

BIODEGRADABLE POLYMER: THE PROMISES AND THE PROBLEMS

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The depletion of petroleum resources and more stringent environmental issues led to considerable research efforts on development of biodegradable polymeric materials. Introducing nanocomponents into biodegradable polymer matrix to produce nanocomposites is the most effective approaches to enhance the properties of pristine polymers. By modifying the naturally occurring inexpensive natural renewable resources, both durable and environmentally acceptable materials can be developed. An increasing availability of biodegradable polymers will allow many consumers to choose them on the basis of their environment friendliness.

Introduction

The interest in using biodegradable polymers as an alternative to petroleum based polymers has increased in recent years due to the limited resources of crude oil, global warming and environmental awareness. Development of biodegradable polymers generally catches the attention of researchers due to environmental problems associated with the disposal of petroleum based polymers. In this context, polymers obtained basically from renewable sources are a new generation of material capable of significantly reduce the environmental impact in terms of satisfying certain technical requirements and are fully biodegradable. Both synthetic and natural polymers that contain hydrolytically or enzymatically labile bonds or groups are degradable. The advantages of synthetic polymers are obvious, their batch-to-batch uniformity and can be tailored easily. Therefore, natural polymer based materials offer a feasible alternative to the traditional polymeric materials when recycling of synthetic polymer is not cost effective or technically impossible. In order to be competitive compared to lost

cost petroleum based polymers, biodegradable polymers need to have acceptable price and equally good performance as petroleum based polymers. The present low-level production and high cost for most of these biopolymers restrict their widespread applications¹⁻². The increasing demand for biodegradable materials leads to the responsibility to develop products with better properties compared with those of existing petroleum based polymers.

Depending on the production process and resources, biopolymers are generally divided into three main groups³:

- Polymers extracted directly from biomass – polysaccharides, proteins, lipids etc
- Biodegradable polymeric materials based on: (i) renewable biobased monomers – poly(lactic acid) and (ii) oil based monomer – poly(ϵ -caprolactones)
- Polymeric materials produced by microorganism and genetically modified bacteria – poly(hydroxyalkanoates)

Cellulose Based Biodegradable Polymer

Among the natural polymers, cellulose is of great interest. Cellulose is the world's most abundant renewable polymer resource. Cellulose is the main structural component of cell wall which confers strength and stability

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to the plant cell walls. Its function is closely related to its hierarchical structure. The fundamental unit of cellulose is the microfibril (CMF), constituting of a bundle of β -1,4-glucane that are formed by intra- and intermolecular hydrogen bonding of glucan chains, forming a crystalline array. These microfibrils are around 10 to 38 nm diameter and 30-100 cellulose molecules in extended chains, depending on their origin.⁴ Microfibrils are the basic structural unit produced during photosynthesis. Cellulose microfibrils exhibit outstanding mechanical properties with high young's modulus (138 GPa) and with an estimated tensile strength well beyond 2 Gpa. These mechanical properties are comparable to those of aramid fiber, a well known high-strength synthetic fiber. With very low coefficient of thermal expansion, CMFs makes them promising candidate for reinforcement material in nanocomposites. Cellulose nanofibers isolated from plant sources contain either single CMF or microfibril aggregates, thus exhibiting high reinforcing efficiency because of the high aspect ratio. The parallel cellulose chains forms microfibrils embedded in non-cellulosic matrix of hemicelluloses and lignin. The non-cellulosic components such as pectin, lignin and hemicelluloses are deposited between the cellulose fibrils. So they have amorphous and semi-crystalline zones. The presence of amorphous region lowers the mechanical strength of the fibril. So the structure of the microfibrils is required to alter by different mechanical and chemical treatment. Cellulose microfibrils have been isolated by researchers from natural sources by using different chemical treatments⁵⁻⁶. Mechanical treatment to isolate the microfibrils involve cryocrushing, homogenization etc.⁷ and it yields high viscous suspensions of individual CMFs. These nanosized microfibrils contribute towards producing composite materials of very high strength suitable for biocomposites in packaging materials and medical devices at low cost in an environment friendly manner.

Studies on the development of polymeric nano composites based on cellulose microfibrils obtained from mature banana rachis, sugarcane bagasse, bamboo fiber and pineapple farming residue are in progress at our organization. These agro wastes are abundant in the North Eastern Part of India and are considered as a viable source of natural cellulose from agricultural waste due to relatively low cost. These generate a considerable amount of residue and it causes environmental problem in the farming region. Sugarcane is one of the major commercial crop in India and its fibrous stack called bagasse are mainly used for paper, fuel or animal feed. In recent years there has been an increasing trend towards for more efficient utilization of agro-industrial residues. These residue resources are rich

in cellulose and have attracted the attention for its potential use as a reinforcing component in composite materials. Microfibrils from these sources can be successfully isolated by different chemo-mechanical treatments.

Surface Grafting of Cellulose Microfibril for Biodegradable Nanocomposites

When cellulose fibers are used as reinforcing agents in composites, it is crucial and often difficult to obtain a sufficient fiber-to-matrix adhesion. So to obtain a maximum adhesion the properties of cellulose fibers need to be improved. Surface grafting of polymer chains is one of the most versatile tools to modify and control the properties of a surface. Various chemical methods such as ring opening polymerization (ROP), atom transfer radical polymerization (ATRP), Reversible addition-fragmentation chain transfer polymerization (RAFT), click chemistry have been used by researchers for this purpose.⁸ By using these methods different kinds of polymer chains have been covalently coupled on the cellulose fiber to alter its property. Polyesters such as poly (lactic acids) (PLA), poly (glycolide), poly(ϵ -caprolactone) (PCL) etc play important roles in the design of biodegradable and biocompatible polymers. Among the numerous polyesters, PCL and its copolymers are the most attractive and useful class of biodegradable polyesters because of their high biocompatibility and good material properties. PCL has excellent thermal property with high decomposition temperature ($T_d = 350$ °C) and low melting temperature ($T_m = 65$ °C). The ability to synthesize hydrophobic-hydrophilic biodegradable polymers containing polyesters and polysaccharides provides a way to materials with novel physical properties and applications. CMF as solid substrate has been thoroughly studied as macroinitiator for synthesis of high molecular weight comb block copolymers consisting of CMF backbone, inner blocks of PCL and outer blocks of different lengths of epoxides using a combination of ROP and ATRP. The resulting grafted products are of interest due to their biodegradability and the possibility to tailor their degree of crystallinity. Ongoing work is focused on the development of super hydrophobic graft-on-graft cellulose surface for packaging applications with self cleaning properties using a combination of two living polymerization techniques.

Chitosan Based Biodegradable Polymer

Chitosan is the fully or partially deacetylated polysaccharide of naturally abundant chitin having the similar structure with cellulose. It displays interesting properties such as biocompatibility, biodegradability,

bioactivity and its end products are non-toxic, non-immunogenic and non-carcinogenic⁸⁻⁹. Despite its unique biological activities and physicochemical properties, chitin still remains an unutilized biomass due to its intractable nature, it is insoluble in common solvents. Many attempts have been made to modify the molecular structure of the chitosan to develop advanced material with improved properties. The reactions often encounter difficulties because of the heterogeneous reaction conditions, multifunctionality with three kinds of functional groups, and poor reactivity. The structure-property relationship of the products is also difficult to explain. Partially deacetylated water-soluble chitin and its derivatives have been proved useful for surface modification in a controlled manner.¹⁰ The grafting modification of chitosan has been explored as a convenient method to develop novel hybrid materials such as chitosan-grafted-poly(methyl methacrylate), chitosan-grafted-poly(vinyl acetate), chitosan-grafted-poly(ethylene glycol).¹¹ Almost all were achieved by free radical polymerization but all these polymers have limited biodegradability because the presence of non-degradable branches. To develop the high potential of chitosan, it is necessary to introduce substituent at specific position in a controlled manner. Chitosan based graft copolymers with well defined structures can be achieved by graft copolymerization of biodegradable polymeric components onto chitosan. Phthaloyl chitosan¹² is also used as a precursor for efficient surface modification.

One of our targets is to introduce multiple polymeric components onto phthaloyl chitosan by ROP of ϵ -caprolactone (CL) and lactides followed by grafting of epoxy monomers by ATRP. These biodegradable polymeric materials have immense potential in biomedical applications. This graft-on-graft architecture onto phthaloyl chitosan was achieved by using the protection technique.¹³

Starch Based Biodegradable Polymer

Among the natural polymers, starch possesses many unique properties and simultaneously some shortcomings also. Starch has received more attention because of its low cost, ready availability and total degradability after usages. However virgin starch has the disadvantage of strong hydrophilic behavior, poor mechanical properties and dimensional stability especially in presence of water and humid environments. By combination of individual advantages of starch and synthetic polymers, starch-based biodegradable polymers have potential for applications in biomedical and environmental field.¹⁴ To improve the properties of starch, various physical or chemical modification of starch such as derivatization and graft

copolymerization have been investigated. One inherited problem for starch based polymers is that starch and many polymers are non-miscible, which leads to the poor mechanical properties of starch/polymer blends. So, it is essential to modify the starch chemically to improve its physical properties suitable for end usage. To prepare completely biodegradable starch-based composites, Polylactide or PCL segments were introduced onto starch by ROP and starch composites with predetermined physical properties were developed. The graft copolymers of starch-g-PCL and starch-g-PLA are completely biodegraded under natural conditions and exhibit improved mechanical performances.

The introduction of an ester group into polysaccharide constitutes an important synthetic task because it permits to modify their original hydrophilic nature and also to obtain enhanced or new thermal and mechanical properties. Starch acetate with degree of substitution (DS) 0.01-0.2 is approved by FDA to improve binding, thickening, stability and texturizing. On the other hand, high DS starch acetate is used as a replacement for cellulose acetate. As a biodegradable material starch acetate also has many potential usages in pharmaceutical applications. It is observed that natural starch exhibit typical B-type crystalline structure. This is due to the presence of amylopectine in natural starch. On esterification the crystallinity decreases and almost amorphous pattern is obtained.

Nanocomposites as Packaging Applications

By nanoprocessing, the poor quality of biobased plastics can be improved to a level near to the petroleum based plastic materials. Though polymer nanocomposites containing nanoclay particles are currently in major use in the food packaging market, biobased nanocomposites with cellulose nanofibers/microfibrils are also being developed. In some cases, these materials have superior properties to the clay based nanocomposites including heat resistance. Microfibril based composites have highly nanoporous structure and can be used as support matrixes for additional functionality as they do the lowest thermal conductivity.

Food packaging and edible films are two major uses of the biodegradable polymers. Traditional food packaging materials such as polyethylene and polypropylene have the environmental pollution and disposal problems. The natural polymer based biodegradable polymers can be a possible alternative for food packaging to overcome these disadvantages and also to keep the advantages of packaging materials. Starch based edible films are odorless,

tasteless, colourless, non-toxic and biodegradable. They are good barriers for oxygen at low humidity and useful for food protection to improve quality and shelf life without impairing consumer acceptability. At present, our strategies are on the development of starch and CMF based biodegradable polymers of appropriate biocompatibility with rapid degradation.

Standard Test Methods for Biodegradable Polymer

Standards organizations such as ASTM and ISO have published several test methods for biodegradable polymeric materials. Degradation of polymer is induced by different factors and mechanisms and depending on the nature of the agent that initiates degradation (i.e. UV light, moisture, heat, and microorganisms), the process is generally classified as photo-oxidative degradation, thermal degradation and biodegradation. Degradation of polymers that occur by any one of these mechanisms can be assessed by measuring changes in physical properties, loss in molecular weight (MW), amount of carbon-dioxide evolved and by calculating the microbial growth on polymer surface after exposure to natural environments. There are several standard test methods (Table 1) which are frequently used to assess biodegradability of polymers by measuring MW and molecular weight distribution, tensile properties, weight loss, extent of fragmentation, enzyme assays, biochemical oxygen demand and carbon dioxide production. Instead of a single procedure, a combination of test procedures is used during evaluation to confirm that biodegradation has actually occurred. It is recommended that selection of test methodology be based on potential fields of application of the test polymer and its fate at the end i.e. compost, soil, fresh or marine water. Some of the widely used standards are: ASTM D5338; ASTM D6400; ISO 14855 (for compost exposure); ASTM D5988; ASTM D 6002 (for soil exposure); ASTM D6691; ASTM D6692; ISO 15314 and ISO 16221 (for marine exposure).

It became increasingly clear that standard test methods are needed to establish and quantify the degradability of polymers, and to confirm the benign nature of the products of breakdown. As a result ASTM committee D-20 on plastics commenced the development of standards in the area of degradable plastics. The ASTM work effectively culminated in 1999 with the publication of ASTM D6400-99 which also refers a number of other ASTM documents including several test methods. The stringent European standard for biodegradability is EN 13432-2000. This standard is a reference point for all European producers and it specifies the requirements and procedures to determine the compostability of plastic packaging materials

TABLE 1: Standard Test Methods for Biodegradation

Standard	Description
ASTM D 6400-99	Standard specifications for compostable plastics
ASTM D6954-04	Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation
ASTM D 5338-98	Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions
ASTM D 6002-96	Standard guide for assessing the compostability of environmentally degradable plastics
ASTM D6340-98	Standard test methods for determining aerobic biodegradation of radio labeled plastic materials in an aqueous or compost environment
ASTM D 5988-03	Standard test method for determining aerobic biodegradation in soil of plastic materials or residual plastic material after composting
ISO 14855-99	Determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions – method by analysis of evolved carbon dioxide
ISO15314-04	Plastic-Methods for marine exposure
ISO 16221-01	Water quality – guidance for the determination of biodegradability in the marine environment
EN 13432-2000	Requirements for packaging recoverable through composting and biodegradation – test scheme and evaluation criteria for the final acceptance of packaging

based on four main areas, biodegradability, disintegration during biological treatment, effect on the biological treatment process and the effect on the quality of the resulting compost.

With the advent of published standard test methods, the claims on biodegradability or compostable nature of polymers must conform to the standards. The only other method might be a full scale demonstration for a potential user of the products. A need for review of these test methods has come to light as industry expands its use of biopolymers. The biodegradable polymer industry has a positive future, driven mainly by the environmental benefits of using a renewable resource feedstock sources. The ultimate goal of the industry is to find a fully biodegradable material with optimum technical performance. □

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