Properties and Applications of Biodegradable Polymers

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Abstract: Biodegradable materials are one of the major discussable matters in the modern world. To keep and produce environment-friendly products for our daily usage the utilization of degradable materials is increasing at a high rate. The modern world wants sustainable products which will not bring about any harm to the environment. Products made from plastics are sustainable but they cause great harm to our environment due to lack of degradation property. After the end of our usage, these materials can sustain for a long time without any degradation which causes a supreme level of loss to our environment. But if we can produce products by using biodegradable raw materials, they will be degraded by the action of bio-organisms hence our environment will be protected from a great loss. So, it has become a crying need for us to use biodegradable raw materials in our products. The materials which are not biodegradable cause a great pollution especially soil pollution. To protect the world from the cruel humiliation of waste, it has become an overwhelming necessity to manufacture biodegradable products, which can quickly be degraded in the environment. Already these materials have been using in several sectors and showing their applications for their friendly properties.

Keywords: Degradable, sustainable, bio-organisms, crystallinity, natural, synthetic.

1. INTRODUCTION

Plastics with same durability properties are ideal for many applications such as in building materials, packaging and commodities, as well as for hygiene products. This may lead to waste-disposal problems in case of traditional petroleum-derived plastics, because these materials are not promptly biodegradable and for their microbial degradation resistance. In recent times, oil prices have been increased markedly. Such facts have helped to promote interest in biodegradable polymers and especially in biodegradable biopolymers. Biodegradable polymers represent a growing field. Biodegradable plastics are environmentally-friendly because of their production from renewable feedstocks, decreasing greenhouse gas emissions. Fossil fuel and gas can be partially replaced by green agricultural resources, which would also participate in reducing the CO₂ emissions. There are several sources of biodegradable polymers, from natural to synthetic polymers. Natural polymers are available in huge quantities from renewable sources, and synthetic polymers are produced from non-renewable petroleum resources [1-2].

Though natural polymers have been used bio medically for thousands of years, research of synthetic degradable polymers into biomedical applications is relatively new, it started in the 1960s. Biodegradable polymers become increasingly important for a large range of applications including medical implants and drug delivery devices and also as disposable packaging products and plastic consumer products. Biodegradable plastics and polymers were first introduced in the 1980s. There are many sources of biodegradable plastics, from synthetic to natural polymers. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources. Biodegradability depends not only on the origin of the polymer but also on its chemical structure and the environmental degrading conditions. The mechanical properties of biodegradable materials depend on their chemical composition, the production, and the processing characteristics, the aging process and the application conditions [3-6].

2. BIODEGRADABLE POLYMERS

the action living micro-organisms' By of biodegradable polymers become degraded. The meaning of biodegradable is degradable into biomass and gases (like CO2 and CH4) in the presence (aerobic) or absence (anaerobic) oxygen because of action of microbes (mostly fungi and bacteria). In different environmental conditions, biodegradable polymers show significant changes. For all biodegradable polymers, it is required that they should be stable and durable enough when they are used in their particular application, but they should easily be broken down upon disposal. Biodegradable polymers have extremely strong carbon backbones that are difficult to break, such that the degradation of polymers often is started from the end-groups [7].

When a polymer contains both hydrophobic and hydrophilic portions, it appears to have a higher

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biodegradability than those polymers which contain either hydrophobic or hydrophilic structures only. A number of general rules enable the determination of the evaluation of biodegradability. As an example, the increase in parameters such as- the macromolecules molecular weights, the hydrophobicity and the size of crystalline domains decreases the biodegradability. Through the action of enzymes and chemical deterioration associated with living micro-organism's biodegradation takes place. To be biodegradable biomaterials, some important properties must be considered. These materials should be (a) possess a degradation time coinciding with their function; (b) not bring a sustained inflammatory response; (c) include appropriate permeability and process ability for designed application; (d) have appropriate mechanical properties for their intended use; and (e) produce nontoxic degradation products that can be readily excreted [8-10].

3. CLASSIFICATION OF BIODEGRADABLE POLYMERS

Biodegradable polymers are classified according to several properties. On the basis of origin from which the polymers are extracted, biodegradable polymers are classified into two classes: a) Natural biodegradable polymers; b) Synthetic biodegradable polymers. Natural biodegradable polymers are originated from natural sources and synthetic polymers are from petroleum sources [11].

4. PROPERTIES OF BIODEGRADABLE POLYMERS

Biodegradable polymers illustrate some special properties of their own. Biodegradable polymers have biodegradability obviously. Other properties are described here step by step.

4.1. Properties of Natural Biodegradable Polymers

Natural biodegradable polymers are extracted directly from natural sources. The important properties of some common natural biodegradable polymers are discussed below:

4.1.1. Collagen

Collagen is a protein found largely in mammals (25% of our total protein in mass) and is the major strength provider to tissue. A regular collagen molecule consists of three entangled protein chains that form a helical structure. Collagen is non-toxic, produces only a minimal immune response and is excellent for

attachment and biological interaction with cells. It may also be processed into different formats, such as porous sponges, gels, and sheets, and can be crosslinked with chemicals to make it stronger or to alter its degradation rate. Depend on how it is processed, collagen can potentially cause alteration of cell behavior, have unsuitable mechanical properties, shows contraction or, shrinkage [12].

4.1.2. Chitosan

Chitosan is one type of polysaccharide derived from chitin, is present in the hard exoskeletons of shellfish like shrimp and crab. Recently chitosan has become popular in the tissue-engineering field due to several desirable properties [13-14]:

- a. Easily controllable mechanical/biodegradation properties (such as scaffold porosity or polymer length)
- b. The availability of chemical side groups for attachment to other molecules.
- c. Less amount of foreign body reaction
- d. Easier processing conditions (chitosan will dissolve in water based on pH, while synthetic polymers often need to be dissolved in harsh chemicals)

Chitosan can easily be combined with other materials in order to increase the strength and cellattachment potential. It may produce mixtures with synthetic polymers such as poly (vinyl alcohol) and poly (ethylene glycol), or natural polymers such as collagen [15-17].

4.1.3. Gelatin

Gelatin is one of the most common biopolymers. It is obtained either by partial acid hydrolysis or by partial alkaline hydrolysis of animal collagen, it's a denaturized fibrous protein. According to a recent report, the production of gelatin from pigskin is the highest (44%), bovine hides (28%), bovine bones (27%) and other sources (1%). Gelatin is about tasteless and odorless. It is a vitreous, brittle solid faintly yellow in color. Gelatin is soluble in aqueous solutions of polyhydric alcohols such as glycerol and propylene glycol. It's insoluble in fewer polar organic solvents, including benzene, acetone, primary alcohols, and dimethyl formamide. Gelatin's color depends on the extraction method and the raw materials used. Gelatin's two most useful properties are gel strength and viscosity. Gelatin can be used as an emulsifying, foaming and wetting agent in the food industry in medicine and cosmetics. Gelatin maintains a standard pH range from 3.8 to 5.5 [18-21].

4.1.4. Alginate

Generally, alginate is derived from brown seaweed, it's a polysaccharide. Alginate can be processed easily in water as chitosan and is fairly non-toxic and noninflammatory, enough so that it has been approved in some countries for wound dressing and use in food products. It has been proved that alginate is biodegradable, it has controllable porosity, and may be linked to other biologically active molecules. Alginate can form a solid gel under mild processing conditions, which allows it using for entrapping cells into beads and other shapes. The interesting matter is that encapsulation of certain cell types into alginate beads may actually enhance cell growth and survival. Alginate has been explored for use in liver, nerve, heart, and also cartilage tissue-engineering. Like others, alginate has some drawbacks including mechanical weakness and poor cell adhesion. To overcome these limitations, the strength and cell behavior of alginate has been enhanced by mixtures with other materials, including the natural polymers agarose and chitosan [22-28].

4.1.5. Lactose

This is also called milk sugar. Lactose is a disaccharide that is found in milk. In the milk cow, it aparts from fat and protein, which is the principal component of milk solids of this product. Lactose is hydrolyzed by lactase in the intestines. The intolerance lactose occurs when a person has difficulty or is not able to digest milk due to lack of lactase. The LGI (Lactose Glycemic Index) is less than half that of maltose and glucose and almost 50% lower than that of sucrose. In fresh cow's milk lactose concentration ranges between 4.5 to 5.2%, but in human milk it reaches to 7% [29-33]. Lactose has good water solubility, it exists in a ring form, with oxygen bonds between the first and fifth carbon atoms. Lactose takes on an aldehyde form in an alkaline environment and is readily oxygenated to lactobionic acid which, due to its chemical form belongs to the group of polyhydroxyacids. An important role of lactose is the correct development of new-born mammals as it is an important source of energy, indispensable for such organs as the liver, heart and kidneys. Lactose breakdowns to lactic acid, which decreases the pH of the gastric contents [34-35].

4.1.6. Starch

Starch is a storage form of glucose in the body. Starch is made up of amylose and amylopectin. Starch contains amylopectin (80-90%) and amylase (10-20%). In the structure of starch, the linkage between glucose residues is 1-4 and at branch point linkage is of 1-6. The size of starch granules ranging from 0.1 to 200 µm diameter, and its morphological shape varies in different such as ellipsoidal, oval, spherical, smooth, angular and lenticular, which depends on the botanical source. Starches from wheat and rice with high phospholipid contents produce pastes with low transmittance power compared to potato or corn starch pastes which is determined by the presence of number of phospholipids. Starch from potato demonstrates high transmittance because of its phosphate monoester [36-39]. Greater crystallinity found in starch granules due to presence of a higher proportion of amylopectin. Deformation is associated with loss of birefringence in starch granules due to its modification. When starch molecules are heated in water excess, the semicrystalline structure is broken, and water molecules associate by hydrogen bonding to hydroxyl groups exposed the amylose and amylopectin molecules. This association causes swelling and increases granule size and solubility. The solubility and swelling capacity of starch describe the interactions of the polymeric chains comprising the crystalline and amorphous granule fractions. Starch granules are insoluble in cold water due to the hydrogen bonds and crystallinity of the molecule. If starch is dispersed in hot water below its Tg, the starch granules swell and increase several times in size, breaking the molecules and consequently leaching amylose to form a three-dimensional network and increase the viscosity [40-43].

4.1.7. Cellulose

Cellulose is a common type of carbohydrate. There are three available hydroxyl groups for reaction in each repeating unit of cellulose, the structure of cellulose being largely affected by hydrogen bonds and van der waals forces. The hydrogen bonds within neighboring cellulose chains may use to determine the straightness of the chain and impart improved thermal stability and mechanical properties to the cellulose fibers. Hydrogen bonds might introduce order or disorder into the system depending on their regularity. Normally cellulose is a water-insoluble polymer and contains rigid linear structure. It is characterized by its chemical inertness, its insolubility and its physical rigidity. Animals such as cows. sheep. horses, etc. can digest this polysaccharide as these animals have bacteria in their

stomachs whose enzyme systems break down cellulose molecules. Humans cannot digest cellulose due to lack of cellulase enzyme [44-45].

4.1.8. Pectin

Pectin is a biodegradable polymer, a complex mixture of polysaccharides that makes up about one third of the cell wall dry substance of higher plants. These are soluble in pure water. The monovalent cation salts of pectinic and pectic acids are generally soluble in water: but divalent and trivalent cations salts are insoluble or weakly soluble. The concentrations of pectin are highest in the middle lamella of the cell wall, which gradually decreases as one passes through the primary wall toward the plasma membrane. 10-15% of pectin found in apple pomace on a dry matter basis while citrus peel contains 20-30%. Citrus pectins are light cream in colour; apple pectins are often darker. Actually, the distribution of free carboxyl groups along the pectin chains is somewhat regular, and the free carboxyl groups are isolated largely from one another. More than 72% degree of esterification (DE) in pectin forms gel at lower soluble solids and higher levels than pectin of slow-set (i.e. pectin with the degree of esterification between 58- 65%). The most important use of pectin is based on its ability to form gels. Gels can be formed by HM-pectin with sugar and acid. The formation of gel is caused by hydrogen bonding between free carboxyl groups on the pectin molecules and also between the hydroxyl groups of neighboring molecules [46-48].

4.2. Synthetic Biodegradable Polymers

Synthetic biodegradable polymers are not extracted directly from natural sources, extracted from petroleum sources. The important properties of some common synthetic biodegradable polymers are discussed below:

4.2.1. Polylactide (PLA)

PLA, [-O(CH3) 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. PLA can be synthesized by condensation polymerization of lactic acid or from lactide by its ring opening polymerization in the presence of a catalyst. PLA production from lactic acid was established by Carothers in 1932 [49-50]. Poly (lactic acid) or polylactide (PLA) is the most extensively researched and utilized biodegradable and renewable aliphatic polyester. L-lactic acid and D-lactic acid, the two isomers of lactic acid. Pure L-lactic acid or D-lactic acid, or mixtures of both components are needed for the synthesis of PLA. PLA has a degradation half-life in the environment ranging from 6 months to 2 years, depending on the size and shape of the article, its isomer ratio, and the temperature. Properties such as tensile properties of PLA can vary widely depending on whether in which it is annealed or oriented, or its degree of crystallinity [51].

4.2.2. Polycaprolactone (PCL)

(PCL) Polycaprolactone is а well-known biodegradable synthetic aliphatic polyester, which is prepared by the ring-opening polymerization of caprolactone in the presence of metal alkoxides such as aluminium isopropoxide. The melting point of PCL is low, between 58-60°C, with low viscosity and it is easy to process. PCL is completely degraded by thermotolerant PCL-degrading microorganism identified as, Aspergillus sp., isolated from the soil after 6 days incubation at 50°C. Degradation of PCL can also be processed by enzymes such as esterases and lipases. The rate of degradation of PCL depends on its molecular weight and degree of crystallinity. The enzymatic degradation of PCL by Aspergillus flavus and *Penicillium funiculosum* is faster in the amorphous region. The improvement of biodegradability of PCL may be caused by copolymerization with aliphatic polyesters due to copolymers have lower Tm and lower crystallinity as compared to homopolymers, and hence are more prone to degradation [52-58].

4.2.3. Polyglycolide (PGA)

Poly (glycolic acid) (PGA) is a rigid thermoplastic material with high crystallinity (46-50%). The glass transition and melting temperatures of PGA are 36°C and 225°C respectively. Because of high crystallinity, PGA is not soluble in most organic solvents; the exceptions are highly fluorinated organic solvents such as hexafluoro isopropanol. Solvent casting, particular leaching method and compression moulding are also used to fabricate PGA based implants [59].

4.2.4. Polyanhydrides

One of the most extensively studied classes of biodegradable polymers is polyanhydrides with demonstrated biocompatibility and excellent controlled release characteristics. Due to limited mechanical properties of polyanhydrides, they show restricted the use in load-bearing applications such as in orthopaedics. Poly[1,6-bis(carboxyphenoxy) hexane] has Young's modulus of 1.3 MPa which is well below the modulus of human bone (40 to 60 MPa). Depending on the monomers used, the mechanical properties as well as degradation time can be varied. Tensile strengths of 15-27 MPa and compressive strengths of 30-40 MPa. An important property is that polyanhydrides are biocompatible, have well-defined degradation characteristics. Polyanhydrides show hydrolytic instability thus they should be stored under moisture-free frozen conditions and low mechanical strength [60-66].

4.2.5. Poly Orthoesters

Polyorthoesters are another successful biodegradable family of biodegradable polymers. The principal characteristics of this polymer family are that they contain orthoester linkage which is acid labile and undergo surface erosion like polyanhydrides. With the addition of lactide segments as part of the polymer structure, tunable degradation times ranging from 15 to hundreds of days can be achieved. When the degradation of lactide segments processed, it produces carboxylic acids, which catalyze the degradation of the orthoester [67-68].

5. 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 which play an important role in the biodegradation processes are surface area, hydrophilic and hydrophobic character, the chemical weight, structure. molecular glass transition temperature, melting point, elasticity and crystal structure etc. of polymers. Generally, 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, the biodegradability of 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 also crystallinity is а key factor affecting biodegradability. This is because the molecules in the amorphous part of the 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 the closer packing of the molecules. The rate of degradation of PLA decreases

with an increase in the crystallinity of the polymer. The melting temperature (Tm) of polymers also has a large effect on the enzymatic degradation of polymers. The increased amount of melting point of the polymer causes the decreased amount of the biodegradation of the polymer [69-73].

$Tm = \Delta H/\Delta S$

In this equation, ΔH is the enthalpy change on melting and ΔS is the entropy change on melting.

Some general rules enable the determination of the biodegradability evolution. For example, an increase in parameters such as- the macromolecules molecular weights, the hydrophobicity and the crystallinity decrease the biodegradability. When a polymer contains both hydrophobic and hydrophilic portions, it appears to have a higher biodegradability than those polymers containing either hydrophobic or hydrophilic structures only. Long repeating units containing synthetic polymers would be less likely to crystallize and thus might be biodegradable; indeed, a series of poly (amide-urethane) were found to be readily degraded by subtilisin. Other factors include [74-77]:

- Shape
- Processing conditions
- Physicochemical factors (ion exchange, ionic strength and pH)
- The presence of unexpected units or chain defects
- The configuration structures
- Sterilization process
- Distribution molecular-weight
- Annealing
- Storage history
- Site of implantation
- Adsorbed and absorbed compounds (water, lipids, ions etc.)
- Physical factors (shape and size changes, variations of diffusion coefficients, mechanical stresses, stress-and solvent induced cracking, etc.)
- Mechanism of hydrolysis (water versus enzymes).

6. APPLICATIONS OF BIODEGRADABLE POLYMERS

A wide range of sectors where applications for biopolymers have introduced including medicine, packaging, agriculture, and the automotive industry [78]. 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 three main sectors where biodegradable polymers have been introduced include medicine, packaging and agriculture. Due to having degradability, biodegradable polymers applications include not only pharmacological devices, as matrices for enzyme immobilization and controlled-release devices but also therapeutic devices, as temporary prostheses, porous structure for tissue engineering. Biopolymers have a low solubility in water and a very important water uptake, so they can be used as absorbent materials in healthcare, horticulture and agricultural applications. Packaging waste has caused increasing environmental concerns. Biodegradable packaging materials development has received increasing attention [79-81].

6.1. Applications in Medicine and Pharmacy

Current applications of biodegradable polymers include surgical implants in vascular or orthopedic surgery and plain membranes. Because of having good strength and an adjustable degradation speed, biodegradable polyesters are widely employed as porous structure in tissue engineering. These are also used as implantable matrices for the controlled release of drugs inside the body or as absorbable sutures. Gelatin is natural polymer that used for coatings and microencapsulating various drugs for biomedical applications and also employed for preparing biodegradable hydrogels. Poly(3-hydroxybutyrate-co-3hydroxyvalerate), commonly known as PHBV has the unique property of being piezoelectric, using in applications where electrical simulation is applied. Synthetic polymers are widely used in biomedical implants and devices because they can be fabricated

into various shapes. PGA fabrics (nonwoven) have been investigated as scaffolding matrices for tissue regeneration. The use of chitin and its derivatives include in drug carriers and anti-cholesterolemic agents, blood anticoagulants, anti-tumor products [82-86]. Collagen, Chitin poly-L-leucine have been used to prepare skin substitutes or wound dressing. The gels of alginate have been extensively used in controlled release drug delivery systems. Good cell adhesion property is shown by PLGA thus it can be used for tissue engineering applications. PLGA is used as polymeric shell in nanoparticules used as drug delivery systems. Polyanhydrides have been investigated in controlled release devices for drugs treating eyes disorder and using as local anesthetics. chemotherapeutic agents, anticoagulants, neuro-active drugs and anticancer agents [87-90].

6.2. Applications in Packing

Packaging is another important area where biodegradable polymers are used. In order to reduce the volume of waste, biodegradable polymers are often used. Biopolymers show characteristics as air permeability, low temperature sealability etc. PLA has a medium permeability level to water vapor and oxygen. It is used in packaging applications such as films, cups, bottles [91-93]. PCL is also using in soft compostable packaging. The new trend in food packaging is thus the use of mixtures of different types of biopolymers. Chitosan is used in paper-based packaging as a coating, to produce an oil barrier packaging etc. Chitosan coatings can be used as fat barriers, but the treatment cost was relatively high compared to the fluorinated coatings usually used. Films based on chitosan have proven to be effective in food preservation and can be potentially used as antimicrobial packaging [94-96].

6.3. Applications in Agriculture

The agricultural chemicals concerned are pesticides and nutrients, fertilizer, pheromones to repel insects. Some natural polymers used in controlled release systems are starch, cellulose, chitin, alginic acid and lignin [97]. In marine agriculture, biopolymers are used to make ropes and fishing nets. In mulching and lowtunnel cultivation, to enhance sustainability and environmentally friendly agricultural activities, a promising alternative is the use of biodegradable materials. The agricultural films placed in the soil are susceptible to degradation and aging during their useful lifetime, so they need to have some specific properties. When starch is placed in contact with soil microorganisms, it degrades into nontoxic products. This is the reason why starch films are used as agricultural mulch films [98].

6.4. Applications in Other Fields

Automotive: The automotive sector aims to prepare lighter cars by the use of bioplastics and biocomposites.

Electronics: PLA and kenaf are used as a composite in electronics applications. PLA has already used to make a computer case by Fujitsu company.

Construction: PLA fiber is used for the padding and the paving stones of carpet. Its inflammability, lower than that of the synthetic fibers, offers more security.

Unusual applications: There are a lot of other applications which do not fit into any of the previous categories. Thus combs, pens and mouse pads made of biodegradable polymers have also been invented, mostly for use as marketing tools. As food and feed additives chitin and chitosan are largely used [99-100].

7. CONCLUSION

An increased amount of analysis has been doing about biodegradable polymers for the last two decades. These polymers show a significant contribution to sustainable development in view of the wider range of disposal options at the lower environmental impact. Now it is needed to take steps to the development of biodegradable products and maximize the environmental, social, and industrial benefits. It's the success of such highly innovative products is the achievement of high quality (environmental quality) standards. Biodegradable polymers have already proven their ability for the development of advance, new and efficient drug delivery systems. They are capable of delivering a wide range of bioactive materials. Natural polymers have an important role in the controlled release of drugs and their targeting to selective sites. The polymers have kept significantly more consideration in the most recent decades due their potential applications in the fields identified with natural insurance and the support of physical wellbeing. For enhancing the properties of biodegradable polymers, considerable measures of techniques have been created, for example, arbitrary and piece copolymerization or joining. Such kind of strategies enhance both the biodegradation rate and

the mechanical properties of the polymers. Biopolymers are environment friendly polymers. If these polymers can displace an equivalent amount of fossil fuel-based polymers, then about 192 trillion of fossil-derived fuel will be saved per year, which results in the reduction in the emission of CO_2 by 10 million tons. To avoid the disorder of ecosystem, processes should be cyclic without creating any chemical or biological imbalance.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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