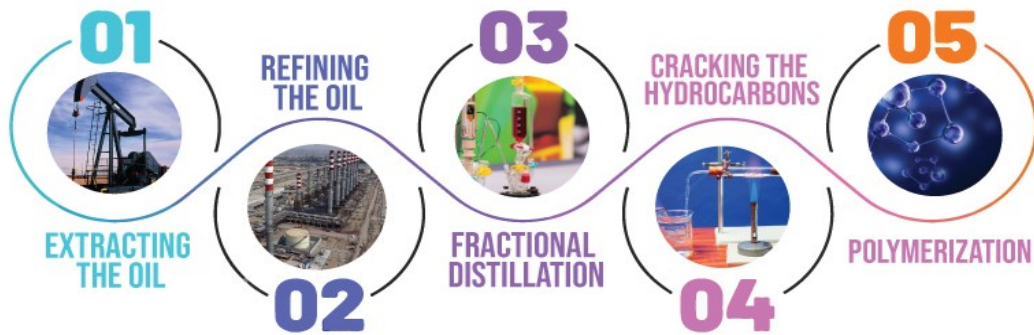


Figure (3): Processing of plastic from crude oil

1.4. Plastic Production

Plastic production and consumption rate increased exponentially due to its non-degradable nature, easy availability and management. China accounted for 32 percent of global plastic materials production in 2021, making it the world's largest plastic producer by far. North America was the second-largest plastics producing region that year, accounting for almost 20 percent of global production, The small two-island nation of St Kitts and Nevis is a popular Caribbean destination that is addressing the problem of single-use plastic to preserve its natural beauty and tourist appeal..

The plastics industry began in the early 1900s when the first synthetic plastic was created in the U.S. Since the industry began, annual global plastic production has exploded from some 1.5 million metric tons in 1950 to 359 million metric tons in 2018 .(Vijayakumar and Sebastian, 2018).

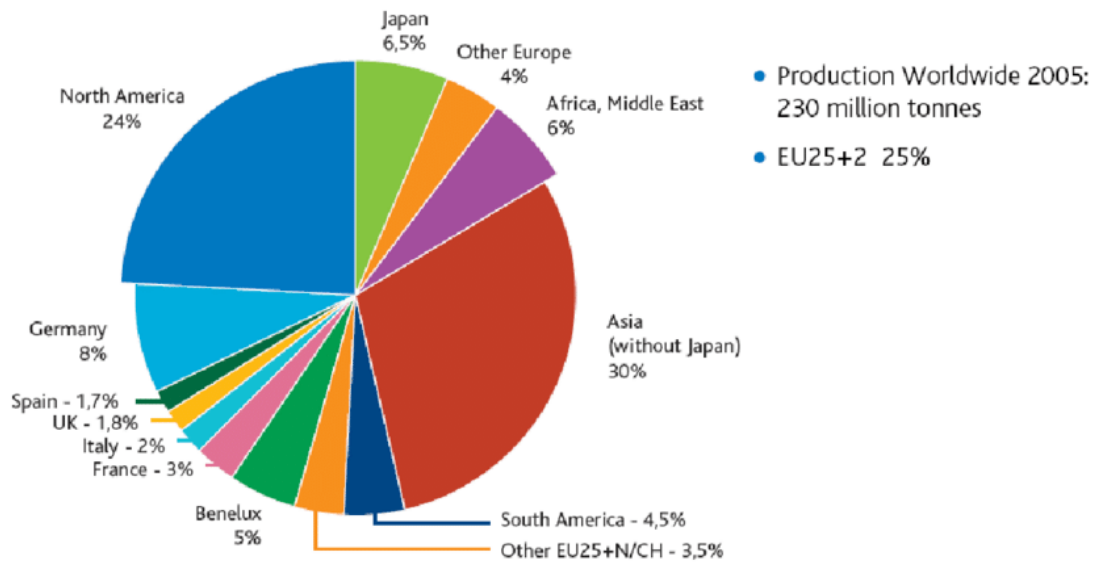


Figure (4): World plastics production per country/region

1.5. Degradation

In science, the degradation of a substance is the process of its breaking down into its separate parts or elements. Plastic degradation is defined as any physical or chemical change in the polymer resulting from light, heat, moisture, chemical action that results in a decrease in the average molecular weight.

The polymer characteristics such as its mobility, tacticity, crystallinity, molecular weight, the type of functional groups and substituents present in its structure, and plasticizers or additives added to the polymer all play an important role in its degradation. The near-UV light quanta (400–290 nm) have energies from 3.1 to 4.3 eV which corresponds to 72–97 kcal/mol. This means that these UV quanta have energy for breaking the most chemical bonds. Under normal conditions, photo and thermal degradation are similar. (Ranby, 1989).

Conventional plastic materials are very resistant to degradation in general. The longevity of plastics is estimated to be hundreds or even thousands of years depending on properties of the plastics as well as the surrounding environmental conditions (PlasticsEurope 2019).

Polymer degradation refers to a process in which the chemical and physical properties of polymers, as well as their appearance, are depleted. Traditional polymer degradation methods have included photo oxidative, thermal, ozone, mechanochemical, catalytic, and chemical methods.(Kulkarni and Dasari, 2018).

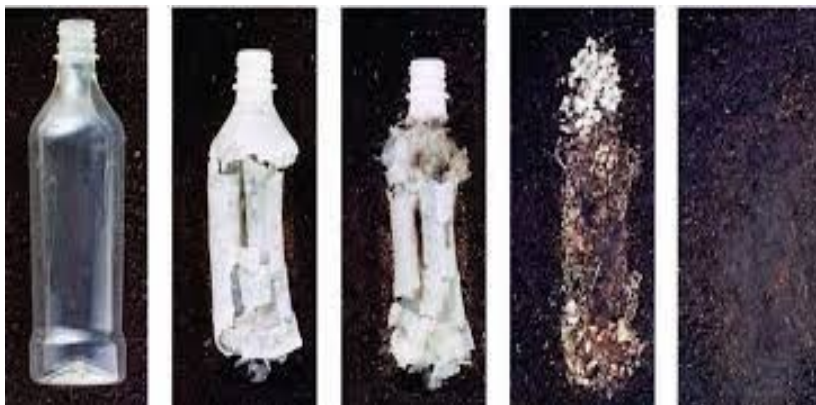


Figure (5): plastic degradation

1.6. Factors affecting polymer degradation

1.6.1. Internal effect

1.6.1.1. Chemical composition

Chemical composition of the polymers plays a very important role in their degradation. Presence of only long carbon chains in the plastics makes these polymers non-susceptible to degradation by microorganisms. By the incorporation of the hetero groups such as oxygen in polymer chain makes polymers labile for thermal degradation. Presence of heteroatom in the polymer chain affects the strength of neighboring C-H bonds of the polymer and promotes carbanion formation in the presence of bases. (Barnes et al., 2009).

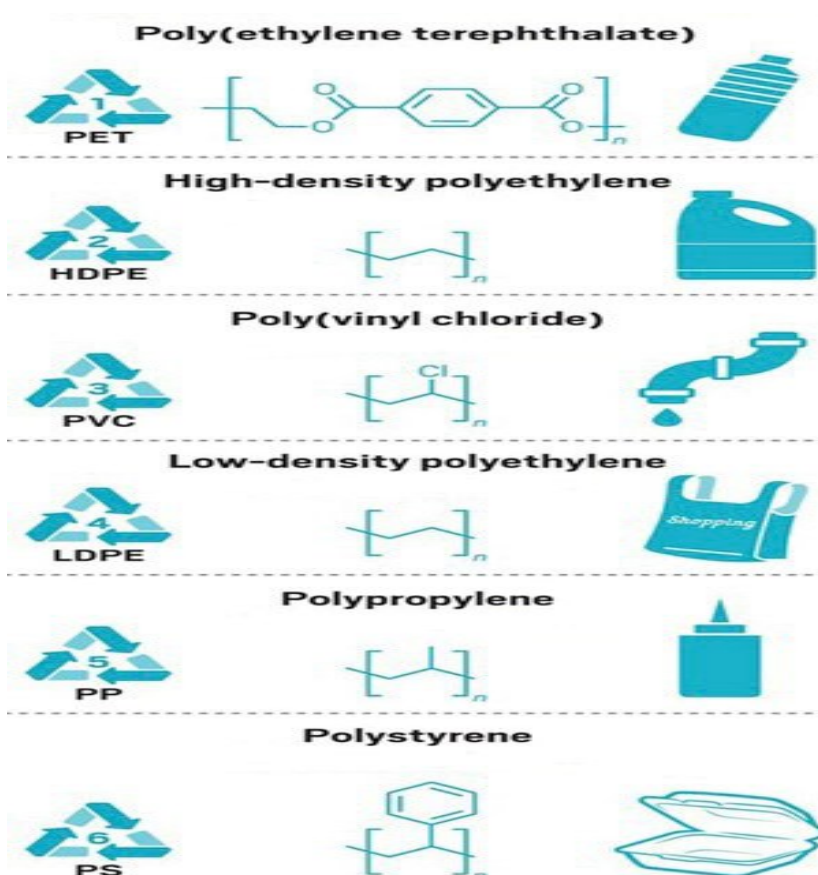


Figure (6): Chemical structures of plastics

1.6.1.2. Molecular weight

Increase in molecular weight of the plastic decreases the rate of plastic degradation. It has been reported that some microorganisms utilize polymers with low molecular weight faster as compared to high molecular weight polymers. Linear polymers with molecular weight lower than 620 support microbial growth. It is easy to form the ozone adduct in low molecular weight olefins which rearranges to ozonide and during this operation, if the polymer chain is under tension during reaction, the broken chain ends separate out before rearrangement to ozonide occurs. (Tokiwa et al., 2009).

1.6.1.3. Chemical bonding

Linkage affects the degree of degradation in plastic. In thermoplastic, head-to-head addition of monomer units and tail-to-tail addition of monomer units during addition polymerization create weak points which make the plastic susceptible for degradation. Branching in polymer chain increases thermal degradation. Crosslinking decreases the rate of photodegradation by locking the polymer structure and preventing lamellar unfolding because these actions prevent the separation of photo-produced radicals and favor the radical-radical combination. Under sunlight irradiation condition, polymers, which mainly consist of C-H and C-C bonds such as PP and PE, have an extremely slow rate of degradation. However, the addition of other chemical bonds can cause a different initiation reaction which in turn can speed up the degradation of the polymer (Wang et al., 2019).

1.6.2. External effect

1.6.2.1. Hydrophobic character

The vast majority of plastic waste is made of hydrophobic polymers such as polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC), which means that they have a natural tendency to separate from water molecules and thus not water-wet. Hydrophobic surfaces have the property of repelling water, they do not easily become wetted in contact with water. The phenomenon is due to unbalanced molecular forces at the water/solids interface causing surface tension. (Law et al., 2010).

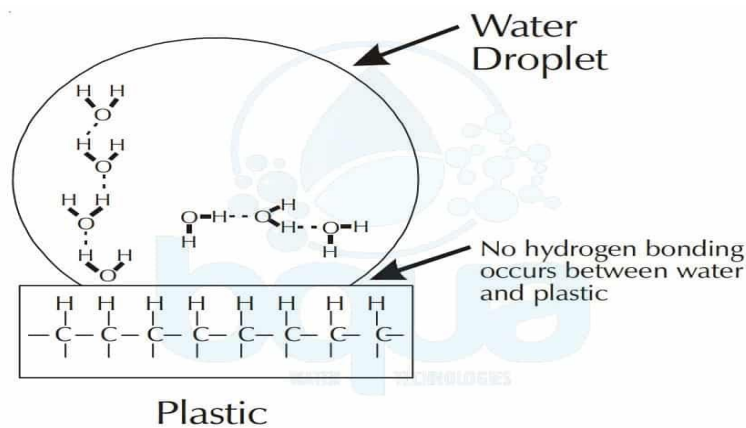


Figure (7): Surface tension

1.6.2.2. Effect of stress

Stress has significant effect on polymer degradation. Tensile stress increases the rate of degradation whereas compressive stress retards the degradation rate. Stress changes the quantum yields of the reactions that lead to bond photolysis, the efficiency of radical recombination following homolysis, and changes the rate of the radical trapping reaction. The polymer morphology is one of the key factors to interpret the effect of stress on degradation rates. Higher stress causes significant morphological changes, including the straightening of the polymer chains in the amorphous regions. When stretched bonds are cleaved by light, the probability of radical recombination decreases as compared to non-stressed polymer because entropic relaxation of the chain drives the radicals apart and prevents their efficient recombination because of their increased separation. (Barnes et al., 2009).

1.6.2.3. Environmental conditions

Degradation of polymer depends upon environmental conditions such as moisture, temperature, oxygen, and suitable population of microorganisms. In warm climates when the relative humidity exceeds above 70%, the rate of polymer degradation by the microorganisms increases. High temperature and high humidity enhance hydrolytic degradation of the polymers. Temperature of the material and the presence of moisture show a considerable synergistic effect on the photodegradation of the polymeric materials. Moisture promotes the light-induced degradation due to the fact that under high humidity soluble photo-stabilizers might leach out of the plastic matrix, reducing the effectiveness of the light stabilizer and leading to degradation. The presence of high humidity, particularly at the higher temperatures tends to increase the photo-damage in polymers such as thermoplastic polyester elastomers.(Ghosh et al., 2013).

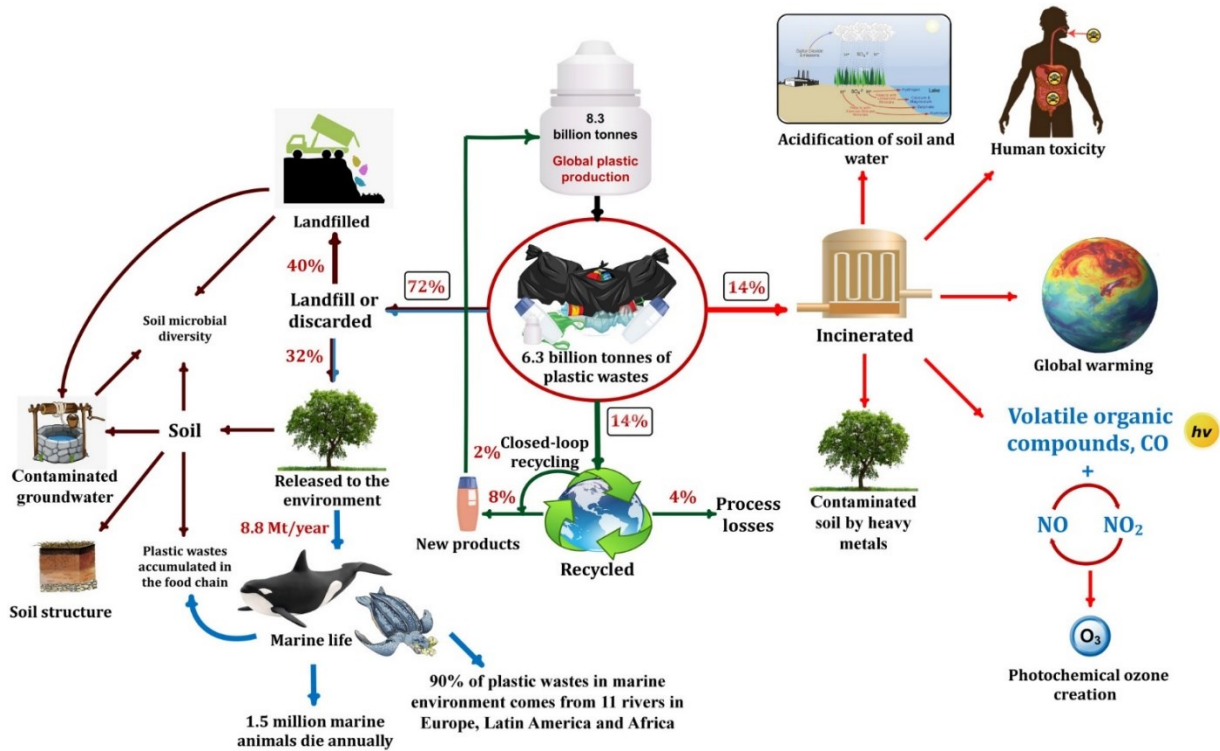


Figure (8): Degradation of conventional plastic wastes in the environment

1.7. Degradation time

Many single-use items are made of plastic. While some plastics are reusable or recyclable, packaging and thicker plastic items are not. Plastic can take anywhere from 20 to 500 years to decompose, depending on the material's structure and environmental factors such as sunlight exposure. Plastic bags are usually made out of one of two materials: high-density polyethylene (HDPE), low-density polyethylene (LDPE). The strongest is HDPE used to make sturdy supermarket bags and wrapping that can easily tear. It takes around 20 years for a standard supermarket plastic bag to fully degrade. (Urbanek et al., 2018).

Traditional plastic bottles are made out of polyethylene terephthalate (PET). It's a lightweight and flexible material that doesn't degrade easily, mainly because bacteria cannot consume and break down the chemicals used in PET. A plastic bottle made from PET takes around 450 years to degrade. Plastic erodes into smaller, often undetectable nanoplastics, which can make their way into our ecosystem. (Ghosh et al., 2013).



Figure (9): The lifecycle of plastics

1.8. Types of degradation

1.8.1. Photo oxidative degradation

Photo-oxidative degradation involves both oxygen and ultraviolet radiation which results in the breaking of chemical bonds and polymer chains, produces radicals, and reduces the molecular weight. The primary source of polymers damage is light. This process is started by light absorption and examples of this degradation process are photo degradation and photo-oxidation.

The lifetime of polymeric material, used for various applications, is determined by UV radiations ranging from 290 to 400 nm and sunlight is the source of such radiations.

Photo oxidative produces ester, aldehyde, propyl and format groups at the soft segments of polymers where degradation occurs. The C–C bonds are easily cleaved by UV radiations.

Photo oxidative degradation of polymers, which include processes such as chain scission, crosslinking and secondary oxidative reactions, and takes place via radical processes, similar to thermal oxidation reactions. (Ranby, 1989)

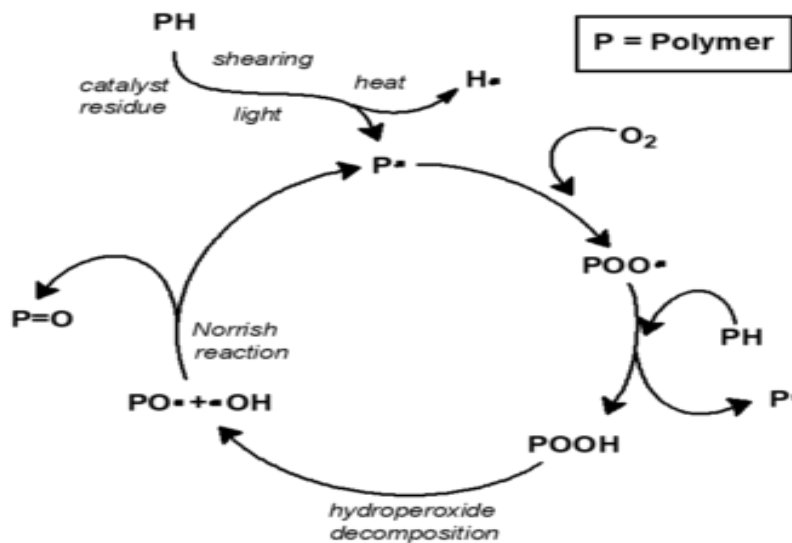


Figure (10): Photo-oxidation of polymers

1.8.2. Thermal degradation

Thermal and photochemical degradation are considered as similar processes and both are classified as oxidative processes or oxidative degradation. In thermal degradation, reactions occur on the whole part of the polymer while in photochemical degradation reactions occur only on the polymer surface.

Thermal degradation takes place by accidental or depolymerization reaction. For its initiation, temperature and UV light are required.

Due to imperfections the bonds (peroxide /ether link) present in the chain become weak and depolymerization usually starts at such weak bonds. At high temperature, a large amount of polymers is depolymerized e.g. PE is decomposed at high temperature and produces small monomers. Polymethylmethacrylate (PMMA) can also be converted quantitatively back to monomers (Tyler, 2004).

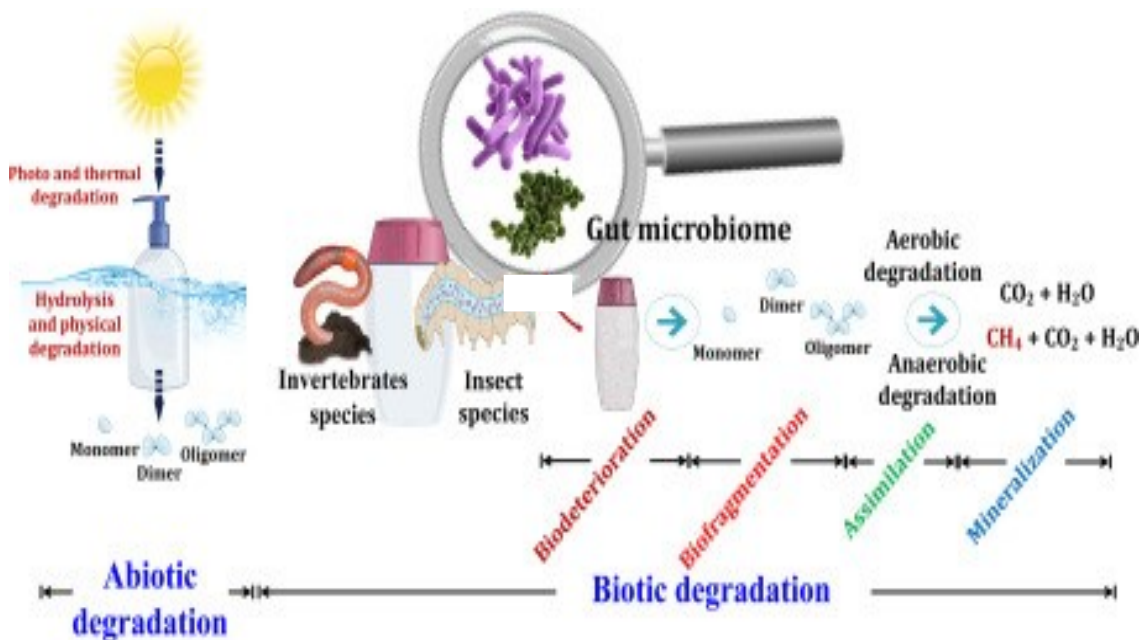


Figure (11): Photo and thermal degradation of plastics

1.8.3. Ozone degradation

Ozone normally present in the atmosphere causes polymeric degradation. Polymers are lasting for a longer time when oxidative processes are not active.

Ozone in the atmosphere is present in very small amount but has a markedly great effect on polymers. Ozone degrades polymeric materials by the formation of reactive oxygen species (ROS).

These ROS are formed by the reduction in molecular weight, by change in electrical and mechanical properties of polymers. When polymers are exposed to ozone then it results different types of carbonyl and unsaturated carbonyl products are formed. These products are based on ketones, lactones, esters and aromatic carbonyl. These all are further associated with another phase known as styrene phase.

Chains in polymer that contain C–C bonds and others saturated hydrocarbon links, aromatic ring ozone reactions occur. During these reactions, intermediates (bipolar ions/peroxy radicals) are formed that are unstable and cause the degradation of large molecules or polymers. (Teare et al., 2000).

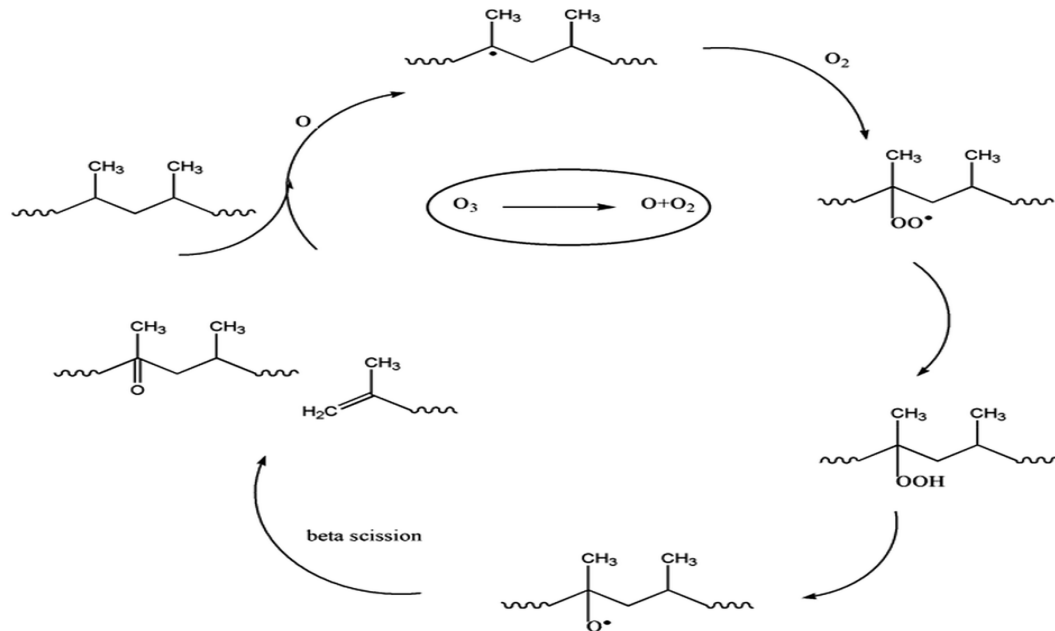


Figure (12): Ozone degradation on the structure polypropylene.

1.8.4. Mechanochemical degradation

It involves polymer chains breakdown under the mechanical stress and ultrasonic irradiations.

Due to chain-side radical reaction, branches in long chains are increased in numbers. The width of weight distribution function of molecules is decreased (correlation between crosslinks and ruptures), double bond concentration is also changed.

In air, the molecular weight of polyvinyl chloride is reduced by mechanochemical dichlorination with different oxide powders e.g., SiO₂, CaO, Al₂O₃ and Fe₂O₃ (Gol'Dberg and Zaikov, 1987; Li et al., 2005).

1.8.5. Catalytic degradation

Catalytic waste polymers transformation into hydrocarbons is a field of great interest. Catalytically degraded polyolefins produce oils and gases. By using this degradation method, not only quality of obtained products (obtained after pyrolysis of plastics) has been improved but it also provides an opportunity to achieve the desired products. Different types of catalysts used for polymers degradation have been reported e.g. Pt-Mo, Pt-Co maintained by SiO₂.

transition metal catalysts (chromium, nickel, molybdenum, cobalt and ferrous) with provision of Al₂O₃ and SiO₂.

Zeolite catalysts and non-zeolite catalysts. The degradation mechanism for polypropylene (PP) is a free radical mechanism, in which Fe/activated carbon used as a catalyst. In catalytic degradation, when polymers are heated above 380 C, their depolymerization takes place, and they are degraded by free radical chain reactions (Gimouhopoulos et al., 2000).



Figure (13): Upcycling and catalytic degradation of plastic wastes.

1.9. Types of Plastics

Plastics are the most abundant products in the world and therefore also represent the largest volume of materials found in the sea. Their resistance to degradation makes them dangerous for the marine environment. The degradation of plastics found in the sea was observed for 6.5 months as they were exposed to UV irradiation in a marine environment. Data on changes in the physical and chemical properties of each of them were collected in order to evaluate the possibilities of material (mechanical) recycling.(Iñiguez et al., 2018).








RIC number	Plastic name	Abbreviated name	Product use
	polyethylene terephthalate	PET or PETE	water, soft drink and juice bottles, carpet, polar fleece
	high-density polyethylene	HDPE	milk jugs, bottles, shopping bags
	polyvinyl chloride	PVC	wrapping and packaging, pipes
	low-density polyethylene	LDPE	plastic bags, squeezable bottles
	polypropylene	PP	refrigerated food containers, dishware
	polystyrene	PS	disposable plates, cutlery, protective packaging
	other	O	acrylic, nylon, composite plastics

Figure (14): Types of plastics

1.9.1. Polyolefins

Polyolefins have received significant attention recently because of their combination of flexibility, toughness, excellent barrier properties, easy manufacturing, and good chemical resistance; this has made them excellent materials for various packaging applications, especially in food packaging. However, the polyolefins do not easily degrade in the natural environment.

The degradation of polyolefins is due to a variety of impurities. These impurities could be carbonyls and hydroperoxide groups which are formed during the fabrication or processing of the polyolefin products.(Ammala et al., 2011).

It degrades to produce two radicals, each of which can participate in a chain reaction process. The presence of carbonyl groups in a degraded polymer indicates that oxidation has taken place and also, means that the material is vulnerable to further degradation since these groups are photolabile. (Elahi et al., 2021).

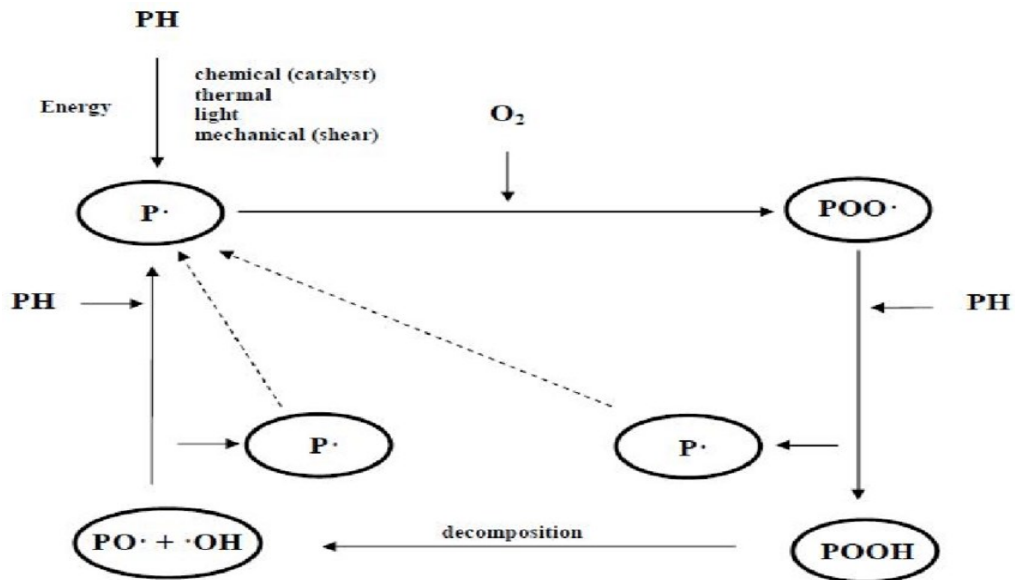


Figure (15): General representation of polyolefin degradation, and PH is a polyolefin and P· an alkyl macro radical.

1.9.2. Polypropylene

PP is a thermoplastic material used in a wide variety of applications including packaging, labeling, textiles, etc. Due to high processability and low cost, PP is one of the most extensively produced polymers, especially, for auto industry. Pristine PP is resistant to photo-oxidation and thermal oxidation at moderate temperatures. However, PP is sensitive to various external aging environments (such as heat, light, and radiation), and, hence, has a relatively low service temperature. When PP is exposed to high temperatures or to an irradiation environment, the tertiary hydrogen atoms present in PP chains are susceptible to be attacked by oxygen.

It is well known that PP oxidation depends on both light and temperature in outdoor aging conditions. PP can also be photo-degraded because several molecular chains are affected in the wavelength range from 310 to 350 nm (Zhao and Li, 2006).

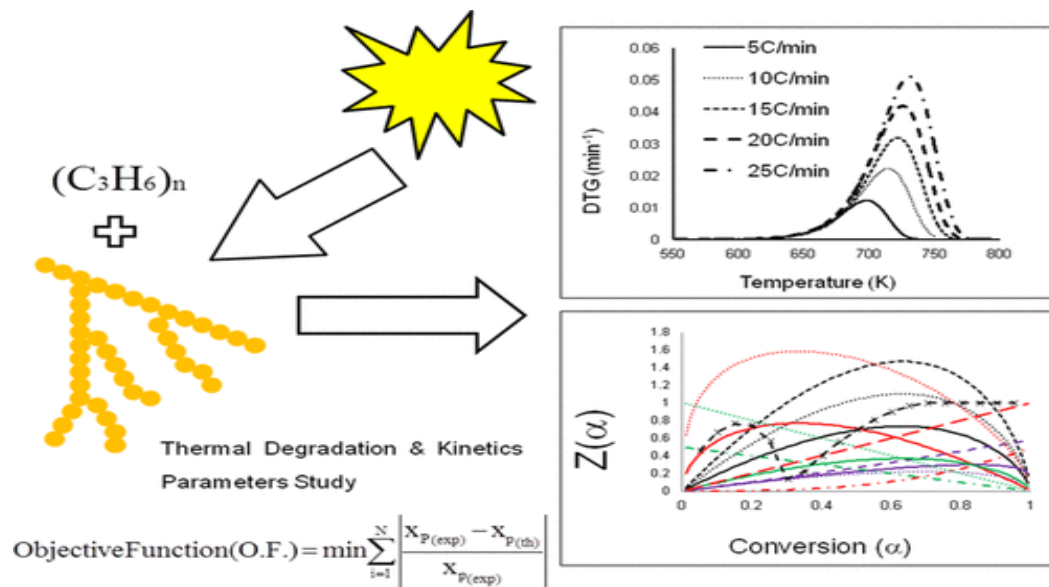


Figure (16): Thermal Degradation Kinetics of Virgin Polypropylene (PP) and PP with Starch Blends Exposed to Natural Weathering.

1.9.3. Polyethylene Terephthalate

Polyethylene terephthalate (PET) is the third most widely diffused polymer exploited in the packaging industry, monopolizing the bottles market for beverages, and covering almost the 16% of the European plastic consumption in the packaging industry. (RobertoNisticò, 2020).

PET when exposed to UV light degrades rather rapidly leading to deterioration in physical and mechanical properties and develops intense yellow color. Traditional plastic bottles are made out of polyethylene terephthalate (PET). It's a lightweight and flexible material that doesn't degrade easily, mainly because bacteria cannot consume and break down the chemicals used in PET. A plastic bottle made from PET takes around 450 years to degrade.

They polymerize and the polymers thermally degrade to give yellow or brown polyenes that discolor the final polymer. The formation of highly conjugated species is catalyzed by carboxyl groups. The formation of colored species is followed by increase of more carboxyl terminated species. Hence, the product having higher carboxyl value is subject to more discoloration. Furthermore, as the carboxyl content increases, the thermo-oxidative stability decreases. The carboxyl end groups act as catalysts for further degradation.

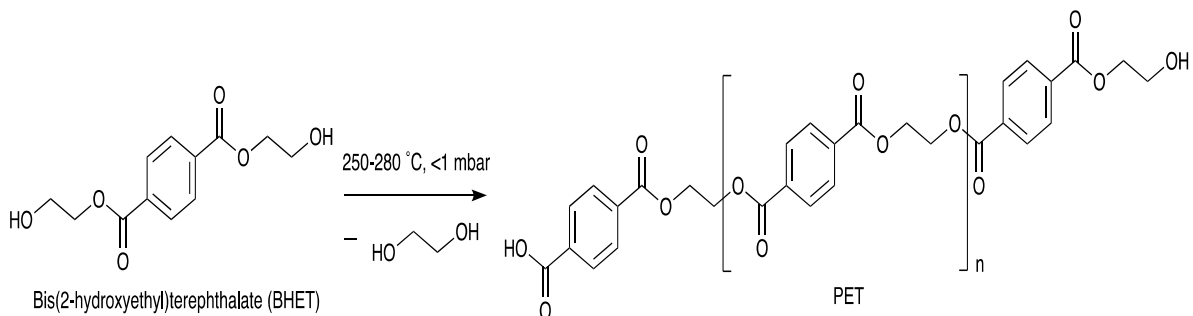


Figure (17): Formation and Molecular structure of PET

The degradation rate increases significantly with temperature, especially above the T_g of PET, as well as with increased relative humidity levels. Wet soil conditions or the presence of iron compounds also increased the degradation rate of the PET, but distinctive results were only seen at temperatures above the T_g . It has been suggested that during hydrolysis, water first diffuses into the amorphous polymer regions and causes cleavage of the ester bonds. The hydrolysis rate will therefore be highly dependent on the degree of crystallinity of the PET material, as well as on the temperature and humidity. (S. Venkatachalam, 2012).

1.9.4. Polyesters

Aromatic polyesters such as PET constitute an important class of polymers with wide spread applications such as fibers, films, and beverage containers. PET is considered to be one of the friendliest synthetic polymers used for food packaging. However, the presence of PET residues in the waste stream is substantial because of its extremely high resistance to atmospheric and biological agents.

The degradation of polyester can lead to several changes in the articles made out of the polymer. These changes include discoloration, chain scissions resulting in reduced molecular weight, formation of acetaldehyde and cross-links or gel formation and fish-eye formation in films. (Li J, 2008)

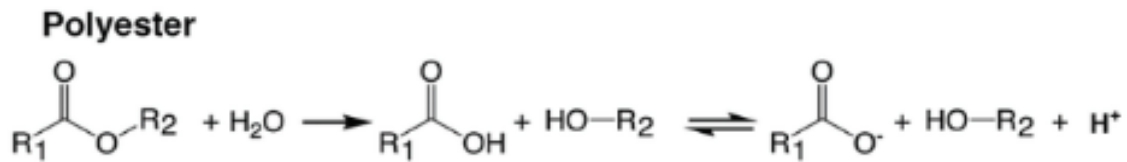


Figure (18): Hydrolytic degradation of polyester

1.9.5. Polystyrene

PS is more susceptible to outdoor weathering. When the polymer is irradiated with UV-light, the phenyl ring gets excited and the excitation energy is transferred to the nearest C-H bond. This causes cleavage of the hydrogen and the formation of a polymer radical. Cross-linking and chain scission are the results with the formation of ketones and olefins. Because end-chain scission is predominant, styrene monomers have been identified as the main volatile product of degradation. (Li J, 2008).

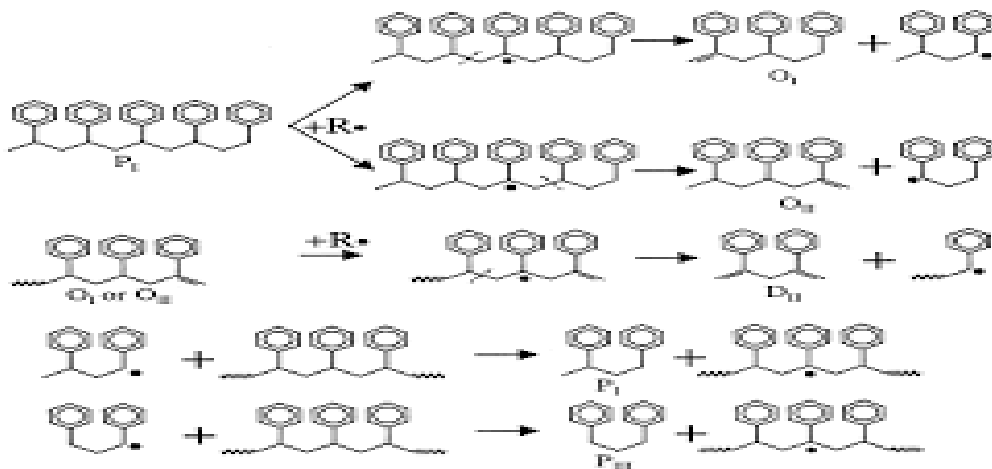


Figure (19): Thermal degradation of polystyrene

1.9.6. High-Density Polyethylene

High-density polyethylene (HDPE) is a widely used organic polymer and an emerging pollutant, because it is very stable. Several fungal species that produce delignifying enzymes are known to be promising degraders of recalcitrant polymers. Thermally pretreated HDPE degrades easily as oxidized polyethylene chain leads to the carbonyl group formation (B. Nowak, 2011).

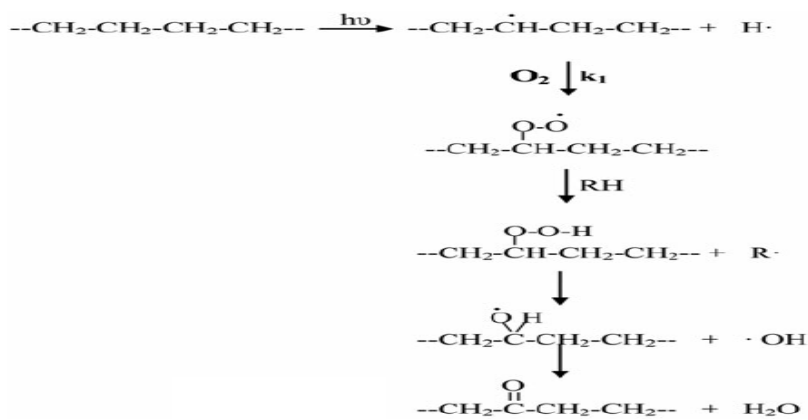


Figure (20): Degradation of HDPE

1.9.7. Low-Density Polyethylene

LDPE is what plastic grocery bags are made of. If exposed to ultra violet light, these bags have been estimated to break down in as little as 500 years with a conservative average time of 1000 years. If there is no exposure to a light source, say at the bottom of a landfill, the plastic may remain intact indefinitely.

The degradation of LDPE by microbes was facilitated by the formation of biofilm on the surface which enables them to breakdown the high molecular weight polymer into smaller fragments through enzymatic processes. (B. Nowak, 2011)

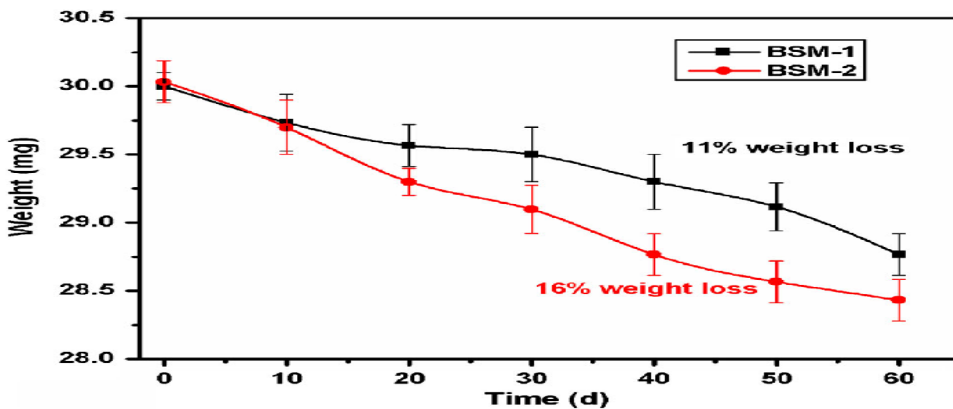


Figure (21): Degradation of LDPE films

1.9.8. Poly (Vinyl Chloride) (PVC)

PVC is the least stable of the high tonnage polymers as it has the highest sensitivity towards UV radiation and therefore photo-degradation is of highest importance. Since PVC monomer units contain only saturated chemical bonds, impurities are required for photo-initiation by UV radiation. When exposed to sunlight, dechlorination of PVC is the first step, which leads to the formation of conjugated double bonds in a polyene polymer and hydrochloric acid, along with a very low amount of other products. The first step is associated with the elimination of chlorine, and the second step is related to the degradation of remaining part which decomposes at the same temperature as observed for other plastics. (Gewert *et al.*, 2015).

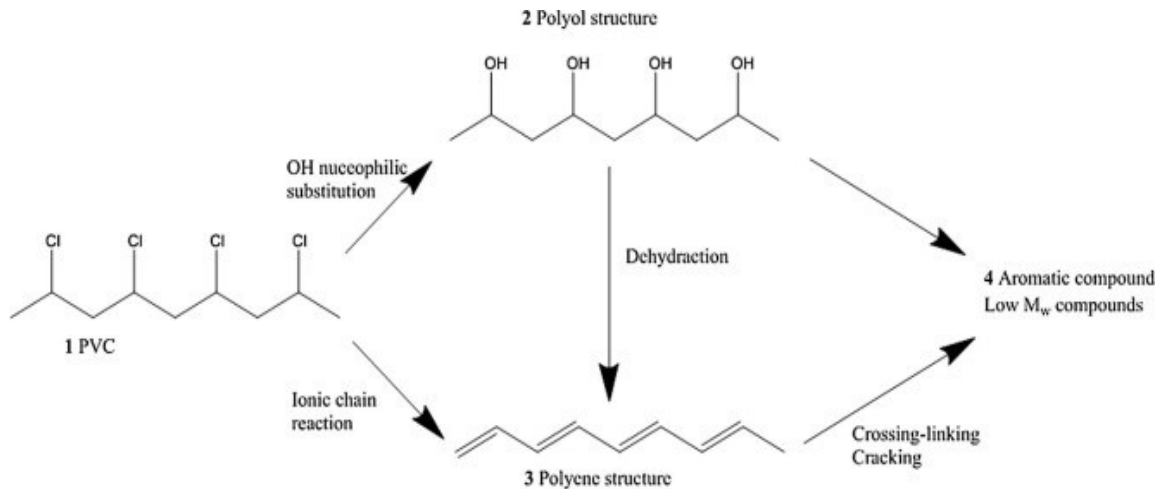
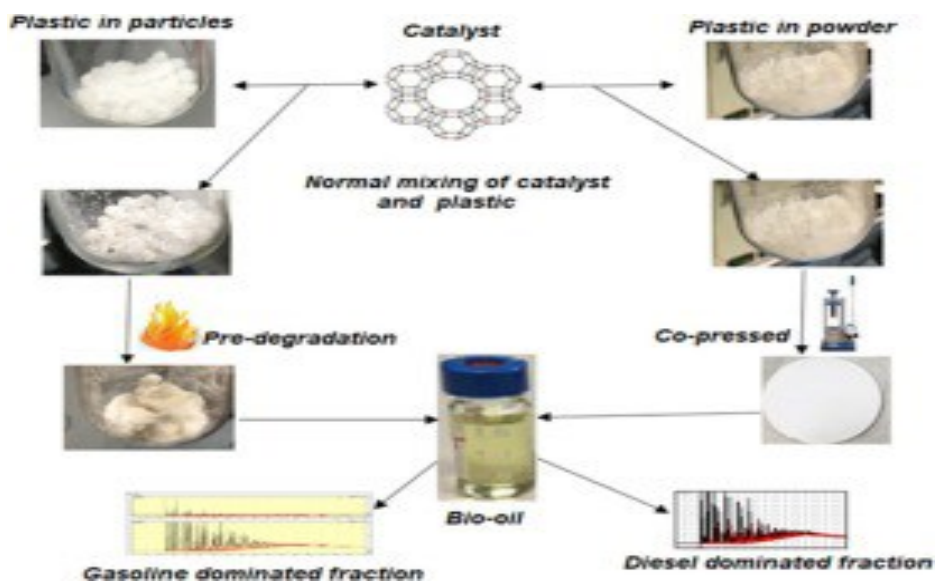


Figure (22): Thermal degradation of PVC

1.10. Catalysts increase degradation of plastics

A wide range of catalysts have been employed in plastic pyrolysis processes, but the most extensively used catalysts are ZSM-5, zeolite, Y-zeolite, FCC, and MCM-41. The catalytic reaction during the pyrolysis of plastic waste on solid acid catalysts may include cracking, oligomerization, cyclization, aromatization and isomerization reactions.

Several studies reported the use of microporous and mesoporous catalysts for the conversion of plastic waste into liquid oil. carried out catalytic pyrolysis of polyethylene (PE) with HZSM-5 catalysts. The use of HZSM-5 increased liquid oil production with the composition of aromatics and isoalkanes compounds. (Serrano et al., 2012).



Figure(23): pretreatment and catalytic conversion of polyolefins into hydrocarbon fuels over acidic zeolite catalysts

1.11. Conclusion

Here we report the degradation of several plastic materials with different compositions in the environment. Degradation of plastics depend on the material's structure and environmental factors. Plastic pollution can alter habitats and natural processes, reducing ecosystems ability to adapt to climate change, directly affecting millions of people's livelihoods, food production capabilities and social well-being.

We see that log time of plastic degradation is harmful for the environment, polyethylene terephthalate (PET) need the longest time to degrade approximately 450 years, while polyethylene and polypropylene are chemically similar, both are degrade rapidly, the faster degradation of plastics the more better for environment.

1.12. References:

1. Wellfair, (2008) 'Testing the Degradation Rates of Degradable, Non-degradable and Biodegradable Plastics Within Simulated Marine Environments', *The Plymouth Student Scientist*, 1(2), pp. 243-301.
2. Kale, S.K., Deshmukh, A.G., Dudhare, M.S. and Patil, V.B., 2015. Microbial degradation of plastic: a review. *Journal of Biochemical Technology*, 6(2), pp.952-961.
3. RaziyaFathima, M.P.P.K., Praseetha, P.K. and Rimal, I.R.S., 2016. Microbial degradation of plastic waste: a review. *Chemical and Biological Sciences*, 4, pp.231-42.
4. Senanayake, I.C., Pem, D., Rathnayaka, A.R., Wijesinghe, S.N., Tibpromma, S., Wanasinghe, D.N., Phookamsak, R., Kularathnage, N.D., Gomdola, D., Harishchandra, D. and Dissanayake, L.S., 2022. Predicting global numbers of teleomorphic ascomycetes. *Fungal Diversity*, 114(1), pp.237-278.
5. Chamas, A., Moon, H., Zheng, J., Qiu, Y., Tabassum, T., Jang, J.H., Abu-Omar, M., Scott, S.L. and Suh, S., 2020. Degradation rates of plastics in the environment. *ACS Sustainable Chemistry & Engineering*, 8(9), pp.3494-3511.
6. Elahi, A., Bukhari, D.A., Shamim, S. and Rehman, A., 2021. Plastics degradation by microbes: A sustainable approach. *Journal of King Saud University-Science*, 33(6), p.101538.
7. Dimassi, S.N., Hahladakis, J.N., Yahia, M.N.D., Ahmad, M.I., Sayadi, S. and Al-Ghouti, M.A., 2022. Degradation-fragmentation of marine plastic waste and their environmental implications: A critical review. *Arabian Journal of Chemistry*, p.104262.
8. Rose, R.S., Richardson, K.H., Latvanen, E.J., Hanson, C.A., Resmini, M. and Sanders, I.A., 2020. Microbial degradation of plastic in aqueous solutions demonstrated by CO₂ evolution and quantification. *International journal of molecular sciences*, 21(4), p.1176.
9. Vijayakumar, A. and Sebastian, J., 2018, August. Pyrolysis process to produce fuel from different types of plastic—a review. In *IOP conference series: Materials Science and Engineering* (Vol. 396, No. 1, p. 012062). IOP Publishing.
10. Ranby, B., 1989. Photodegradation and photo-oxidation of synthetic polymers. *J. Anal. Appl. Pyrolysis* 15, 237–247.
11. Leal Filho, W., Saari, U., Fedoruk, M., Iital, A., Moora, H., Klöga, M. and Voronova, V., 2019. An overview of the problems posed by plastic products and the role of extended producer responsibility in Europe. *Journal of cleaner production*, 214, pp.550-558.
12. Kulkarni, A. and Dasari, H., 2018. Current status of methods used in degradation of polymers: a review. In *MATEC Web of Conferences* (Vol. 144, p. 02023). EDP Sciences.

13. Barnes, D.K., Galgani, F., Thompson, R.C. and Barlaz, M., 2009. Accumulation and fragmentation of plastic debris in global environments. *Philosophical transactions of the royal society B: biological sciences*, 364(1526), pp.1985-1998.
14. Tokiwa, Y., Calabia, B.P., Ugwu, C.U. and Aiba, S., 2009. Biodegradability of plastics. *International journal of molecular sciences*, 10(9), pp.3722-3742.
15. Ryberg, M.W., Hauschild, M.Z., Wang, F., Averous-Monnery, S. and Laurent, A., 2019. Global environmental losses of plastics across their value chains. *Resources, Conservation and Recycling*, 151, p.104459.
16. Law, K.L., Morét-Ferguson, S., Maximenko, N.A., Proskurowski, G., Peacock, E.E., Hafner, J. and Reddy, C.M., 2010. Plastic accumulation in the North Atlantic subtropical gyre. *Science*, 329(5996), pp.1185-1188.
17. Ghosh, S.K., Pal, S. and Ray, S., 2013. Study of microbes having potentiality for biodegradation of plastics. *Environmental Science and Pollution Research*, 20, pp.4339-4355.
18. Daglen, B.C. and Tyler, D.R., 2010. Photodegradable plastics: end-of-life design principles. *Green Chemistry Letters and Reviews*, 3(2), pp.69-82.
19. Singh, B. and Sharma, N., 2008. Mechanistic implications of plastic degradation. *Polymer degradation and stability*, 93(3), pp.561-584.
19. Iñiguez, M.E., Conesa, J.A. and Fullana, A., 2018. Recyclability of four types of plastics exposed to UV irradiation in a marine environment. *Waste management*, 79, pp.339-345.
20. Vaverková, M., Kotovicová, J. and Adamcová, D., 2011. Testing the biodegradability and biodegradation rates of degradable/biodegradable plastics within simulated environment. *Infrastruktura i Ekologia Terenów Wiejskich*, (12).
21. Li, Y.S., Wu, L.H., Lu, X.H., Zhao, L.M., Fan, Q.L. and Zhang, F.S., 2006. Soil microbial biomass as affected by non-flooded plastic mulching cultivation in rice. *Biology and Fertility of Soils*, 43, pp.107-111.
22. Nisticò, R., 2020. Polyethylene terephthalate (PET) in the packaging industry. *Polymer Testing*, 90, p.106707.
23. Venkatachalam, S.G.S.V.J.R.P., Nayak, S.G., Labde, J.V., Gharal, P.R., Rao, K. and Kelkar, A.K., 2012. *Degradation and recyclability of poly (ethylene terephthalate)* (pp. 75-98). Rijeka, Croatia: InTech.
24. Shan, Z.W., Li, J., Cheng, Y.Q., Minor, A.M., Asif, S.S., Warren, O.L. and Ma, E., 2008. Plastic flow and failure resistance of metallic glass: Insight from in situ compression of nanopillars. *Physical Review B*, 77(15), p.155419.

25. Nowak, B., Pająk, J., Łabużek, S., Rymarz, G. and Talik, E., 2011. Biodegradation of poly (ethylene terephthalate) modified with polyester" Bionolle®" by *Penicillium funiculosum*. *Polimery*, 56(1), pp.35-44.
26. Serrano, D.P., Aguado, J. and Escola, J.M., 2012. Developing advanced catalysts for the conversion of polyolefinic waste plastics into fuels and chemicals. *Acs Catalysis*, 2(9), pp.1924-1941.



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