A Review on Biodegradations of Polymers and its Effect on Environment

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Abstract: Biodegradation refers to the chemical dissolution of materials by microorganisms or other biological means. Biodegradability of a material refers to the ability of that material to be decomposed by biological agents, especially bacteria. Carbon dioxide and water are produced during aerobic biodegradation and carbon-dioxide, water and methane are produced during anaerobic biodegradation. The process of degradation induces changes in polymer properties resulting in bond scission, chemical transformation and formation of new functional groups. Most of the polymers are non-degradable and some are degraded after longtime and causes environmental pollution. Biodegradation of polymers have both positive and negative impact on environment but the negative impacts are more remarkable. Because some polymeric materials take about million year to degrade in environment. Disposal problem will be introduced from these materials and finally destroy our ecological balance. To protect the environment some advisory steps should be taken such as development of standards and testing, life cycle assessment, determination of appropriate disposal environments. Environmental benefits that may be derived from the use of biodegradable polymers.

Keywords: Biodegradation, polymer, environment, microorganism, decompose.

1. INTRODUCTION

Approximately 140 million tons of synthetic polymers are produced worldwide every year. Since polymers are extremely stable, their degradation cycles in the biosphere are limited. In the Western Europe alone it is estimated that 7.4% of municipal solid wastes are plastic, which are classified as 65% polyethylene/polypropylene, 15% polystyrene, 10% PVC, 5% polyethylene terephthalate and remaining others. Environmental pollution by synthetic polymers, such as waste plastics and water soluble synthetic polymers in waste water has been recognized as a major problem. In view of this, energetic, chemical and biological polymer degrading techniques have been studied extensively during the last three decades. The energetic agencies can be either thermal or radiant. While chemical degradation is caused by using certain chemicals like acids and alkalis etc. Usage of certain microorganisms and enzymes to degrade polymers are classified as the biodegradation method of polymers.

Some types of plastics have been shown to be biodegradable and their degradation mechanisms are different. Very small variations in the chemical structures of polymer could lead to large changes in the biodegradability. The biodegradability depends on the molecular weight, molecular form and crystallinity. It decreases with increase in molecular weight; while monomers, dimmers and repeating units are degrade easily. Two categories of enzymes are involved in the process, namely extracellular and intracellular depolymerases. Exo-enzymes from the microorganism's first breakdown the complex polymers giving short chains that are small enough to permeate through the cell walls to be utilized as carbon and energy sources. The process is called deploy-merization. When the end products are carbon dioxide, water or methane, the process is called mineralization. Different end products are formed depending upon the degradation pathway. (Figure **1**).

The biodegradation of polymers plays an important role because polymers are used in high amounts in our daily life. In order to understand the big picture on polymers one has to remember that polymers may occur in many different forms such as solid materials or even (water) soluble compounds used in huge amounts in the pharmaceutical, personal care products, dyes and lacquers, glues, construction and oil and gas field industry. This review aims to investigate the general aerobic and aerobic biodegradation of synthetic polymers in environment. The main focus is to:

- Summarize known information on biodegradation of polymers both in the land and aquatic environment.
- Identify if standard biodegradation tests may be used for the evaluation of polymer biodegra-dation and to identify potential shortfalls.
- Compare the biodegradation potential and biodegradation pathways in environment.

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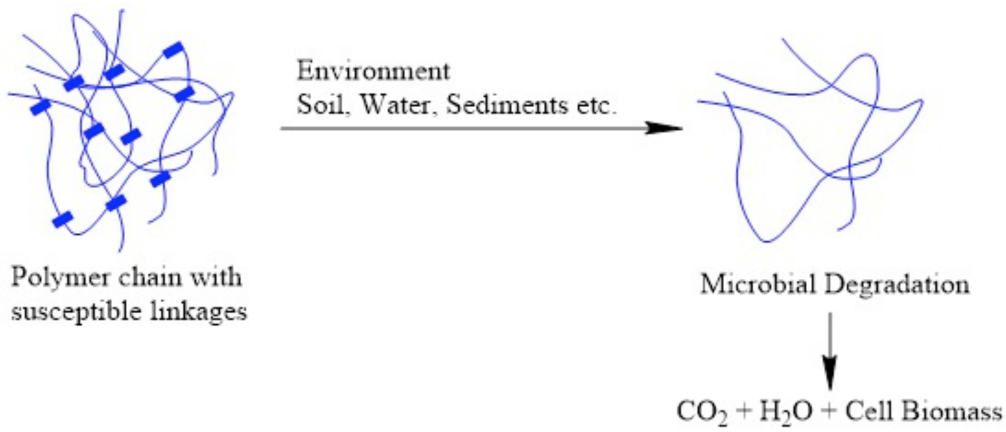

Figure 1: Biodegradation of Polymer.

- Check whether molecular or structural properties of the polymers may have influence on the biodegradation in different environments.
- Confirm the possible pathways of biodegradation and identify similarities and differences.
- Partially investigate the microorganism community link the composition of microbial communities to the biodegradation potential.
- Check whether it may be possible to accelerate marine biodegradation tests and what options are available if standard test cannot be applied to investigate marine biodegradation.
- Inventories/assess the manufacturing status of biodegradable plastics industries manufacturing units in India with reference to processing technologies and environmental issues etc.
- Establish the degradation rate w.r.t change in chemical structure, decrease in mechanical strength, fragmentation and weight loss of polymeric material degradability under laboratory scale composting conditions.
- Evaluate the self-life and its impact on environment.
- Evaluate its effect on food stuffs w.r.t natural color/additives.

2. MAIN APPLICATION OF POLYMERIC COMPOUNDS ARE MENTIONED BELOW

- Packaging (food containers, wraps, nets, foams).
- Film including over wrap, shopping bags, waste and bin liner bags, composting bags, Mulch film, silage wrap, body bags/coffin liners, landfill covers and packaging–incl. O_2 and H_2O barriers, bait bags, nappy backing sheet, and cling wrap.
- Catering products (cutlery, plates, cups straws etc.).
- Agriculture (mulch films, plant pots, nursery films etc.).
- Hygiene products.
- Medical and Dental Implants (sutures etc.).
- Plastic bags for collection and composting of food waste and as supermarket carrier bags.
- Flushable sanitary products.
- Sheet and non-woven packaging.
- Liquid paper board.
- Planter boxes and fishing nets.
- Food service cups, cutlery, trays, and straws.

3. DEGRADATION OF POLYMER

The process of degradation induces changes in polymer properties resulting in bond scission, chemical transformation and formation of new functional groups as the end products that are stable and found in nature. Various polymeric compounds are synthesizing and using tremendously without any awareness. But the negative effect comes from the waste of these materials. Different polymeric compound takes different time to degrade. Negative effect depends on the stability of these materials [1]. More stability is the more harmful for environment. Degradation time of some polymeric compounds are shown in the Table **1**.

Table 1: Degradation Time of Some Polymeric Compounds

SL NO.	Polymeric Materials	Degradation Time
1	Cotton rags	1-5 months
2	Paper	2-5 months
3	Rope	3-14 months
4	Orange peels	6 months
5	Wool socks	1 to 5 years
6	Cigarette butts	1 to 12 years
7	Plastic coated paper milk cartons	5 years
8	Plastic bags	10 to 20 years
9	Nylon fabric	30 to 40 years
10	Aluminum cans	80 to 100 years
11	Plastic 6-pack holder rings	450 years
12	Glass bottles	1 million years
13	Plastic bottles	100 years
14	Paper towel	2–4 weeks
15	Newspaper	6 weeks
16	Apple core	2 months
17	Cardboard box	2 months
18	Wax coated milk carton	3 months
19	Plywood	1–3 years
20	Painted wooden sticks	13 years
21	Tin cans	50 years
22	Disposable diapers	50–100 years

From the Table **1**, it is recognized that, more uses of these materials which has the long degradation time, create more disposal problem on the environment and this condition rapidly destroying our ecological balance.

3.1. TYPES OF DEGRADATION

There are different mechanisms were research, for degradation of polymeric materials. The main importance fact in degradation of synthetic polymer is to reduce it mechanical strength by different technique to solve very important problem of polymer disposals. Degradation of polymer can be occurred by the following types [2]:

(a) **Thermal Degradation:** It occurs due to use or processing at high temperature.

(b) **Photo Degradation:** It occurs due to exposure to the energetic part of sunlight i.e. UV radiation or other high energy radiation.

(c) **Compostable Degradation:** Maximum number of microorganism in compost increases the rate of degradation.

(d) **Mechanical Degradation:** It occurs due to the influence of mechanical stress strain.

(e) **Ultrasonic Degradation:** The application of sound at certain frequencies may induce vibration and eventually breaking of chains.

(f) **Chemical Degradation:** Corrosive chemicals such as ozone or sulphur in agrochemicals may attack the polymer chain causing bond breaking or oxidation.

(g) **Biodegradation:** Specific to polymer with functional groups that can be attacked by micro-organisms.

(h) **Hydrolytic Degradation:** For polymer containing functional groups which are sensitive to the effect of water.

4. BIODEGRADATION

Biodegradation is defined as a process which occurs due to the action of enzymes that are secreted by living organisms (bacteria, fungi etc.) leading to its chemical decomposition. [3] Primary biodegradability depends upon the formation of biofilm, which is defined as a layer of deposition of the microorganisms and their secreted polysaccharides etc. on the polymer surface. This is followed by the breakdown of the polymer to low molecular weight oligomers (probably due to the enzymes that are secreted by the microorganisms) and then they are easily assimilated by the microbes. The ultimate degradation leads to the formation of CO_2 and

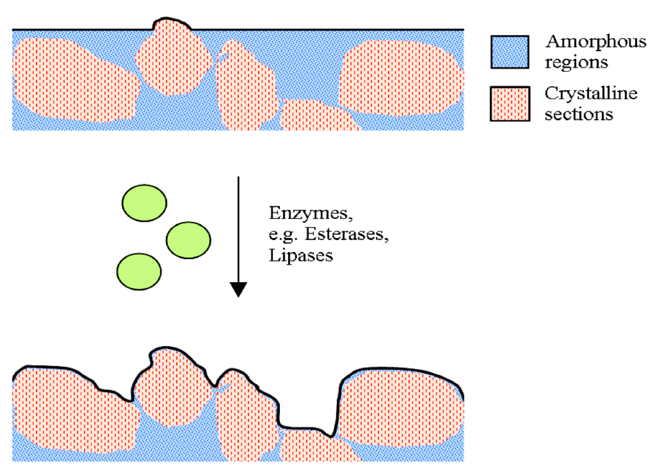

Figure 2: Schematic representation of the effect of polymer crystallinity on enzymatic biodegradation.

water. The prerequisite for this process to take place is that the microorganism should be able to use the polymer as its sole carbon source. In natural conditions, the degradation of plastics is a very slow process and it is a function of environmental factors such as temperature, humidity of air and moisture in the polymer, pH and solar energy; polymer properties and biochemical factors. The most problematic plastics are polyolefin as they are resistant to microbial attack, due to the absence of any active functional groups. (Figure **2**).

5. FACTORS AFFECTING THE RATE OF BIODEGRADATION OF POLYMER

Factors affecting the rate of biodegradation of polymer include the following [4].

5.1. Environmental Factors

- Physical Factors: Temperature and Mineral Structure,
- Chemical Factors: pH, Salt, Nutrient present, Oxygen and Moisture content,
- Biological Factors: Microorganism and Enzyme present.

5.2. Nature of the Polymeric Substance

- Chemical condition.
- Branching.
- Hydro-philicity.
- Stereochemistry.
- Molecular weight.
- Crystallinity.

6. GENERAL STEPS OF BIODEGRADATION

Biodegradation of polymer involves the following steps:

- Attachment of microorganism to the surface of the polymer.
- Growth of microorganism utilizing the polymer as a carbon source.
- Primary degradation of the polymer and,
- Ultimate degradation.

Biodegradation is expected to be the major mechanism of loss for most chemicals released into the environment. This process refers to the degradation and assimilation of polymers by living microorganisms to produce degradation products. The most important organisms in biodegradation are fungi, bacteria and algae [5].

Enzymes markedly take part in polymer degradation in an organism. Due to the bulky molecular weight and size they cannot normally get into a polymeric implant but attack it from the surface or in a surface. Bacteria is the main degradation agent for enzymatic degradation.

7. DIFFERENT STEPS OF POLYMER DEGRADATION BY ENZYME / MICROORGANISMS / BACTERIA

Several steps occur in the polymer biodegradation process and could be identified by specific terminology:

- **Bio-deterioration** defines the action of microbial communities and other decomposer organisms responsible for the physical and chemical deterioration that resulted in a superficial degradation that modifies the mechanical, physical and chemical properties of the plastic.
- **Bio-fragmentation** refers to the catalytic actions that cleave polymeric plastics into oligomers, dimers or monomers by action of enzymes or free-radicals secreted by microorganisms.
- **Assimilation** characterizes to the integration of molecules transported in the cytoplasm in the microbial metabolism.
- **Mineralization** refers to the complete degradation of molecules that resulted in the excretion of completely oxidized metabolites (CO_2, N_2, CH_4, H_2O).

Natural polymers (i.e., proteins, polysaccharides, nucleic acids) are degraded in biological systems by oxidation and hydrolysis [6]. Biodegradable materials degrade into biomass, carbon dioxide and methane. In the case of synthetic polymers, microbial utilization of its carbon backbone as a carbon source is required [7].

Biodegradation of the polymer induced by the aqueous environment takes place by the following possible three mechanisms [8, 9].

7.1. Mechanism-1: Solubilization by Backbone Cleavage

In this category, high molecular weight water insoluble polymers are converted to small water soluble molecules by cleavage of labile bonds in the polymer backbone. These types of polymers are most useful in the systemic administration of therapeutic agents from subcutaneous, intramuscular or intraperitoneal implantation sites. It is essential that the degradation products of these polymers must be completely non-toxic.

7.2. Mechanism-2: Solubilization by Hydrolysis, Ionization and Protonation of Pendant Groups

By this mechanism all polymers that are initially water insoluble but become water soluble as a consequence of hydrolysis, ionization or protonation of pendant groups, because no backbone cleavage takes place. The solubilization does not result in any significant change in molecular weight. Consequently, such polymers are not generally useful for systemic applications because of difficulty in the elimination of such molecules.

7.3. Mechanism-3: Degradation or Solubilization by Crosslink Cleavage

In this system, water-soluble polymers are insoluble by means of hydrolytically unstable cross-links. Consequently, the matrix in highly hydrophilic and completely permeated by water, since active agent is in aqueous environment, its water solubility becomes an important consideration and compounds with appreciable water solubility will be rapidly leached out, independent of matrix erosion. (Figure **3**).

If oxygen is present, aerobic biodegradation occurs and carbon dioxide is produced. If there is no oxygen, an anaerobic degradation occurs and methane is produced instead of carbon dioxide [10, 11]. When conversion of biodegradable Materials or biomass to gases (like carbon dioxide, methane, and nitrogen compounds), water, salts, minerals and residual biomass occurs, this process is called mineralization. Mineralization is complete when all the biodegradable materials or biomass are consumed and all the carbons converted to carbon dioxide.

Biodegradable materials have the proven capability to decompose in the most common environment where the material is disposed, within one year, through natural biological processes into non-toxic carbonaceous soil, water or carbon dioxide [12]. The chemical structure (responsible for functional group stability, reactivity, hydrophobicity and swelling behavior) is the most important factor affecting the biodegradability of polymeric materials. Other important factors are inter alia, physical and physicco-mechanical properties, e.g., molecular weight, porosity, elasticity and morphology (crystalline, amorphous) [13, 14].

8. NECESSITY OF BIODEGRADABLE POLYMERS

- A large number of polymers are quite resistant to the environmental degradation process and are thus responsible for the accumulation of polymeric solid waste materials.
- These solid wastes cause acute environmental problems and remain under graded for quite a long time.

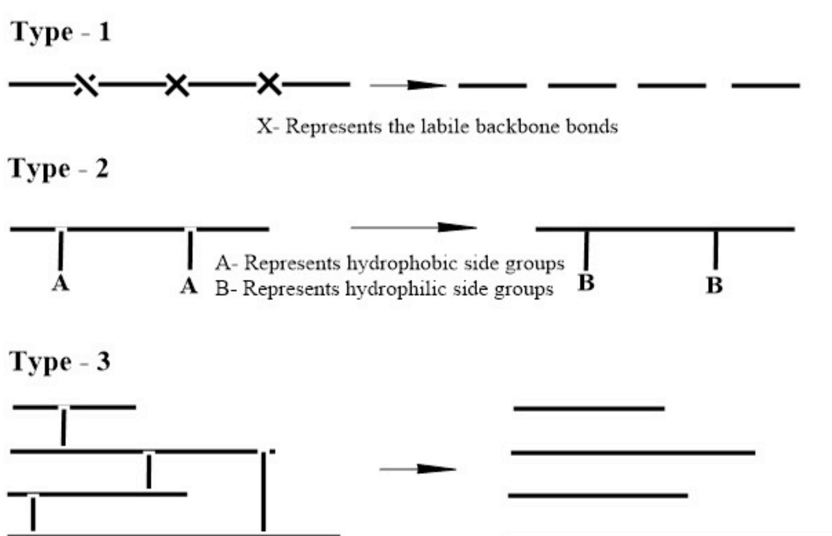

Figure 3: Biodegradation mechanism of the polymer induced by the aqueous environment.

- In a view of the general awareness and concern for the problems created by the polymeric solid wastes, certain new biodegradable synthetic polymers have been designed and developed.
- These polymers contain functional groups similar to the functional groups present in biopolymers.

9. POLYETHYLENE (PE) BIODEGRADATION

Polyethylene is widely used for various one-trip applications like food packaging, retail industry uses and agricultural uses. These applications lead to a large quantity of plastic waste, causing serious environmental problems [15]. PE is the most problematic plastic that is resistant to microbial attack. Polyethylene subjected to 26 days of artificial UV irradiation before being buried in soil evolved less than 0.5% carbon by weight after 10 years. Without prior irradiation, less than 0.2% carbon dioxide was produced. Similarly, a polyethylene sheet that had been kept in contact with moist soil for a period of 12 years showed no evidence of bio-deterioration. However, some studies demonstrated partial biodegradation of polyethylene after shorter periods of time. It showed that UV photo oxidation, thermal oxidation or chemical oxidation with nitric acid of polyethylene prior to its exposure to a biotic environment did enhance biodegradation [16].

Polyethylene is a synthetic polymer with –CH2-CH2 repeating units in the polymer backbone. This polymer is resistant to biodegradation, which results from highly stable C-C and C-H covalent bonds and high molecular weight. The mechanism of biodegradability of polyethylene includes alteration by adding a carbonyl group (C=O) in the polymer backbone. The altered polyethylene molecule undergoes biotic oxidation. In the process of biodegradation, PE molecules containing carbonyl groups first get converted to alcohol by the monooxygenase enzyme. After that, alcohol is oxidized to aldehyde by the alcohol dehydrogenase enzyme. Next, aldehyde dehydrogenase converts aldehyde to the fatty acid. This fatty acid undergoes β-oxidation inside cells. Biotic factors that may bring about polyethylene biodegradation included inter alia bacteria, fungi, bio-surfactants produced by microbes to attach on PE surface, biofilm growth on PE surface, uptake of shorter chain PE polymers membranes and assimilation of such short chains *via* β-oxidation pathway inside cells using intracellular enzymes. And abiotic factors are: sunlight and photo oxidation, the addition of carbonyl radicals into -CH2-CH2- backbone due to photo oxidation and propagation of Norrish type I and II degradation, diffusion of O_2 into PE crystals and chain [17, 18]. (Figure **4**).

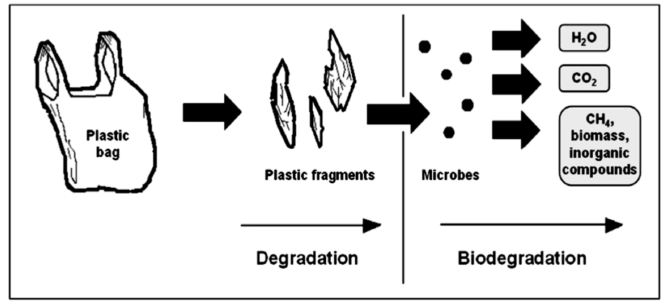

Figure 4: Degradation and Biodegradation of plastic bags (polyethylene).

10. DISPOSAL ENVIRONMENT FOR BIODEGRADABLE POLYMER

The rate of biodegradation of biodegradable plastics is dependent on the disposal environment and its conditions [19].

The major disposal environments for biodegradable plastics are:

- Composting facilities or soil burial;
- Anaerobic digestion;
- Wastewater treatment facilities;
- Plastics reprocessing facilities;
- Landfill;
- Marine and freshwater environments; and
- General open environment as litter.

To a large extent, the nature of the biodegradable plastic application should dictate the disposal environment.

11. SYNTHETIC WATER SOLUBLE POLYMERS

Synthetic water-soluble polymers are substances that dissolve, disperse or swell in water and, thus, modify the physical properties of aqueous systems in the form of gellation, thickening or emulsification/ stabilization. These polymers usually have repeating units or blocks of units; the polymer chains contain hydrophilic groups that are substituent or are incorporated into the backbone. The hydrophilic groups may be nonionic, anionic, cationic or amphoteric [20, 21].

12. NON-BIODEGRADABLE POLYMER

Non-biodegradable polymers are those polymers which are not degraded by Micro-organisms Major portion of synthetic polymers are being used as throw away containers and packing materials. These do not disintegrate by themselves (are non-biodegradable) over a period of time. This is not an advantage; rather, it has presented mankind with a serious waste disposal problem. With the ever increasing use of plastics, soon the civilization will have a pile of plastic debris.

13. NON-BIODEGRADABLE WASTE AND THEIR DISPOSAL

Following methods are used for disposal of non-biodegradable waste-

13.1. Recycling

Separate glass, plastic and metal from non-biodegradable waste for recycling. Many urban and suburban areas have curbside recycling programs. Recycling saves space in landfills and reduces the amount of materials that must be manufactured to make new products, saving energy and reducing global climate change in the process.

13.2. Combustion

Some non-biodegradable waste like rubber tiles and plastic can be burned at combustion facilities. Most of these facilities use the heat generated by incineration to make energy in the form of steam or electricity, which reduces their demand for other nonrenewable resources including coal and petroleum.

13.3. Landfills

Landfills provide long term storage for non-biodegradable waste. Ideally, Landfills are carefully situated to prevent contamination from entering surrounding soil and water and managed to reduce odor and pests as much as possible.

14. SUGGESTIONS AND FUTURE DIRECTIONS

14.1. Development of Standards and Testing

For the successful management of polymeric compound as well as introduction of degradable polymer it is essential for any new application that the following are clearly identified:

- Disposal route.
- Appropriate recovery systems.
- Processing infrastructure required and,
- The product has been tested against nationally agreed standards to ensure that the disposal route is appropriate and is environmentally sustainable. For this to be achieved it will be necessary to establish a national framework for standards and testing. This could be based upon appropriate international standards.

14.2. Life-Cycle Assessment

Further work is also required to understand the fate and consequence of recalcitrant residues such as small aromatic compounds, small polymer particles and other residues in the environment from the degradation and incomplete degradation of biodegradable plastics. Full Life Cycle Assessment (LCA) work on the production, use and disposal of biodegradable polymers, with reference to conventional polymers, should be carried out to determine the real environmental and social benefits and impacts of their introduction into a range of applications.

This would cover:

- Sources of raw materials (renewable resources, energy and water usage, farming practices, greenhouse gas emissions etc.)
- Production of materials;
- Uses and reuses; and
- Disposal environments (including residuals and greenhouse gas potentials). Comprehensive LCA data and analysis would assist in the development of appropriate policy.

14.3. Minimization of Impact on Reprocessing

The introduction of competing products to those which are currently recovered and reprocessed *via* sorting facilities, such as some plastics bags, HDPE and PET bottles, should only occur after industry is fully satisfied that failsafe sorting systems are available. As with other plastics, biodegradable polymers could be given a unique polymer identification code to minimize confusion and assist in sorting. Research on the impacts of the incorporation of biodegradable plastics into established plastics reprocessing systems may be required. Small variations in the ratio of biodegradable to non-biodegradable material could significantly alter the quality of the end material and failure rate in uses reliant on strength. Further research would allow for appropriate policies, labeling, sorting procedures and mechanisms to be developed to minimize the impact on this industry.

14.4. Determination of Appropriate Disposal Environments

Extensive consultation with the product supply chain and potential disposal chain, including sorting, reprocessing, and composting bodies, will be necessary before the widespread introduction of biodegradable products that may impact on existing recycling and composting systems. This could be carried out in a similar manner to the National Packaging Covenant and incorporate COAG (Council of Australian Governments) principles. Composting as a planned disposal route, particularly for film and sheet, should only occur once a system is in place to identify these materials as distinct from non-degradable products.

One possible solution is to introduce a unique standard color (i.e. bright lime green) so they can be easily differentiated from non-biodegradable plastics in a composting environment. These way non-biodegradable plastics can still be manually removed while the biodegradable plastics can be left *in situ*. Unique color-based identification of biodegradable plastics would also assist plastic recyclers identifying those plastics that are not compatible with mechanical recycling processes. A parallel identification system involving a logo such as the ‘Compost OK’ mark would allow consumers to identify these products There does not appear to be any significant impediment, however, to the introduction of biodegradable products destined for landfill disposal, such as garbage bags, landfill covers, and non-recycled shopping bags, provided that they meet the appropriate testing standards.

14.5. Education and Training for Awareness Development

With the introduction of biodegradable plastics into the consumer packaging market, effective education is essential. It will be important to educate the public that biodegradable plastics do not degrade instantaneously to avoid the potential to increase the incidence of littering. In addition, clear disposal routes must be identified and available to consumers to appropriately manage this waste stream. For example, to stipulate that an item should be disposed of to the consumer’s green organics bin which is destined for a commercial composting operation would result in issues where residents are not provided with these services.

CONCLUSION

Now a days worldwide peoples are dependent on the uses of polymer. Daily life, house hold purpose, Industrial sectors, Medical sectors, Agricultural sectors etc. in everywhere the uses of polymers are increasing day by day. Due to the availability, low cost, replaceable and easy handling, peoples are using polymers haphazardly in everywhere without any precautions. At present most of the using polymers are non-degradable and some are degradable, but takes long time to degrade in the nature. Actually polymer degradation is a change in the properties- tensile strength, color, shape, molecular weight etc. of a polymer or polymer-based product under the influence of one or more environmental factors. Degradation of polymers depends on some vital factors, such as-chemical structure, molecular weight, heat, light, pressure and also presence of microorganism and chemicals etc. Degradation of polymers can be useful for recycling/reusing the polymer waste to prevent or reduce environmental pollution. Degradation can also be induced deliberately to assist structure determination of a polymer. Polymer degradation has some remarkable negative impact on the environment, such as -emissions of greenhouse gas, enhancement of aquatic COD and BOD, decreasing of land fertility, compost toxicity, serious water pollution, disposal problem of unmanageable residues etc.

To protect the environment some advisory steps should be taken such as Development of standards and testing, Life cycle assessment, Determination of appropriate disposal environments. Environmental benefits that may be derived from the use of biodegradable polymers through the use of renewable energy resources and reduced greenhouse gas emissions. Awareness of the waste problem and its impact on the environment has awakened new interest in the area of degradable polymers. The major advantages of biodegradable polymers are that they can be composted with organic wastes and returned to enrich the soil, their use will not only reduce injuries to wild animals caused by dumping of conventional plastics but will also lessen the labor cost for the removal of plastic wastes in the environment because they are degraded naturally, their decomposition will help increase the longevity and stability of landfills by reducing the volume of garbage, they could be recycled to useful monomers and oligomers by microbial and enzymatic treatment. Recently, the development of the manufacture of such polymers has been observed. Using biodegradable polymers in many fields of industry, instead of synthetic materials, may significantly help to protect the natural environment.

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