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Plastic Degradation Using Different Techniques-A Review

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Abstract:- Due to its versatility and cost effectiveness, the widespread use of plastic has led to significant environmental problems such as pollution and waste accumulation. This review examines various methods of plastic degradation, focusing on their mechanisms, efficiency and environmental impact. It deals with microbes, chemicals, and mechanical degradation processes and emphasizes the role of enzymes, photochemical reactions, and physicochemical changes in the degradation of polymers into ecologically benign components. Particular attention is paid to emerging approaches such as photocatalysis and the use of extremophilic bacteria, the persistent and widespread nature of plastic pollution severe conditions. Despite progress, the persistent and widespread nature of plastic pollution requires continues research and the development of innovation, scalable solution to reduce the impact on ecosystems. This review highlights the importance of reducing plastic use and developing degradation technologies to address global environmental health threats.

I. INTRODUCTION

Nowadays plastic is been widely used all over the world due to its highly versatile properties such as chemical resistance, low weight, excellent thermal stability, user-friendly designs, and outstanding electrical insulation. Plastic has been introduced due to growing urbanization, rapid industrialization, and increasing population. This has resulted in many severe man-made environmental problems. Plastic plays an important role in our lives; it is very essential for economic purposes. It is cheap, light, durable, and easy to use. Mass production of plastic was begun in the 1940s as the demand for plastic has increased very fastly due to its nature. The amount of plastic that is being produced or used is increasing day by day. The plastic that is been dumped in the oceans or the water bodies is exposed to direct sunlight which causes the degradation of the plastic and the release of the polymers which cause marine pollution. The common plastic types or the plastic that is being used are polystyrene (PS), polyurethane (PU), polyethylene (PE), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polypropylene (PP). in the year 1950 annually 2 million tons of plastic used to be produced which has turned into 370 million tons annually in the year 2019.

Currently (MSW) municipal solid waste generated is 2 billion tons which were expected to turn 3 billion tons in the year 2025 in the worldwide range. On the average US and Europe produce one-third of the plastic annually. Plastic has only one positive thing which is cost-effective and is expected to increase its market by 722.6 billion USD by the year 2027. Plastics due to their multiple applications in human society have become omnipresent material. The plastic concentration is being increased in the water bodies. According to the current senses for every 5 fish 2 plastic bodies but nearly after 10 years there will be 5 plastic bodies for every 3 fish.

II. IMPACTS DUE TO PLASTIC ACCUMULATION

During the manufacturing of plastic, there will be a huge release of hazardous gaseous substances into the air, which includes nitrogen oxide, dioxins, hydrogen cyanide, and carbon monoxide. Low-density particles in the air effects more, there was a report which was reported by Royal et al (2018) that the traces of the gases produced from the low-density polyethylene (LDPE) increases with incubation time (212 days) and there will be an increase in the density effect. After 212 days it will reach to 5.8nmol methane/g/day, 9.7 nmol propylene/g/day, 14.5 nmol ethylene/g/day and 3.9 nmol ethane/g/day. Their emission rates are nearly 2 times higher for methane and 76 times higher for ethylene. From the year 1950 to 2022 nearly 4.2 billion ended up wasted as there were used just once before disposal, and 6.4 billion metric tons of plastic were disposed of in between. In this, nearly 4.6 billion tons of plastic waste was disposed on landfills, as the complete decomposition of plastic takes more than 500 years and plastic releases toxins during its composition in the soil there are affecting the microbial action or microbial content in the soil changes the whole soil into infertile lands. While we take the bio-degradable plastics, there are plenty of microorganisms that help in the acceleration of the degradation of the plastic waste that is being disposed of, few of those bacteria are Microorganisms from diverse taxa, including **Firmicutes, Proteobacteria, Ascomycetes and Basidiomycetes**, can degrade bioplastics. These microbes are distributed throughout many ecosystems, including terrestrial and marine soil, compost facilities, and even insect guts, bacteria like *pseudomonas* sp., are nylon-eating bacteria, and flavobacteria have the nylonase enzyme which breaks down the nylon.

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Fig 1 Dump yard Filled with Plastic Waste

In the year 2021, a total of 195 countries were estimated to produce about 405 metric tons of plastic waste, with about 9 metric tons entering the water bodies. Based on the data given by UNCRD (United Nations Centre for Regional Development) that the southern countries of Asia (Vietnam, Sri Lanka, Malaysia, China, Philippines, Bangladesh, and Indonesia) are ranked first in the disposal of plastic or mismanagement of plastic waste in the water bodies, nearly 88% of plastic water is ending up in the oceans. The abiotic degradation of plastic releases highly toxic compounds, damaging all the soil and the water. The water bodies consist of nearly 5.3 trillion macro, micro, and nano plastic particles which weigh 280 tons. As the problems are being increased day by day the government has taken a few sets of rules like increasing the size of the plastic from 40 to 50 microns for making it thicker for easy collection and recycling. Segregating the plastic waste from the remaining waste and handing it over to authorized persons for taking care of the plastic waste.

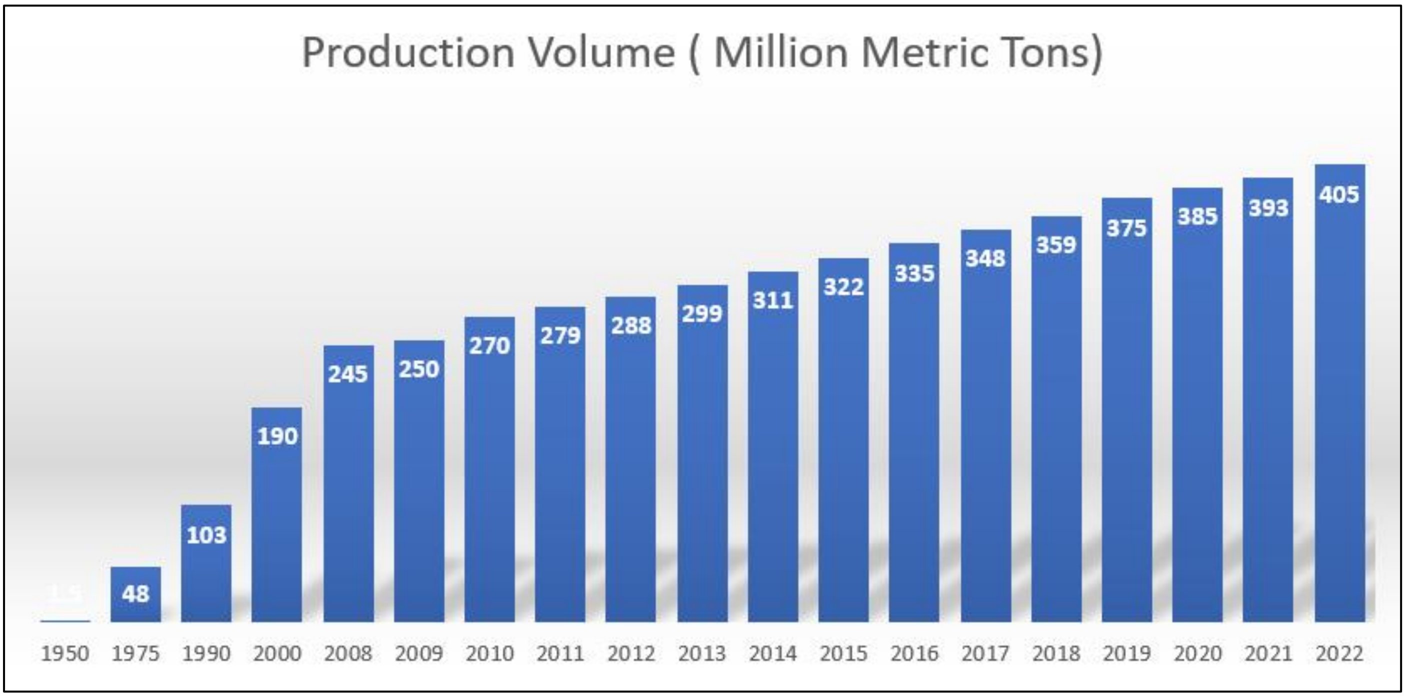

Fig 2 Plastic Production in Million Metric Tons each year

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A. Types of Methods or Techniques:

There are various types of plastic degradation techniques like microbial degradation, biodegradation, physiochemical degradation, photocatalytic degradation, biological treatment by using marine bacteria, photo-oxidation degradation, etc. in these degradation techniques all the polymeric complexes will break down. All these processes will lead to the breakage into low molecular weight compounds, which can now be treated with microbes, but this process takes centuries to complete the degradation.

➢ *Microbial Degradation:*

This is a process of degradation in which a group of living organisms breaks down the polymeric chain into monomers and oligomers. Now, other components or compounds use these molecules to make themselves simpler substances or elements and, the remaining parts are left as waste material. Microbes with the help of enzymes participate in the degradation process, which is h resin the converting the residues of the plastic degradation into environmental components like the carbon in the polymer chain is converted into carbon dioxide and hydrogen in presence of oxygen to the water. So, this helps the soil to become more fertile but the problem is it takes centuries for this process. This process even helps to get the metabolites like oligomers and monomers. The degradation process is influenced by various properties like the presence of functional groups that promote higher hydrophilicity, the quantity of crystalline and amorphous types, weight, length of the carbon chain, and the presence of polar covalent (amide or ester bonds, C-C bonds), size and form (pellets, fibers, films, powder), environmental factors like temperature, pressure, moisture, pH, UV, enzyme characteristics. According to the biodegradation rate of the plastic, they are been divided into 2 main groups – biodegradable and non-biodegradable. Mostly non-biodegradable plastic is Fossil based plastic for example PVC, PP, PE, and PS. Most of the polymers cannot be degraded directly by the microbes they are reasonable for only the primary degradation and then it is continued by the secondary degraders. Biodegradation occurs in mainly four steps;

- Bio-degradation – cracks and aggravates physical properties and changes in the matrix by pH change as a result of the release of the acid.
- Bio-fragmentation – the activity of enzymes by microbes on the long chain polymers releases the oligomers.
- Degradation of oligomers to monomers – oligomers enter the cells, and the secondary degraders remove the carbon sources and increase the microbe's biomass.
- Assimilation of oligomers and releasing the oxidized metabolites to N_2, CO_2, CH_4, and H_2O.

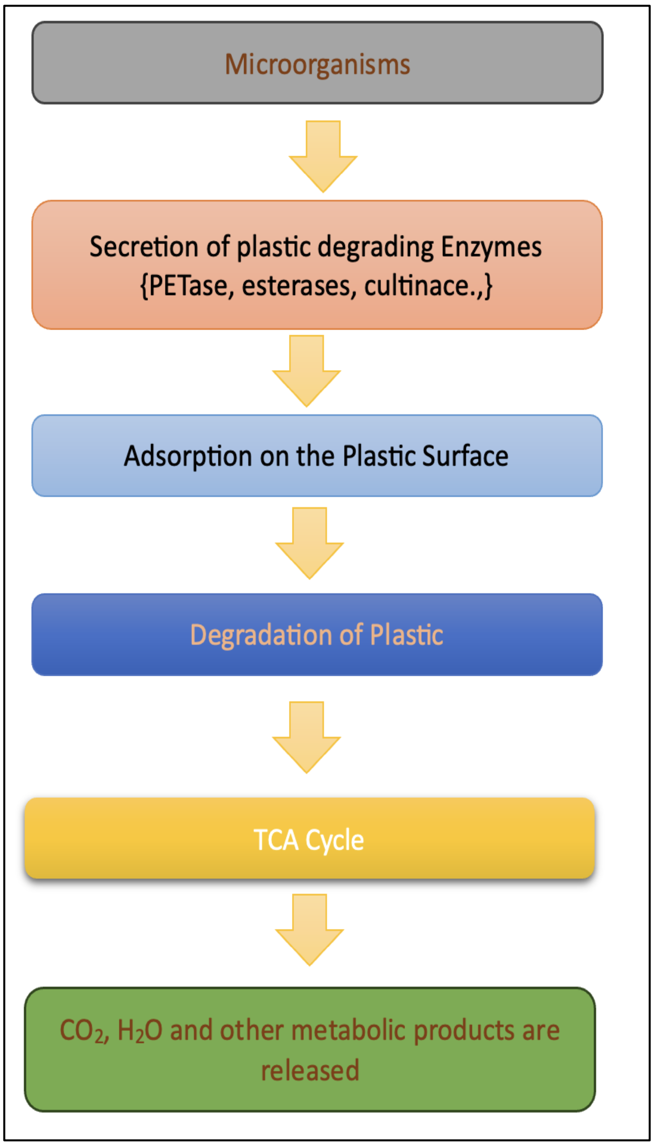

Fig 3 Stepwise Microbial Degradation

➢ *Physiochemical Degradation:*

Abiotic degradation of plastic occurs naturally, now if we take in case of mechanical degradation is done by abrasion by stones, tidal forces, and waves. Plastic debris is produced by the fragmentation process. The effect of the hydrolysis process, photo-oxidation can help to form micro and nano plastic very easily. When we take the chemical degradation the polymer weight is decreased when it is compared to the mechanical degradation in the mechanical degradation process the molecular weight remains constant, and this process is controlled by various factors like mechanical stability, plastic weight, polymer chain length, polymer crystallinity and intramolecular forces between polymer chains.

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- *Photodegradation*

It is one of the most important abiotic degradation techniques in presence of air (aerobic outdoor environment). Photo-oxidation is a technique that oxygenates the plastic's surface and then enhances the microbial biofilm formation on the surface of the polymer and increases the hydrophilicity of the polymer. Plastic photodegradation consists of three steps; they are – initiation, propagation, and termination. In the first stage, the chemical bonds are broken down by the process of heat or light to form free radicals. Usually, the polymers contain unsaturated chromophoric groups that absorb light energy, few plastic types like PP and PE do not contain any unsaturated double bonds in their polymeric structure, and these substances are resistant to the photodegradation process. Like wisely, few impurities might enter the polymer and it initiates the first step of photodegradation. Now during the propagation step, the free radicals will react with the oxygen and react into the peroxy radicals. The complex radicals take up the reactions and auto-oxidation take place. Finally, this step leads to the crosslinking or the chain scission. Termination of the reaction occurs when the inert product is formed from the combination of two radicals. So, random chain scission is performed to produce oxygen-containing functional groups like ketone, aldehyde, and olefin compounds due to oxidation. These compounds are considered more susceptible to photo-oxidation as they contain unsaturated double bonds. And now the molecular weight of the plastic will decrease. Due to more fragmentation, the surface area is increased.

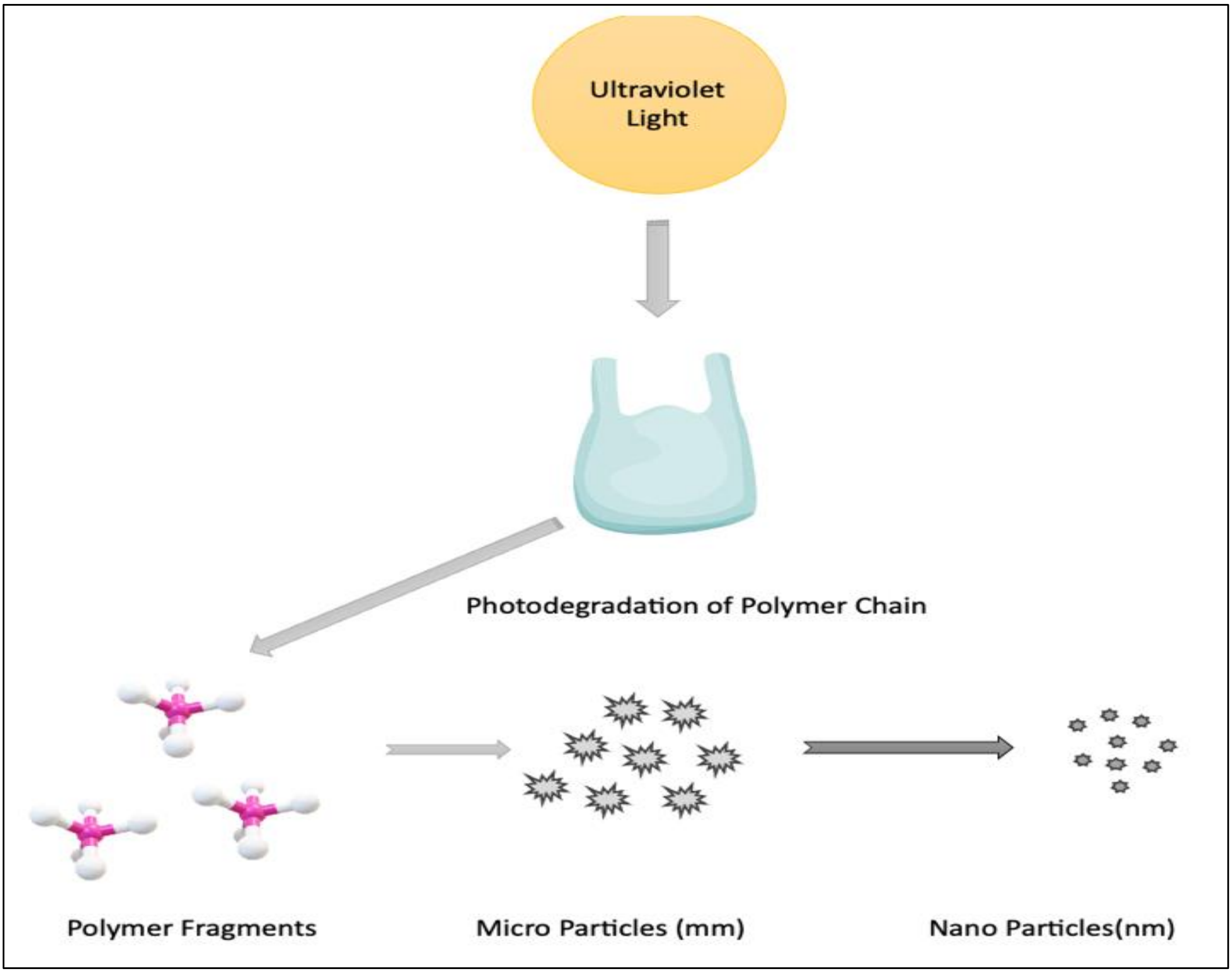

Fig 4 Photodegradation of Plastic

- *Hydrolysis*

It is one of the main steps in the abiotic degradation pathway. This process contains a catalyst that speeds up the reaction like ions released in the reaction process. The rate of the reaction depends on the susceptibility of the water effect on the chemical bonds, and the concentration inside the material, and the critical factor is the water diffusion rate into the polymeric material. This process is catalyzed chemically or biologically and the physicochemical changes occur as the water reacts with the polymer. In the acid-base catalyzed reactions, the mechanism involves a nucleophilic attack on the carbonyl group in esters or amide bonds. Several factors affect this processing rate, which includes the molecular weight of the polymeric molecules, in which as the molecular

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weight increases the rate of the process will decrease. same as, hydrophilicity or hydrophobicity and mobility of the molecules affect the rate of the reaction. The rate even depends on the chain's stereochemical composition, in which the oxygen, carbon, and hydrogen atoms interfere sterically with rotations of other groups.

- *Thermal Degradation*

This process is conducted or performed at a high temperature, likely which is higher than the boiling temperature of water (>100ºC), the temperature depends on the plastic polymer type and characteristics. The additives like antioxidants which are incorporated by the plastic manufacturers prevent thermal oxidation at a lower temperature. Stress and exposure to reactant compounds, like ozone, accelerate the degradation process. The chemical composition decides the resistance of the degradation process of the polymer, PP, PBD (polybutadiene), and PVC are highly susceptible to this process (thermal degradation). Polymers such as polysiloxanes, polyether ketone, and polysulfone are highly thermal resistant and have a strong bond as their backbones. The contribution for this process by the normal environment globally is considered zero, particularly in the cold, marine environment as this process requires high temperature for completion.

- *Photocatalytic Degradation*

In this process, a photocatalyst participates in the photochemical reaction process, a semiconductor is used to accelerate the rate of photoreaction and absorb light. It is many applications like water splitting for green hydrogen generation, removal of bacteria and pollutants and energy conversion. A basic photocatalyst should be non-toxic, absorb light at room temperature and have high stability toward the photo corrosion.

When TiO_2 is one of the photocatalyst is exposed with the UV light with irradiation energy which is equal or more than its bandgap, the (e^-) electron are excited from its valence bond to conduction bond, creating an energetic electron (e^-) hole (h^+) pair.

Now, the parts of the electrons (e^-) will rejoin with holes in fraction of second, and now this has longer life. The recombination of the electron-holes reduces the number of holes transported to the TiO_2 surface for oxidation-reduction chemical reaction and reduce the number of photogenerated electrons. So, the presence of incorporation of trap sites and scavengers, which helps in the reduction of holes in the bulk of semiconductors and the recombination of electrons (e^-), these are the attractive strategies for the catalytic activity to increase. Now, the holes and the electrons (e^-) are transferred to the surface of the semiconductor which is undergoing interfacial charge-transfers to carry out the oxidation-reduction chemical reaction.

Now, in the reductive reaction, electrons (e^-) in the conduction bond of photocatalyst produces superoxide by reacting with the oxygen, hydrogen peroxide is produced by the process of reduction of the superoxide, hydroxyl and hydroxides radicals with electrons (e^-) are produced from the hydrogen peroxide.

Where, in the oxidation reaction, holes present in the valency bond of the photocatalyst reacts in with water molecules in the air and forms hydroxyl radicals and protons. Organic pollutants will be decomposed into carbon dioxide and water in the presence of hydroxyl radicals. So, hydroxyl radical is known as essential elements in photocatalysis. On the surface of the semiconductors the interfacial charge transfer is regarded as important producing hydroxyl radicals, that is affecting the photocatalytic degradation rate.

UV light only represents only 5-8% of the solar spectrum which is at the sea level, where it limits the efficiency of photocatalytic degradation for most photocatalysts as ZnO and $TiO_{2.}$ This process crucially requires more solar energy so it done under the visible light. The energy band gap is reduced to increase the activity of the degradation process under visible light. This can be achieved by introducing structural imperfections into the crystal, called as chemical doping. Impurities such as Fe^{3+}, C, N are used to know the controlled process.

- *Biological Treatment by using Marine Bacteria*

Most of the places of our planet are cold less than 5ºC, and uninhabited by human beings. The reason behind this is nearly 70% of our planet is covered by seawater, mostly deep ocean, and in this two third part has approximately 2ºC temperature. We can see that bacteria can even live at this extreme temperature and are able to resist all these conditions poses few unique features. As these microbes live in cold areas, it was assumed that the degradation of plastic ability increases. As the amount of plastic that is being dumped into oceans is increasing might provide a new environment for the benthic organisms. In the seawater plastic releases dissolved organic carbon, which stimulates the microbes. New features may be added as a new environment is formed by the presence of carbon and particularly due to the production of cold active enzymes. And these enzymes give various opportunities to decompose the plastic waste. It is huge advantage as the enzyme activity is done at lower temperature, as the power requirement will be lower which is reduced which is used for heating. The microorganisms from cold habitat can be cultivated in open areas. The microbes used for this process are belong to the species – *Corynebacterial, Rhodococcus, Pseudomonas, Arthrobacter, Streptomyces* and *Micrococcus* these are the bacteria found in the cold places. *Micrococcus and Pseudomonas,* the bacterial isolated strains are *Micrococcus, Agreia, Leif Sonia, Polar monas, Flavobacterium, Subtercola and Cryobacterium* were isolated from cryoconite. These 12 strains were able to produce lipase, it is an enzyme which hydrolyses ester bonds present n lipids and in some polyesters. Lipase activity is found in the microbial strains that are been isolated from the Artic Sea ice of the Canada Basin. Microbes that are identified here belong to the genera *Pseudomonas, Colwellia, Shewanella, Pseudoalteromonas and Marinomonas.* These strains lipase activity was found to be 10 – 30% and 20 – 40% at 0ºC of psychrotolerant and psychrophilic strains. They have a great lipase activity which can be used for biodegradation of hydrolyze polyesters such as PCL. When additives are added which disturb their thermal stability will increase the degradation rate. At 1ºC the greatest quantity of proteases are released, which help in the production of more enzyme which degrades the plastic.

➢ *Photo-Oxidation Degradation*

It is a type of degradation process in which decomposition of the material is done by action of light, which is a primary source of damage exerted upon polymeric substrates. Degradation is done normally in presence of visible and UV light. UV radiations have the sufficient power or energy to brake C—C bond. PP and PE materials are exposed to UV radiations and they lose their strength, extensibility and mechanical integrity even its molecular weight decreases. At any given moisture cont. and temperature, the rate of weathering increases with the increase in UV flux.

- *Mechanism.*

The mechanism of oxidation and degradation reactions are determined by the impurities in the polymer, which absorb light and form into the excited state. Now, short lives single state is transformed into long lives triple state, which now breaks the polymer chains and forms radical pairs or by hydrogen transfer it forms pairs of unsaturated or saturated chain ends. The radicals now take up an oxygen and forms peroxide radicals, now takes hydrogen and forms hydrogen peroxide groups, which absorbs UV light, pairs of hydroxyls and alkoxy radicals are formed by the brakage of weak O—O bond, and now reacts in different types like chain scission, hydrogen abstraction, rearrangement reactions which accelerates the photodegradation process. Oxygen molecule enters the single state and the double bond is shifted to the C—C bond and hydroperoxide group is formed. Few synthetic polymers like polyamides and aromatic polyesters have high absorption rate of UV light, chain scission, causing excitation, splitting of small molecules, radical formation, oxygen addition.

✓ *Initiation.*

Absorption of sufficient energy of UV light to break the chemical bonds in the polymer chain initiates the polymer degradation. Which involves the radical chain mechanism for the formation of initial radical. Different initiation steps are noted down here –

- Direct UV initiated photolysis of C—H and C—C bond.
- Photosensitized cleavage
- Catalyst residues as source of generation of radicals
- Incorporation of carbonyl groups
- Introduction of peroxide or site if unsaturation
- Reactions of singlet and triplet stage.

✓ *Propagation Reaction.*

This reaction is common for all the carbon backbone reactions. Hydroperoxide species are formed not directly involving the backbone cleavage but the key intermediates. Hydroperoxide species generated in propagation leads to backbone degradation. Oxidative processes involve 1) formation of hydroperoxides and 2) degradation of hydroperoxide. This oxidation reaction occurs when the hydrogen is removed, thus removed by photooxidation reaction. The newly formed hydroperoxide group is subjected to decomposition and resulting ultimately in chain cleavage into ketones and olefins.

✓ *Termination Reactions.*

Termination of photodegradation is achieved by mopping up the free radicals to crate inert product.

- *Methods for Photodegradation.*

✓ Natural weathering method
✓ Artificial weathering method

III. CONCLUSION

Plastic degradation is one of the most important for damaging the environment. The growing population and urbanization have increased the significance of usage of the plastic. This increased usage of plastic has to be reduced as it take so long to degrade or in few cases it wont even degrade. This is a review which helps us to know the different types of degrading the plastic by the use of microbial, chemical and mechanical methods. Day by day the usage of plastic has been increased and it has to minimized.

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