

# Biodegradable Polymers

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**Abstract:** *Biodegradable materials find application in several fields such as agriculture, medicine, and packaging. Biodegradable polymers have garnered more attention in recent years. One can distinguish between two types of biodegradable polymers: natural and manufactured polymers. Certain polymers are made using feedstocks that come from either biological (renewable resource) or petroleum (non-renewable resource) sources. Natural polymers typically have less benefits than manufactured ones. An overview of the many biodegradable polymers that are now in use, their characteristics, and recent advancements in their synthesis and uses are provided in the review that follows.*

**Keywords:** Biodegradable polymers, polyesters, polyamides, polyurethanes, biopolymers, and biodegradable polymer blends

## I. INTRODUCTION

The same durability qualities that make plastics perfect for a wide range of uses, including hygiene products, building materials, and packaging, can cause issues with waste disposal when it comes to traditional petroleum-derived plastics. These materials are not easily biodegradable and build up in the environment due to their resistance to microbial degradation. Additionally, the price of oil has significantly climbed recently. Interest in biodegradable polymers, and particularly biodegradable biopolymers, has increased as a result of these findings. In the 1980s, biodegradable polymers and plastics were first made available. Biodegradable plastics come from a variety of sources, including natural and manmade polymers. While synthetic polymers are made from non-renewable petroleum resources, natural polymers are readily available in huge quantities from renewable sources.

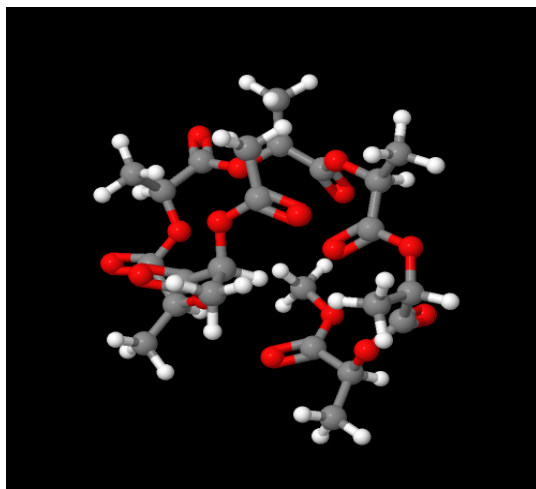
Biodegradation occurs due to the catalytic activity of enzymes and/or chemical breakdown linked to living organisms. There are two stages to this event. The first is the breakage of the polymers into species with lower molecular masses by biotic (degradation by microbes) or abiotic (oxidation, photodegradation, or hydrolysis) events. The polymer fragments are then mineralized after being bioassimilated by bacteria. The chemical makeup of the polymer, the environment in which it degrades, and its place of origin all affect how biodegradable it is. A review of polymer biodegradation mechanisms and estimate methods has been conducted. The mechanical properties of biodegradable materials are contingent upon various factors such as their chemical composition, manufacturing process, storage and processing attributes, aging, and application circumstances (1,2,3,4,5,6).

### Polyesters

Polyester is a synthetic or man-made fiber material. Shortened from its technical name, polyethylene terephthalate (PET), which, if born, would be its legal name, is made by mixing ethylene glycol and terephthalic acid. Made in a lab from chemical compounds, polyester is a kind of plastic[7]

### Aliphatic polyesters:-

Because of its significant diversity and synthetic versatility, this class of biodegradable polymers has been investigated the most. A wide range of monomers are available for use. There are several paths that lead to the creation of synthetic polyesters; these paths have recently been examined [8]. Low molecular weight polymers are preferentially produced through polycondensation of difunctional monomers. When high molecular polymers are wanted, ring opening polymerization is the method of choice. Six or seven membered lactones are polymerized using ring opening to create the majority of biodegradable polyesters [9].



[54]

Fig. 1

Because they are practically the only high molecular weight biodegradable substances [10], aliphatic polyesters have been thoroughly studied. They are biodegradable due to their hydrolyzable ester linkages. Based on the way the constituent monomers are bonded together, aliphatic polyesters can be divided into two categories. The polyhydroxyalkanoates are the first class of compounds. These polymers, HO-R-COOH, are produced from hydroxy acids. Poly(glycolic acid) and Poly(lactic acid) are two examples. This second class is represented by poly(alkene dicarboxylate). (fig no 1).

#### Aromatic copolyester:-

Numerous polyesters and copolyesters featuring aliphatic monomeric units in various sizes have been created. However, these polyesters' mechanical qualities aren't as good as non-biodegradable polymers. Furthermore, aromatic polyesters are resistant to microbiological and enzymatic attack as well as hydrolytic breakdown. Aliphatic-aromatic copolyesters were created in order to enhance them. A combination of aliphatic and aromatic monomers make up aliphatic-aromatic copolyesters. Their foundation is frequently terephthalic acid. A wide variety of aliphatic-aromatic copolyesters in varying diameters have been presented by Shaik [11].

Recent research on a variety of copolyesters, such as aliphatic acid and terephthalic acid used in biodegradable aliphatic polyesters, has been published. Novel biodegradable polymers were prepared by melt reaction using lactic acid [12], glycolic acid [13], or succinic acid [14]. These novel polymers' synthesis and hydrolytic breakdown are explained.

#### Polyamides and poly(ester-amide)s



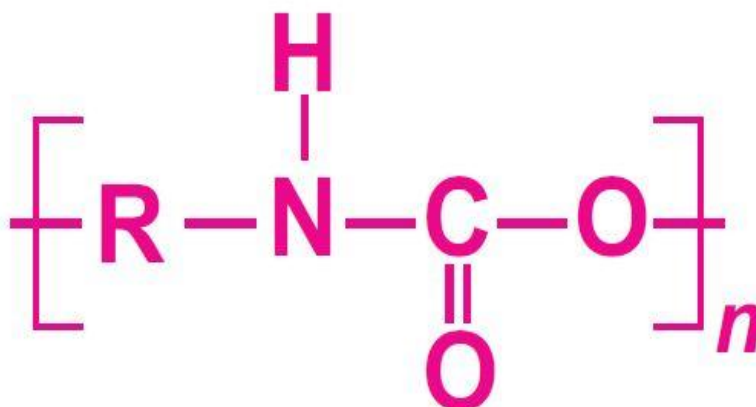
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Fig. 2

The amide bond in polyamides is the same as that in polypeptides. However, compared to polypeptides, polyamides degrade at a slower rate due to their strong chain connections and high crystallinity. Low molecular weight oligomers can be broken down by microbes and enzymes [10,15]. By adding other side groups, such as methyl, hydroxyl, and benzyl groups, by copolymerization, for example, biodegradation may be enhanced.

It is discovered that copolymers containing ester and amide groups break down easily. The more ester content there is, the faster the deterioration happens. Aliphatic poly(ester-amides) with methylene groups ranging from 2 to 8 have been synthesized from glycine, 1,6-hexanediol, and diacids [16]. These are all very crystalline polymers. (fig no.2).

**Polyurethanes:-**



[56]

**Fig. 3**

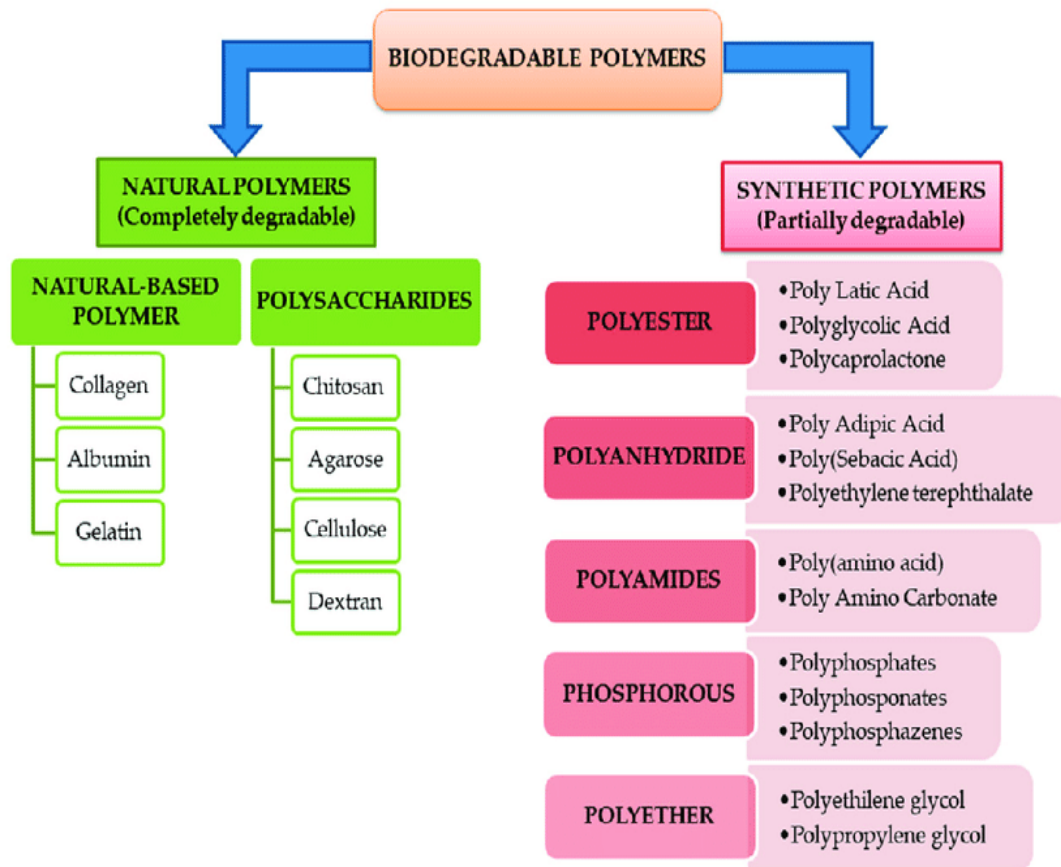
The physical and chemical characteristics of polyurethane, a special kind of polymeric material, have been considerably modified to satisfy the largely varied requirements of contemporary technologies, including coatings, bonds, fiber, lathers, and thermoplastic elastomers (17). Three constituents are used to make polyurethanes polyol, chain extender, and diisocyanate.(fig no 3).

A segmented polymer with interspersing hard and soft parts is formed as a result of their response. Polyols like polyester and polyether polyols are the source of soft members. The diisocyanate and the chain extender combine to form the hard member. The chemical makeup of the parts affects how biodegradable polyurethanes.

A suitable selection of the soft segment allows for customization of the degradation. Polyurethanes derived from polyethers exhibit resistance to biodegradation. Polyurethanes can easily biodegrade if the polyol is a polyester [18]. PCL, PLA, and PGA are examples of biodegradable polyesters [19, 20]. Soft segments, where esters bounds are found, are thought to control the rate of degradation. The urethane bounds in the hard segment are difficult to hydrolyze.

As a result, new biodegradable poly(ester urethane)s have been created. The first is made up of blocks of poly(butylene succinate) and poly(L-lactic acid) [21]. It was created using dihydroxyl terminated PLLA and PBS prepolymers in a chain extension reaction. As a chain extender, toluene-2,4-diisocyanate was used. A PBS segment led to the copolymer's crystallization. The PLLA's flexibility.

**Classification of biodegradable polymers**



[57]

Fig. 4: Schematic representation of biodegradable polymers classification after their nature.

**Polyanhydride:-**

Recently, a summary of polyanhydrides was published [22]. Due to the fact that they have two hydrolysable sites in the repeating unit, polyanhydrides are interesting biodegradable materials. The polymer backbone affects the rate of degradation. Aliphatic polyanhydrides can degrade in a few days while aromatic polyanhydrides take a long time to degrade. They can be made via a number of different processes, including the ring-opening polymerization of anhydrides, interfacial condensation, melt condensation of diacids (or diacid esters), melt condensation of diacyl chloride with coupling agents, and interfacial condensation.[23].

Due to their high crystallinity and quick degradation, aliphatic homo-polyanhydrides are only used in a limited number of applications. In this instance, poly(sebacic anhydride) is involved. By altering the hydrophobic and hydrophilic ratios in the copolymer, polyanhydride degradation can be controlled. Slower degradation was produced by increasing the hydrophobicity of the diacid building blocks of the polymers. As biomaterials, copolymers containing a hydrophobic aromatic comonomer, such as carboxyphenoxypropane, have received a lot of attention [24]. Their degradation byproducts are both biocompatible and non-toxic.

Due to the wide variety of diacid monomers available, various linkages of polyanhydrides have been created. Ether, ester, and urethane linkages are some of these. Copolymers of anhydride and imide were also created in order to enhance the mechanical properties of polyanhydrides for particular medical applications [25]. It's been proven that they perform well mechanically. The addition of acrylic functional groups to the monomeric unit is an alternative strategy. Photocrosslinkable polyanhydrides are the result of this. The type of the monomeric species affects the crosslinked polyanhydrides' mechanical stability and rate of degradation.(fig no 4).

## Polyanhydride

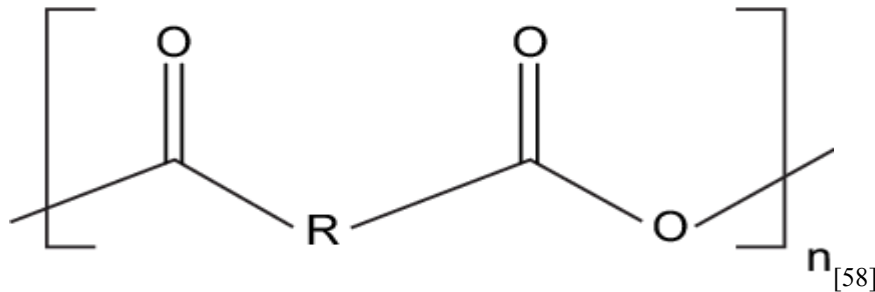


Fig. 4

### Phosphorous:-

Composites made of waste materials containing nitrogen, phosphorus, and polyvinyl alcohol were created and investigated as potential materials for encasing mineral fertilizers. The fillers for the composites included by-products of the production of biodiesel (rapeseed cake, crude glycerol), horn meal (a waste product of haberdashery), and phosphogypsum (a by-product of the production of phosphorus fertilizers). Different fillers or their mixtures were used to create the films for the composites with various amounts of nitrogen and phosphorus.

We looked at mechanical, film-related, hygroscopic, and water-soluble properties. The developed composites were used to encapsulate mineral fertilizers. It was determined that encapsulation caused the fertilizer's time of release to lengthen. The created slow-release fertilizers are a blend of organic and inorganic substances. [26].

### Blends of biodegradable polymers:-

Starch is a completely biodegradable and sustainable substance. Additionally, starch is inexpensive. However, starch's use is restricted because it is highly water-sensible and has inferior mechanical properties when compared to other petrochemical polymers. Combining it with other synthetic polymers might be a solution. Numerous biodegradable thermoplastic blends based on starch have been created and thoroughly researched. The creation of starch-based blends with synthetic biodegradable polymers is a topic of extensive research. These blends offer a number of benefits [27,28]. By changing the composition, the material properties can be tailored to the demands of the application. In comparison to the cost of creating new synthetic materials, the blending process is inexpensive.

#### Starch-poly(ethylene-co-vinyl alcohol) (EVOH):

*Different ratios of native corn starch and EVOH were used to create blown films. Starch, moisture content, and processing all had a significant impact on the mechanical properties. When the blend was processed at a temperature that was 5 °C higher, a higher extension to break as well as lower tensile strength and modulus were obtained. Differential scanning calorimetry and dynamic mechanical analysis have been used to describe interactions between the two components [29].*

#### Starch-PLA:

Due to incompatibility, blends of PLA and starch produced using conventional methods have poor mechanical properties. Utilizing plasticizers or reacting agents during the extrusion process will increase elongation. It has been used to use coupling agents like isocyanates. The isocyanate group and the hydroxyl groups of starch may react, forming urethane linkages and making these systems compatible. Investigations into the impact of starch gelatinization were also conducted [30]. It has been demonstrated that starch can act as a nucleating agent in PLA/gelatinized starch blends, improving the crystallinity of PLA blends and improving their mechanical properties.

*Starch-polyvinyl alcohol:*

Excellent compatibility exists between TPS and PVOH, and their mixtures are of particular interest. TPS and starch can be mixed in a variety of ratios to customize the final material's mechanical properties. Blends have better tensile strength, elongation, and processability when compared to pure TPS materials [31,32]. Recent research has been done on their biodegradability [33]. The amount of PVOH has a significant influence on how quickly starch breaks down; adding more PVOH will slow this process down.

*Starch – PCL:*

TPS and PCL were blended to modify the rheological properties of the melt before the process in order to prepare films using the film-blowing technique [34]. A class of starch blend with various synthetic components is produced by Novamont (Italy). The brand name of it is Mater-Bi®. There are four grades available, one of which contains PCL (Mater-Bi® Z). The fastest rate of PCL degradation is possible with the highest amount of starch. Some PCL-modified starch blends' behavior has been investigated [35]. Modified starch increases the PCL Young's modulus while decreasing the tensile strength and elongation at break values. The mixture loses ductility [36]. To control the rate of biodegradation, some synthetic polymers with lower biodegradability are used.

*Starch – PBS:*

Granular corn starch and PBS were combined [37]. It was demonstrated that elongation at break and tensile strength decreased with increasing starch content. Starch fillers increased the rate of degradation significantly.

*Starch – PHB:*

Prior reviews of blends containing PHB or PHBV were conducted [38]. It was demonstrated that poly(hydroxyalkanoates) can mix well with other polymers that have the right kind of functional group, such as those that can form hydrogen bonds or donor-acceptor interactions. Additionally, the impact of adding starch to PHB was investigated [39]. Blend films in different starch ratios have the same characteristics. All of the semi-crystalline samples are found to have a single glass transition temperature. The PHB/starch ratio of 70/30 (% wt/wt) was optimal for the tensile strength [40]. In this instance, compared to pure PHB, advantageous cost reduction and improved mechanical properties are obtained.

**Application:-**

With a few tweaks to the machinery and processing conditions, biodegradable polymers can be processed using most conventional plastics processing procedures. Among the processing methods employed are thermoforming, blow molding, injection molding, and film extrusion. Biodegradable polymers have been launched in three key sectors: packaging, agriculture, and medicine. Applications for biodegradable polymers extend beyond pharmaceuticals, such as controlled-release and enzyme immobilization matrices [41]; they also include medical devices, such as temporary prostheses and porous structures for tissue engineering.

Biopolymers could be utilized as absorbent materials in horticultural, medical, and agricultural applications because of their significant water uptake and low water solubility [42]. Waste from packaging is causing more and more environmental problems. Growing interest has been shown in the creation of biodegradable packaging materials [43].

## II. MEDICINE AND PHARMACY

A recent review has examined the application of biodegradable polymers as biomaterials [44,45,46]. Biodegradable polymers need to possess three crucial characteristics in order to be utilized as biomaterials: mechanical resistance, bioabsorbability, and biocompatibility. While the use of synthetic biodegradable polymers dates back to 50 years, the use of naturally occurring enzymatically degradable polymers, such as proteins or polysaccharides, in biological applications began thousands of years ago.

Biodegradable polymers are currently being used in simple membranes and surgical implants for orthopedic or vascular surgery. Because biodegradable polyesters typically have considerable strength and a customizable degradation pace,

they are commonly used as porous structures in tissue engineering [47]. The chemical makeup of the polymers, their breakdown products and mechanisms, mechanical characteristics, and clinical limits are all discussed in these studies.

### **Packaging**

Another significant application of biodegradable polymers in daily life is packaging. Biodegradable polymers are frequently utilized to decrease the amount of trash produced. Biopolymers exhibit a variety of additional properties in addition to being biodegradable, such as air permeability and low-temperature sealability [48]. Depending on the product to be packaged and the store circumstances, different physical properties are needed for biodegradable polymers used in packaging.

PLA is utilized for yard waste bags because of its accessibility and affordability in comparison to other biodegradable polyesters. Furthermore, PLA has a medium degree of permeability to oxygen and water vapor. As a result, it is created for packaging uses such as films, bottles, and cups [49,50]. PCL is used in environmental applications, including as soft, compostable packaging.

### **Agriculture:-**

The most crucial characteristic of biodegradable polymers for this use is really their biodegradability [51]. The most common biopolymers in this field are those based on starch. They are biodegradable and have a long enough lifespan to be effective.

In the 1930s, plastic films were first used for mulching and fumigation of greenhouse coverings. Young plants need to be covered since they are vulnerable to frost. Biodegradable cover films work primarily to promote plant growth rate by preserving moisture, raising soil temperature, and suppressing weed growth. The film can be discarded into the soil at the conclusion of the season, where it will biodegrade[52]. An additional application is based on the creation of seed bands. An additional application is based on the creation of seed bands. It is made up of bands that are regularly distributed with nutrients and seeds. Within the realm of geotextiles, the application of geogrids and textiles based on biopolymers for drainage and filtration is noteworthy [53].

Agricultural chemicals can be released under regulated conditions using biodegradable polymers. The active ingredient can be a component of the macromolecular backbone or pendent side chain, or it can be dissolved, distributed, or encapsulated by the polymer matrix or coating. Insect-repellent pheromones, fertilizers, and pesticides are the agricultural chemicals in question. Generally speaking, cellulose, chitin, lignin, alginic acid, and starch are the natural polymers utilized in controlled release systems [10].

Applications for biopolymers in horticulture include threads, clips, staples, fertilizer bags, ensilage envelopes, and seed trays. Other agricultural applications include containers like compostable bags and containers made of biodegradable plant pots. When the plant starts to grow, the pots that are directly seeded in the soil disintegrate.

### **III. CONCLUSION**

Because of their potential uses in the fields of environmental protection and physical health maintenance, biodegradable polymers have attracted a lot more attention in recent decades. Only a small number of the aforementioned biopolymer groups are currently significant in the market. Their price point, which is currently uncompetitive, is the primary cause. Each biopolymer's future depends on society's ability to pay for it as well as its competitiveness. The future appears bright for advancements in the field of biopolymers as materials.

Numerous techniques, including random and block copolymerization and grafting, have been developed to enhance the properties of biodegradable polymers. These techniques enhance the ultimate products' mechanical qualities as well as their rate of biodegradation. Another method for creating biodegradable materials with various morphologies and physical properties is physical blending.

Advanced technologies have been used to give biodegradable polymers additional value. They consist of reinforcements made of natural fibers and active packaging technology. Numerous studies on the application of nano clay with biodegradable polymers—particularly starch and aliphatic polyesters—have been published recently. Research is being done on nano-biocomposites and bio-nanocomposites.

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