Polymer Biodegradation Basics and Approaches to Improve Biodegradability of Polymer: A Review

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Abstract - **Biodegradable polymers have opened an emerging area of great interest because of their wide applications in the environment and biomedical field. The biodegradable polymers are extensively employed for biomedical applications due to their bio-compatibility, biodegradability, flexibility, and minimal side effects. The industrial applications of various polymers are limited to their non-biodegradability. The kinds of parameters that impact the biodegradability of polymers include hydrophobicity, high molecular weight, chemical and structural compositions of polymers that hinder their biodegradation. The different approaches can be useful to improve the biodegradability of existing polymers and to make them eco-friendly. In the present review, the author has discussed biodegradable and non-biodegradable polymers, factors influencing polymer biodegradability, biodegradation pathways, and approaches to improve the biodegradability of polymers.**

keywords - **Polymers, biodegradable, non-biodegradable, eco-friendly polymers**

1. INTRODUCTION

A polymer is a large molecule composed of chain or rings of the linked repeating subunit (monomers). In recent times, polymers have the most popularity and applicability in various filed. They have become more crucial to human life due to their extensive applications in diverse fields. In the pharma and food companies, polymers are playing an imperative job. However, applications of most of the polymers are restricted due to their resistance to chemical, physical, and biological degradation and non-biodegradable (NBD) nature. The non-degradability of these polymers is producing a huge impact on the global environment. Thus, the development of eco-friendly biodegradable (BD) polymers is of vital importance to protect the environment and life on the earth [1, 2].

Therefore, there is an unmet need to develop new BD polymers or to improve the biodegradability of existing polymers by using suitable approaches. Nowadays, there has been significant interest in the development of polymers that degrade in the environment or under physiological conditions. Thus, the research and development of new biodegradable polymeric materials have become a hot topic in science and industry. The various approaches (insertion of weak links into polymers, compounding of polymers with pro-oxidant, blend of biodegradable polymers and non-biodegradable polymers, etc) can be useful to improve the biodegradability of the polymers [3-5].

The present review is mainly focused on BD polymers and NBD polymers, factors affecting the biodegradability of polymers. Degradation pathways, approaches to improve the biodegradability of polymers are also discussed.

2. BIODEGRADABLE POLYMERS:

The polymers which are decomposed by the action of enzyme or chemicals associated with living organisms and their secretion products are called BD polymers [1]. Figure 1 indicates the classification of biodegradable polymers.

2.1. Categories of Biodegradable Polymers [2–5]

Raw materials origin and the process used in their manufacture, categorized BD into three types which are as follows:

2.1.1. Natural Biodegradable Polymers

The natural BD polymers are obtained from natural resources like polysaccharides (starch, cellulose, lignin, chitin, and chitosan); proteins (wool, silk, collagen, gelatin, and casein); bacterial polyesters (polyhydroxyalkanoates (PHAs) and others (lignin, shellac, natural rubber, etc.)

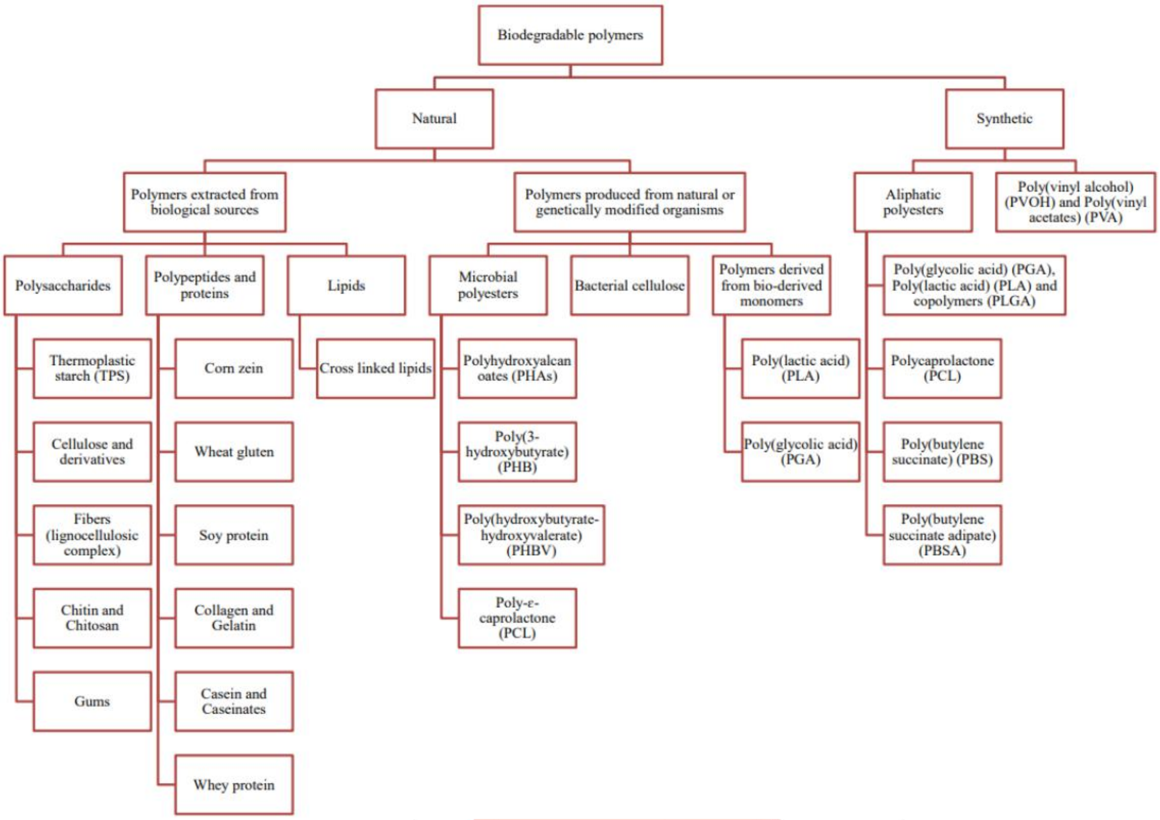

Figure 1: Classification of biodegradable polymers

2.1.2. Synthetic Biodegradable Polymer

Polymers derived from petrochemical or biological resources (feed stocks) include; polyesters, polycaprolactone (PCL), polyamides, polyurethanes, polyureas, polyanhydrides, poly (vinyl alcohol) (PVOH), poly (vinyl acetates) (PVA).

2.1.3. Biodegradable Polymer Blends

The blending of biodegradable polymers from renewable and non-renewable resources is a way of dropping the overall cost of the material and offers a method of modifying both properties and degradation rates.

2.2. Characteristics of an Ideal BD Polymer

- It should be flexible and possess a wide range of properties.
- It should be non-toxic, and possess good mechanical strength.
- It should be inexpensive.
- It should be easy to engineer.
- It should be inert to host tissue and compatible with the environment.

3. NON-BIODEGRADABLE POLYMERS:

The polymers which cannot be decomposed by the action of enzymes or chemicals associated with living organisms and their secretion products are called as NBD polymers. For instance of NBD polymers include; polyethylene poly (methyl methacrylate) polyester, polycarbonate, polyamide (nylon) polyurethane. The difference between the BD and NBD is summarized in Table 1.

Table 1: Difference between NBD and BD

Non-biodegradable Polymers	Biodegradable Polymers
Degradation process is very slow	Degradation process is slow
Rate of biodegradation is very low	Rate of biodegradation is very high
Cannot be decomposed by the living organisms	Can be decomposed by the living organisms
Costly chemicals used for decomposition	Cost free decomposition
Cannot be recycled naturally	Can be recycled naturally
Cannot be broken down into harmless substance(s) by any biological processes	Can be broken down into harmless substance(s) by the action of microorganisms like bacteria
Can pollute the environment	Cannot pollute the environment
Remain unchanged over a long period of time	Change their form and structure over time

4. FACTORS AFFECTING BIODEGRADATION [6–11]:

The various factors affecting the biodegradability of polymers are given below;

4.1. Chemical Structure

The biodegradability of polymers is ultimately controlled by the chemical structures which directly affects on ability of degradation. Functional groups biodegradation ability may be a descendant in such order; aliphatic ester > peptide bond > carbamate > aliphatic ether > methylene.

4.2. Degree and Type of Branching

Branching of the molecular chain inhibits the biodegradation. Polymers with flexible chains are easily biodegradable. Linear polymers are more easily biodegradable than branched and cross-linked polymers.

4.3. Molecular Size

The high molecular weight of the polymer is more resistant to biodegradation due to the presence of less concentration of end group in the form of unsaturation, hydroperoxide in the polymer structure.

4.4. Degree of Hydrophilicity

Polymers containing hydrophilic segments are more biodegradable than hydrophobic polymers of comparable molecular weight. The biodegradability of a polymer can be promoted by increasing the hydrophilicity of the polymer by chemical modifications.

4.5. Crystallinity

Crystalline regions of a polymer are difficult to penetrate and thus affect the rate of degradation. Amorphous areas in the polymers are easier to degrade than crystalline areas.

4.6. Environmental Factors

Temperature, moisture, salts, pH, and oxygen are required for the biodegradation process. Water is necessary for the growth of microorganisms. Polymeric materials can be biodegraded only under certain humidity and temperature has a dual effect on biodegradation. In a convinced assortment, high temperature haste up microbial metabolic processes and causes vigorous growth, this is helpful to degradation. On other hand, the temperature has a greater effect on the biological activities of proteins and enzymes. Therefore, each kind of microorganisms has its own optimal temperature for growth and reproduction. The pH value also has a great effect on the growth of microorganism. Optimal pH can increase microbial metabolism, eventually, speed up the degradation rate.

5. WAYS OF POLYMER DEGRADATION [12–14]:

Polymer degradation in the natural environment occurs in two stages. The first stage is mainly abiotic and the second stage is purely biotic.

a) Abiotic degradation
b) Biotic degradation

5.1. Abiotic Degradation

In abiotic degradation due to structural modification, there is a loss in the mechanical properties of the polymer. The polyethylene, chemical pro-oxidant, or photo-initiators or both used in film formation produce free radicals on the polyethylene chain causing the loss of its physical properties and make them more accessible to microbial degradation. The environmental factors, causing chemical degradation of polymers are as follows;

5.1.1. Thermal Degradation

All polymers can be degraded by the effect of heat, whether present at the service temperature or applied during polymer processing. When heated to increase in the bond rupture, polymer degradation results from the production of free radicals, which causes either random splitting into smaller molecules of varying chain length (e.g. polyethylene) or depolymerization of the polymer to monomer or monomers (e.g. polymethylmethacrylate (PMMA).

5.1.2. Photo-oxidative Degradation:

Chemical bonds in polymers can be broken by the highest-energy UV waves of the solar spectrum, leading to their photo-degradation. Photo-oxidative degradation is a radical-based auto-oxidative process. Chromophoric species such as carbonyl groups, hydroperoxides, unsaturation, metallic impurities such as iron and titanium, polynuclear aromatic compounds (PNA) such as anthracene, phenanthrene, and naphthalene are responsible for the UV absorption.

5.1.3. Hydrolytic Degradation or Bioerosion

It is key way of degradation of biodegradable polymers, especially synthetic polymers. Depending on the erosion mechanism degradable polymers are classified into the surface (or heterogeneous) and bulk (or homogeneous) eroding materials.

5.1.4. Degradation due to Environmental Stress Cracking (ESC)

ESC is defined as the catastrophic failure of a material at a stress much lower than its ultimate strength, due to the combined effects of stress and environment. The stress-cracking agents that occurred in the environment are detergents, alcohols, oils, solvents, chemicals, and vapours of polar liquids.

5.1.5. Chemical Degradation

Chemical degradation of corrosive gases and liquids can affect most polymers, except polytetrafluoroethylene (PTFE) and polyether ether ketone (PEEK). Ozone, atmospheric pollutants (such as nitric and sulphuric oxides), and acids like sulphuric, nitric, and hydrochloric will attack and degrade most polymers.

5.1.6. Mechano-chemical Degradation

Because of their length, polymers have the ability to convert mechanical energy applied in shear into main-chain bond energy resulting in a screw extruder; macro alkyl radicals are formed leading to accelerated oxidation.

5.1.7. Radiation-induced Degradation:

Transfer of energy by gamma-ray or electron beam irradiation onto polymer backbone results in severe degradation of the polymer. Irradiation produces free radicals, which, depending on the chemistry of the polymer, initiates degradation (e.g. polyethylene, polypropylene).

5.1.8. Degradation due to Weathering

All plastics subjected to long-term exposure to weather (heat, light, ionizing radiation, oxygen, ozone, humidity, rain, wind, etc) degrades to a different extent, depending on their composition.

5.2. Biotic Degradation

In this, polymers are broken down into smaller structures by enzymes which are produced by living microbial organism. Low molecular weight products formed by the abiotic degradation are consumed by microorganisms, leaving CO_2, water, and other harmless substances at the end of the metabolic process.

6. APPROACHES TO IMPROVE BIODEGRADABILITY OF POLYMERS [15–22]:

BD polymers break down after its proposed use to result in natural by-products such as gases, water, biomass, and inorganic salts. Polymers with a main chain containing only carbon-carbon bonds (except polymers possessing large number of polar groups on the main chain) show little or no susceptibility to enzyme catalyzed degradation reactions. The approaches like insertion of weak links within the backbones of polymers (polymer modification) to consent the controlled degradation of an initially high molecular weight polymer into a low molecular weight oligomer, which can be utilized and consumed by microorganisms through the biodegradation process. The various methods or modifications used to improve the biodegradability of polymers are discussed below.

6.1. Insertion of Weak Links into Polymers

In this approach, mainly two types of polymer modification used to obtain biodegradable polymers from synthetic polymers which include insertion of functional (ester) groups in the main chain which can be broken by chemical hydrolysis and insertion of functional (carbonyl) groups in the main chain which can be broken by photochemical reactions.

6.2. Compounding of Polymer with Pro-oxidants and Photosensitizer

The thermal and/or photolytic pre-biotic treatment, which constitutes the major route for promoting the eventual biodegradation of polyethylene, could be enhanced by using pro-oxidant additives. The pro-oxidants (divalent transition metal salts of higher aliphatic acids) such as stearic acid, unsaturated elastomers as auto-oxidizable substances, and transition metal complexes such as dithiocarbonates as photosensitizers or photoinitiators.

6.3. Blends of Biodegradable and Non-Biodegradable Polymers

The most frequently adopted approach to the degradability design of polymers is the introduction of pro-degradant additives such as starch and cellulose into synthetic polymers. When these blends are deposited in the environment, easier breakdown of polymer into tiny pieces is produced that increases surface area accessible to microorganisms.

6.4. Modified Natural Polymers

The readily biodegradable polysaccharide polymers (starch, cellulose, cellulose, chitosan, and chitin) can be transformed into new biodegradable polymers by co-blending modification.

6.5. Chemically Synthesized Polymers

These polymers containing ester, amide, and peptide bonds like natural polymers are chemically synthesized. The presence of above functional moieties in the polymer chain can cause rapid biodegradation of polymers. The precursors like L-lactic acid and glycerol can be used to synthesize a biodegradable material (poly (lactic acid-co-glycerol) under the optimal synthetic conditions.

6.6. Microbiologically Synthesized Polymers

The microorganism can utilise organic matters (glucose or starch as food sources) to synthesize complex polymers. Polyhydroxyalkanoates (PHA) is microbiologically synthesized exceedingly biocompatible and biodegradable plastics. The other examples of such polymers include silk, polysaccharides, polyesters, etc. The main limitation of this method is complexity of separation of product.

6.7. Enzymatic Synthesis

It is one of the novel methods for the synthesis of biodegradable polymeric materials with abscence any by-products due to the high specificity of the enzymes. The chief benefits of this method is easy product separation and economic. Besides, the enzymes can be recycled. The method can be employed to synthesize various (fully biodegradable) polymers such polyester, polysaccharide, polyamide, etc.

6.8. Chemo-Enzymatic Synthesis

This method combines the conventional polymerization with the exceedingly proficient and regio-selective enzymatic approach and is therefore, a very promising tactic for the preparation of BD polymers.

CONCLUSION:

BD polymers have gained significant attention in the last decades due to their imminent applications in the field of medicine, agriculture, cosmetics, packaging, environmental protection, and maintenance of physical health, and other areas. Nowadays, BD polymers are augmenting the attraction of the researchers.

Though few BD polymers are available however, they are allied with several restrictions such as strength and dimensional stability, processing problems and are expensive. The recent advances in BD polymers show that polymers are important owing to their inherent biodegradability, biocompatibility, and easy availability. The kinds of new techniques have been devised with objective of improving both BD and mechanical properties of the polymers. Diverse new BD polymer preparation techniques with the advancement of smart design will be explored, and better biodegradable polymers would be developed.

Competing interest
The authors declare that they have no competing interests.

Acknowledgement
We are greatly thankful to our Head of Institute and Institute Management for supporting this research project.

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