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Review on Biodegradable Polymers

Mr.Abhishek Makani, Dr.Vimal Kumar, Dr.Jaswandi Mehetre, Dr.Joyti Tomar,

Ms. Pratiksha B. Kanhere, Ms. Dolly Pawar

Lab-Assistant, Department of Pharmacy, School of Pharmacy, ITM (SLS) Baroda University, Dhanora
Tank Road, Off Halol Highway, Near Jarod, Paldi, Vadodara, Gujarat, India

Dean, Department of Pharmacy, School of Pharmacy, ITM (SLS) Baroda University, Dhanora Tank Road,
Off Halol Highway, Near Jarod, Paldi, Vadodara, Gujarat, India

HOD, Department of Pharmacy, School of Pharmacy, ITM (SLS) Baroda University, Dhanora Tank Road,
Off Halol Highway, Near Jarod, Paldi, Vadodara, Gujarat, India

Asst. Professor, Department of Chemistry, School of Sciences, ITM (SLS) Baroda University, Dhanora
Tank Road, Off Halol Highway, Near Jarod, Paldi, Vadodara, Gujarat, India

Asst. Professor, Department of Chemistry, School of Sciences, ITM (SLS) Baroda University, Dhanora
Tank Road, Off Halol Highway, Near Jarod, Paldi, Vadodara, Gujarat, India

Asst. Professor, Department of Chemistry, School of Sciences, ITM (SLS) Baroda University, Dhanora
Tank Road, Off Halol Highway, Near Jarod, Paldi, Vadodara, Gujarat, India

ABSTRACT: Current trends in biodegradable polymers indicate noteworthy developments in terms of unique design strategies and engineering to offer advanced polymers with comparably good performance. However, there are numerous shortfalls in terms of either technology or cost of manufacture especially in the case of applications in environmental pollution. Hence, there is a need to have a fresh perspective on the design, properties and utilities of these polymers with a view to developing strategies for future developments. The biodegradable polymers can be synthesized from fossil resources but main manufactures are attained from renewable resources. The paper reviews the present state of biodegradable polymers and discusses the salient features of the design and properties of biodegradable polymers. Microbial and enzymatic biodegradation of plastics and some factors that affect their biodegradability are also discussed. Special emphasis is given to the problems and prospects of (i) approaches adopted to make non-biodegradable synthetic polymers such as polyethylene biodegradable and (ii) biodegradable polymers and copolymers made from renewable resources especially poly(lactic acid) based polymers and copolymers which are emerging as the candidate biodegradable materials for the future.

Which is biodegradable super absorbent material?

Polyitaconic acid, polyvinyl alcohol and polysaccharides are some of the key products used as biodegradable superabsorbent materials in the industry.

I. INTRODUCTION

Biodegradation is a natural process by which organic chemicals in the environment are converted to simpler compounds, mineralised and redistributed through elemental cycles such as the carbon, nitrogen and sulphur cycles. Synthetic plastics are resistant to degradation, and subsequently their disposal is stimulating a global drive for the establishment of biodegradable polymers. As the development of these materials rises, industry must discover unique applications of them. Material usage and final mode of biodegradation are reliant on the composition and processing technique employed. An integrated waste management system is also required in order to efficiently use, recycle, and dispose of biopolymer materials. Reduction in the consumption of sources, reuse of existing materials and recycling of rejected materials must also be considered. Polymer materials are solid, non-metallic compounds of high molecular

weights. They are made of repeating macromolecules, and possess varying characteristics depending upon their composition. Each macromolecule that comprises a polymeric material is known as a mer unit. A single mer is called a monomer, while repeating mer units are called as polymers. A variety of materials both renewable and non-renewable are employed as feedstock sources for modern plastic materials. Plastics that are obtained from non-renewable feedstocks are generally petroleum-based, and strengthened by glass or carbon. Renewable resource feedstocks comprise microbial-grown polymers and those extracted from starch and its derivatives. It is likely to reinforce such materials with natural fibres, from plants such as flax, jute, hemp, and other cellulose.

Biodegradable plastics are environmentally-friendly as they can be produced from renewable feedstocks, thus decreasing greenhouse gas emissions. For example, polyhydroxyalkanoates (PHA) and lactic acid (raw materials for PLA, polylactic acid) may be formed by fermentative biotechnological processes by means of agricultural products and microorganisms. The major advantage of biodegradable plastics is the low accumulation of bulky plastic materials in the environment which in turn reduces the cost of waste management. Moreover, biodegradable

plastics may be reprocessed to useful metabolites by microorganisms and enzymes. The degradation of some petroleum based plastics may also be done by biological processes. For example some aliphatic polyester such as PCL and PBS can be degraded with enzymes and microorganisms. Studies have also shown that aliphatic polycarbonates have been found to possess some degree of biodegradability.

II. HISTORY

The first known use of biodegradable in a biological context was in 1959 when it was employed to describe the breakdown of material into innocuous components by microorganisms.

What are the 2 types of biodegradation?

Biodegradation can occur by two different mechanisms: namely **hydro-biodegradation (hydrolysis followed by oxidation)** **oxo-biodegradation**

III. BIODEGRADABILITY OF MATERIALS

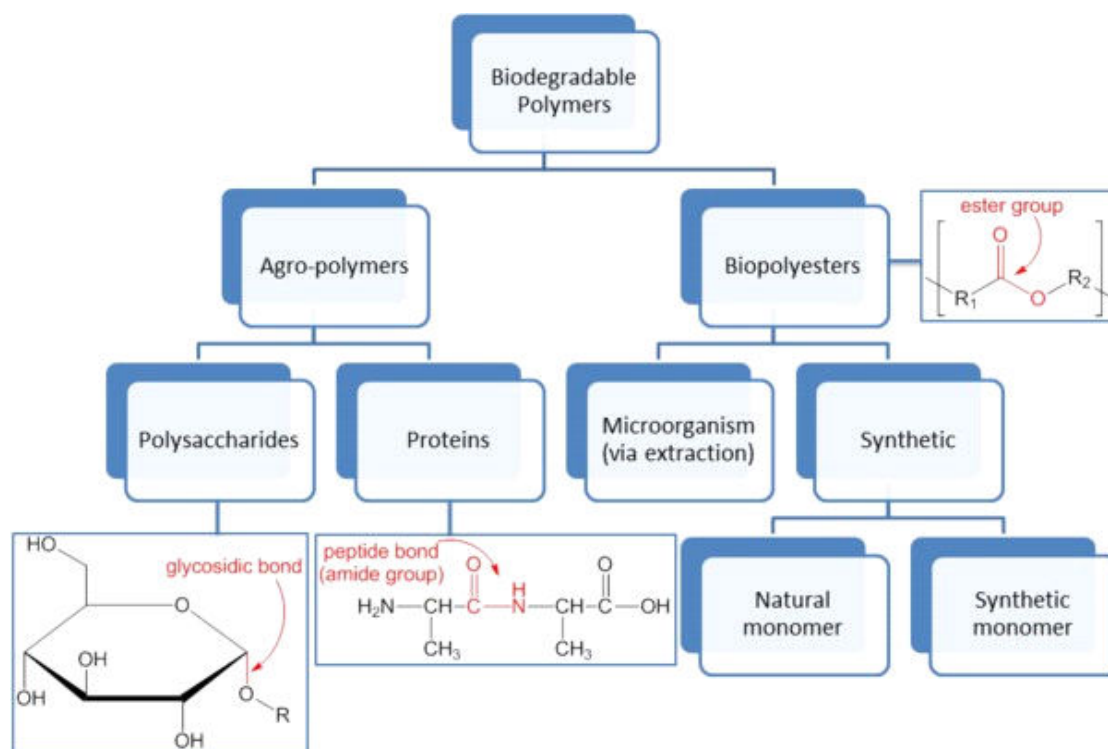
The American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO) define degradable plastics as those which undergo a significant change in chemical structure under specific environmental conditions. These changes result in a loss of physical and mechanical properties. Biodegradable plastics suffer degradation from the action of naturally occurring microorganisms such as bacteria, fungi and algae. Plastics are also categorized as photodegradable, oxidatively degradable, hydrolytically degradable, or those which may be composted. Usually, the adherence of microorganisms on the surface of plastics followed by the occupation of the exposed surface is the main mechanisms taking place in the microbial degradation of plastics. The enzymatic degradation of plastics by hydrolysis occurs by a two-step process. In the first step, the enzyme binds to the polymer substrate and then catalyses a hydrolytic cleavage of the polymer. Polymers get degraded into low molecular weight oligomers, dimers and monomers and lastly to CO₂ and H₂O. The degradation potential of various microorganisms towards a polymer is usually assessed by using a clear zone method with agar plates. Agar Biodegradable Polymers 181 plates having blended polymers are injected with microorganisms. These polymerdegrading microorganisms excrete extracellular enzymes that diffuse through the agar and then degrade the polymer into water soluble substances.

Using this technique, it was observed that poly (hydroxybutyrate) (PHB), polypropiolactone (PPL) and Polycaprolactone (PCL) degraders are extensively dispersed in diverse environments.

Most of the strains which are able to degrade PHB belong to different taxonomy such as Gram- positive and Gram-negative bacteria, Streptomyces and fungi. About 39 bacterial strains of the classes Firmicutes and Proteobacteria have been reported to degrade PHB, PCL, and PBS, but not PLA. Only a few microorganisms have been isolated and identified which can degrade PLA. In the different ecosystems the population of aliphatic polymer-degrading microorganisms have been found to be in the following order: PHB = PCL > PBS > PLA.

Biodegradable polymers comprise ester, amide, or ether bonds. In general, biodegradable polymers can be grouped into two large groups on basis of their structure and synthesis. One of these groups is agro-polymers, i.e. those derived from

biomass. The other consists of bio polyesters, which are those derived from microorganisms or synthetically made from either naturally or synthetic monomers .

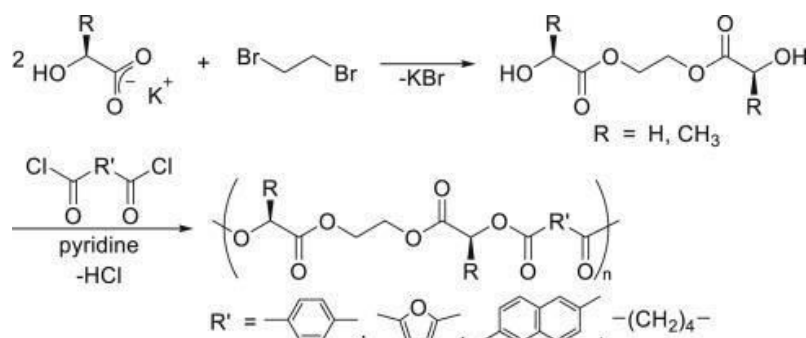


Biodegradable polymers organization based on structure and occurrence

Examples of agro-polymers are polysaccharides, such as starches present in potatoes or wood, and proteins, such as animal based whey or plant derived gluten. Polysaccharides consist of glycosidic bonds, which take a hemiacetal of a saccharide and bind it to an alcohol along with dehydration. Proteins are consisting of amino acids, which have various functional groups.

These amino acids come together again through condensation reactions to form peptide bonds, which are consisting of amide functional groups. Examples of bio polyesters includes polyhydroxybutyrate and polylactic acid.

SYNTHESIS



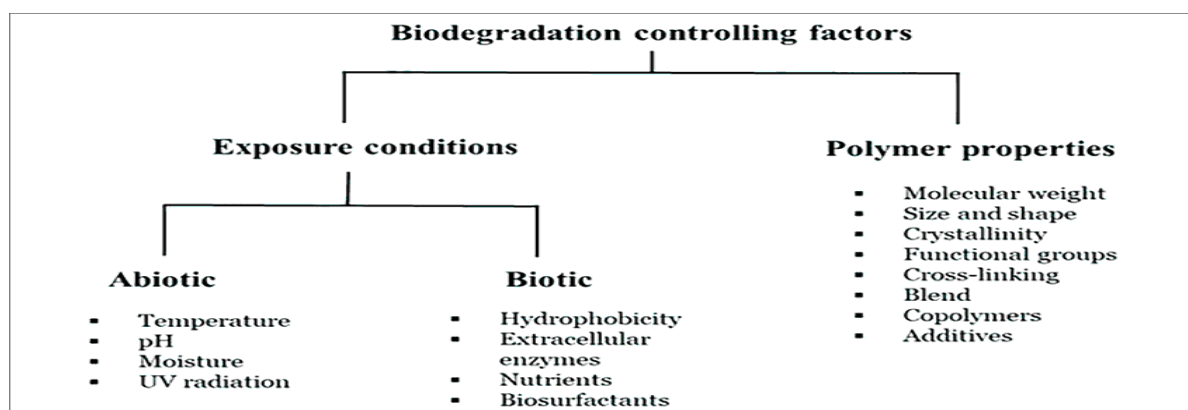
IV. METHODS OF BIODEGRADATION

The breakdown of polymer materials takes place by microbial action, photo degradation, or chemical degradation. All three methods are categorized under biodegradation, as the end products are stable and found in nature. Many biopolymers can be dumped in landfills, composts, or soil. The materials will be broken down, only if the required microorganisms are present. Normal soil bacteria and water are normally sufficient, adding to the appeal of microbial reduced plastics. Polymers which are based on naturally grown materials such as starch or flax fibre are vulnerable to degradation by microorganisms. The material may or may not decompose more rapidly under aerobic conditions, subject to the formulation used, and the microorganisms required. In the case of materials where starch is added as an additive to a conventional plastic matrix, the polymer in contact with the soil and/or water is attacked by the microorganisms. The microbes digest the starch, leaving behind a porous, sponge like structure with a huge interfacial area, and lower structural strength. When the starch constituent has been depleted, the polymer matrix begins to get degraded by an enzymatic attack. Each reaction results in the scission of a molecule, gradually reducing the weight of the matrix until the whole of the material has been digested. Another approach to microbial degradation of biopolymers comprises growing of microorganisms for the specific purpose of digesting polymer materials. This is a more intensive process that eventually costs more, and avoids the use of renewable resources as biopolymer feedstock. The microorganisms required are designed to aim and breakdown petroleum based plastics. Although this method reduces the amount of waste, it does not aid in the conservation of nonrenewable resources.

Photodegradable polymers undergo degradation from the action of sunlight. In many cases, polymers are attacked photo chemically, and broken down to small pieces. Further microbial degradation must occur later for true biodegradation to be achieved. Polyolefin, a type of petroleum-based conventional plastic, are the polymers found to be most vulnerable to photo degradation. Proposed approach for further developing photodegradable biopolymers includes incorporating additives which escalate photochemical reactions e.g. benzophenone, amending the composition of the polymers to comprise more UV absorbing groups (e.g. carbonyl), and synthesizing new polymers with light sensitive groups. An application for biopolymers which experience both microbial and photo degradation is in the usage of disposable mulches and crop frost covers. Some biodegradable polymer materials experience a rapid dissolution when exposed to particular (chemical based) aqueous solutions. As mentioned earlier, Environmental Polymer's product 'Depart' is soluble in hot water. Once the polymer dissolves, the remaining solution consists of polyvinyl alcohol and glycerol. Similar to many photodegradable plastics, total biodegradation of the aqueous solution occurs later, through microbial digestion. The necessary microorganisms are conveniently found in wastewater treatment plants. Procter & Gamble has developed a product similar to Depart, named Nodax PBHB. Nodax is alkaline digestible, which means that exposure to a solution with a high PH causes a fast structural breakdown of the material. Biopolymer materials which disintegrate on exposure to aqueous solutions are desirable for the disposal and transport of biohazards and medical wastes.

Industrial "washing machines" are designed to dissolve and wash away the aqueous solutions to promote microbial degradation.

Factors Affecting the Biodegradability of Polymers



The biodegradability of plastics depends upon their properties. The mechanism of biodegradation is affected by both the physical and chemical properties of plastics. The properties such as surface area, hydrophilic and hydrophobic character, the chemical structure, molecular weight, glass transition temperature, melting point, elasticity and crystal structure of polymers play important role in the biodegradation processes. Usually, polyesters with side chains undergo degradation less easily than those without side chains. Since molecular weight determines many physical properties of the polymers so it also plays an important role in determining their biodegradability. In general, biodegradability the polymer decreases with increasing the molecular weight of the polymer. Furthermore, the morphology of polymers also greatly affects their rates of biodegradation. As enzymes mostly attack the amorphous areas of a polymer hence the degree of crystallinity is also a key factor affecting biodegradability. This is because the molecules in the amorphous part of polymer are loosely packed so make it more prone to degradation. However, the crystalline part of the polymer is more resistant than the amorphous region due to closer packing of the molecules. The studies have shown that the rate of degradation of PLA decreases with an increase in crystallinity of the polymer. The melting temperature (T_m) of polymers also has a large effect on the enzymatic degradation of polymers. The higher the melting point of the polymer, the lower is the biodegradation of the polymer.

$$T_m = \Delta H / \Delta S$$

where ΔH is the enthalpy change on melting and ΔS is the entropy change on melting.

Aliphatic Polyesters from Renewable Resources (Agro-Resources) Polylactic Acid (PLA)

PLA, $[-O(CH_3)CHCO-]_n$ Polylactic acid is a linear aliphatic polyester which is a biodegradable and biocompatible thermoplastic that can be formed by fermentation from renewable resources. It can also be synthesized by condensation polymerization of lactic acid or from lactide by its ring opening polymerization in the presence of a catalyst. The production of PLA from lactic acid was established by Carothers in 1932. Lactic acid is also formed via starch fermentation, as a co-product of corn wet milling. The ester linkages present in PLA are sensitive to chemical hydrolysis as well as enzymatic chain cleavage. PLA is usually blended with starch to enhance its biodegradability and decrease expenses. But, the starch-PLA blend has somewhat brittleness which poses a major drawback in many of its applications. This limitation can be overcome by using various low molecular weight plasticisers such as sorbitol, glycerol and triethyl citrate. The PLA-degraders have not been found to be widely distributed as shown by ecological studies on the population of PLA-degrading microorganisms in diverse environments and therefore PLA is less prone to microbial attack relative to other microbial and synthetic aliphatic polymers.

However several strains of genus *Saccharotrix* and *Amycolatopsis* are capable of degrading PLA. Williams studied the enzymatic degradation of PLA by means of proteinase K, bromelain and pronase enzymes. Among these enzymes, proteinase K from *Tritirachium album* has been found to be the most effective for PLA degradation. Many esterase-type enzymes, especially *Rhizopus delemar* lipase have been reported to accelerate the degradation of PLA oligomers by Fukuzaki et al. PLA are mainly used as thermoformed products such as drink cups, containers, takeaway food trays and planter boxes. Due to its good rigidity characteristics, the material has potential to replace polystyrene and PET in some of their applications.

Poly(3-Hydroxybutyrate) (PHB)

PHB, $[-O(CH_3)CHCH_2CO-]_n$ is a natural polymer formed by several bacteria as a resource to store carbon and energy. This polymer has attracted interest worldwide because it can be produced from renewable low-cost feedstocks and the process of polymerizations can be performed under mild conditions without causing much impact on environment. Moreover, it undergoes biodegradation in both aerobic and anaerobic conditions, without producing any toxic degradation products. Several aerobic and anaerobic PHB-degrading microorganisms have been isolated from soil such as *Pseudomonas lemoigne*, *Aspergillus fumigatus*, *Comamonas* sp., *Acidovorax faecalis* and *Variovorax paradoxus*, from activated and anaerobic sludge such as *Alcaligenes faecalis*, *Illyobacter delafieldi*, *Pseudomonas*, and from seawater and lake water such as *Comamonas testosterone*, *Pseudomonas stutzeri*. The percentage of PHB-degrading microorganisms in the environment has been found to be 0.5-9.6%. Majority of the PHB-degrading microorganisms has been found to be capable of degrading PHB at ambient or moderate temperatures and only a few of them are capable of degrading PHB at higher temperature. Tokiwa et al. emphasized that as composting at high temperature is the most promising technology for recycling biodegradable plastics so the thermophilic microorganisms which can degrade polymers are significant in the composting process. A thermophilic *Streptomyces* sp. Isolated from

soil can degrade PHB, PES, PBS and poly [oligo (tetramethylene succinate)-co-(tetramethylene carbonate)] . A thermotolerant *Aspergillus* sp. has been found to degrade 90% of PHB film after five days cultivation at 50 °C

Aliphatic Polyesters from Fossil Resources (petroleum based) Polycaprolactone (PCL)

Polycaprolactone (PCL) $[-OCH_2CH_2CH_2CH_2CH_2CO-]_n$ is a biodegradable synthetic aliphatic polyester prepared by the ring-opening polymerization of caprolactone in the presence of metal alkoxides such as aluminium isopropoxide, tin octoate...). PCL has a low melting-point, between 58-60°C, low viscosity and it is easy to process.

PCL has been found to be degraded by the action of aerobic and anaerobic microorganisms which are extensively distributed in different ecosystems. Besides, the degradation of high molecular weight PCL when studied using *Penicillium* sp. strain 26-1 (ATCC 36507) isolated from soil, the PCL was found to be nearly totally degraded in 12 days. This strain has also been observed to degrade unsaturated aliphatic and alicyclic polyesters but it does not assimilate aromatic polyesters. PCL has been found to be completely degraded by thermotolerant PCL- degrading microorganism identified as, *Aspergillus* sp. strain ST-01, isolated from soil after 6 days incubation at 50 °C PCL can also be degraded by enzymes such as esterases and lipases.

The rate of degradation of PCL depends on its molecular weight and degree of crystallinity. Enzymatic degradation of PCL by *Aspergillus flavus* and *Penicillium funiculosum* has been observed to be faster in the amorphous region. The biodegradability of PCL may be improved by copolymerization with aliphatic polyesters because copolymers have lower T_m and lower crystallinity as compared to homopolymers, and hence are more prone to degradation. Tokiwa et al. have studied the hydrolysis of PCL and biodegradation by fungi. They have revealed that PCL can easily be enzymatically degraded. The marine biodegradation of PCL has been studied by Janik et. al. (1988) and they have reported that the PCL in seawater was completely decomposed after eight weeks, whereas in salt solution it had lost only 20% of its weight.

Hence it indicates that the enzymes in the seawater support to speed up the biodegradation of PCL and other biodegradable plastics.

Polymer Blends

Blends of Polyester with Other Polymers

The biodegradable polymers are blended with other polymers in an approach to reduce the overall cost of the material and modify the required properties and degradation rates.

Blending is a much easier and rapid way to attain the desired properties relative to copolymerization method.

wamoto et al. obtained blend plastics by mixing PCL with conventional plastics such as low density polyethylene (LDPE), poly(ethyleneterephthalate) (PET), polypropylene (PP), polystyrene (PS), PHB and nylon 6 (NY) and estimated their enzymatic degradabilities. It was observed that the higher the miscibility of PCL and conventional plastics, the tougher the degradation of PCL in their blends by *R. arrhizus* lipase.

Various blends of PHB have been obtained with biodegradable and nonbiodegradable polymers and polysaccharides. The studies of enzymatic degradation of these blends using PHB depolymerase from *Alcaligenes feacalis* T1 showed that the weight loss of the blends reduced linearly with rise in the amount of PBA, PVAc or PCL.

Koyama and Doi estimated the various properties and biodegradability of PHB/PLA blend. It was observed that polymer blends having PHB generally showed improved properties and biodegradability as compared to pure PHB.

Blends of Polyesters and Starch

Blending of synthetic polymers with starch provides cost and performance advantages because starch is renewable, cheaper and is available throughout the year. It has been observed that blends of PCL and granular starch exhibit biodegradation to greater extent.

PLA and starch are preferred for obtaining polymer blends as both are biodegradable and are derived from renewable resources. In their blends, starch improves the biodegradability and lowers the cost of the polymer whereas PLA can regulate the mechanical properties of the blend.

Ratto et al. investigated the properties and biodegradability of PBS/A and corn starch (5%-30% w/w) blends and reported that the tensile strength reduced with rise in starch content. The rate of biodegradation has been observed to increase significantly when the starch content was increased to 20%, using soil burial test.

Applications of biodegradable plastics

Research and development is only a part of the work that is done in order to familiarize the use of biodegradable polymer material. The design of such materials commonly begins with a conceptual application. It is expected to substitute an existing material, or to complement one. Sectors where applications for biopolymers have introduced comprise medicine, packaging, agriculture, and the automotive industry. Many materials that have been developed and commercialized are useful in more than one of these categories. Biopolymers that may be employed in packaging continue to receive more consideration than those designated for any other application. All levels of government, predominantly in China and Germany, are endorsing the widespread use of biodegradable packaging materials in order to lessen the volume of inert materials currently being disposed in landfills, inhabiting scarce available space. It is estimated that 41% of plastics are applied in packaging, and that almost half of that volume is used to package food products. The renewable and biodegradable characteristics of biopolymers are what render them appealing for innovative usages in packaging. The end usage of such products varies widely. The starch material is treated by an acetylation process, chemical treatments, and post-extrusion steaming. Mechanical properties of the material are adequate, and true biodegradability is attained. The biopolymer materials suited for packaging are often used in agricultural products. Ecoflex, generally is used in both areas. Young plants which are particularly prone to frost may be covered with a thin Ecoflex film. At the end of the growing season, the film can be worked back into the soil, where it is broken down by the suitable microorganisms. It is concluded that the use of a clear plastic mulch cover immediately after seeding rises the yield of spring wheat if used for less than 40 days. Therefore, plastic films that commence to degrade in average soil conditions after added. The medical world is continuously changing, and consequently the materials employed by it also see recurrent adjustments. The biopolymers used in medical fields must be compatible with the tissue they are found in, and may or may not be anticipated to break down after a given time period. It is reported that researchers working in tissue engineering are attempting to develop organs from polymeric materials, which are suitable for transplantation into humans. The plastics would need injections with growth factors in order to encourage cell and vascular growth in the new organ. Work accomplished in this area comprises the development of biopolymers with adhesion sites that act as cell hosts in giving shapes that resemble different organs.

V. CONCLUSION

The sectors of agriculture, automotives, medicine, and packaging all need environment friendly plastics and polymers. Because the level of biodegradation may be tailored to specific needs, each industry is able to generate its own ideal material. The various modes of biodegradation are also a key advantage of such materials, because disposal methods may be changed to industry specifications. Biodegradable plastic is an innovative way of resolving the plastic disposal problem from the viewpoint of development of new materials. Environmental responsibility is constantly increasing in importance to both consumers and industry. For those who yield biodegradable plastic materials, this is a key advantage. Biopolymers limit carbon dioxide emissions during manufacture, and degrade to organic matter after disposal. Although synthetic plastics are a more economically feasible choice than biodegradable ones, an augmented availability of biodegradable plastics will permit many consumers to choose them on the basis of their environmentally responsible disposal. The processes which hold the maximum potential for further improvement of biopolymer materials are those which employ renewable resource feedstocks. Biodegradable plastics containing starch and/or cellulose fibres appear to be the most likely to experience persistent growth in usage. Microbial grown plastics are scientifically sound, and a novel idea, but the infrastructure required to commercially expand their use is still exorbitant, and difficult to develop. Time is of the essence for biodegradable polymer development, as society's current views on environmental responsibility make this an ideal time for further growth of biopolymers.

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