REVIEW

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Biodegradable Plastics from Renewable Sources

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ABSTRACT. Plastic waste disposal is a huge ecotechnological problem and one of the approaches to solving this problem is the development of biodegradable plastics. This review summarizes data on their use, biodegradability, commercial reliability and production from renewable resources. Some commercially successful biodegradable plastics are based on chemical synthesis (*i.e.* polyglycolic acid, polylactic acid, polycaprolactone, and polyvinyl alcohol). Others are products of microbial fermentations (*i.e.* polyesters and neutral polysaccharides) or are prepared from chemically modified natural products (*e.g.*, starch, cellulose, chitin or soy protein).

CONTENTS

1 INTRODUCTION

The field of biopolymers, while still in its early stages, is growing in popularity every day (Gross and Kalra 2002). General introduction on biopolymers, a technical overview of biopolymer field, and description of the research in Europe, Japan and USA was summarized by Kennedy and Sundquist (1993). Later, Lenz (1995) published an exhaustive report that summarized the state of the art in development of biodegradable polymers in 27 research laboratories in Japan. *Anonymous* (2000*a*) and Schlechter (2001) published extensive reports analyzing the situation on the market of biodegradable polymers, providing market estimates up to 2005, evaluating new technologies and describing the activities of major corporations.

Biopolymers are polymers that are generated from renewable natural sources, are often biodegradable and nontoxic. They can be produced by biological systems (*i.e.* microorganisms, plants and animals), or chemically synthesized from biological materials (*e.g.*, sugars, starch, natural fats or oils, *etc.*). Two

strategies are applied in converting these raw materials into biodegradable polymers: extraction of the native polymer from a plant or animal tissue, and a chemical or biotechnological route of monomer polymerization.

Biodegradable biopolymers (BDP) are an alternative to petroleum-based polymers (traditional plastics). Some BDP degrade in only a few weeks, while the degradation of others takes several months. In principle the properties relevant for application as well as biodegradability are determined by the molecular structure. According to the *American Society for Testing and Materials*, biopolymers are degradable polymers in which degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae (Shimao 2001). This means that BDP can be produced from natural raw materials such as starch, sugar and cellulose as well as fossil oils. In Europe, EC and DIN (*e.g.*, 54900) are proposing standards for the evaluation of biodegradability based on the composting technique. The EC standard (*Anonymous* 2000*b*) supports the *European Packaging Directive*. Successful efforts (Calmon-Decriaud *et al.* 1998) are underway to harmonize the different methods and definitions for aerobic and anaerobic degradation.

Besides the BDP biodegradability, other aspects relevant for processing are also important, *i.e.* thermal stability and viscosity that allow the use of conventional technologies and machines without large adaptations. The economic value of renewable raw materials will increase to a significant extent (Schlechter 2001) and stimulate new industrial activities (Cahill *et al.* 1999). However, the opinions of several suppliers of biodegradable polymers on the market position of these new products wary widely, from careful approximations of 500 Gg (*i.e.* 500 000 ton) to optimistic approximations of more than 10 Tg (*i.e.* 10 000 000 ton). The final potential will depend on legislation, local directives and sufficient waste treatment capacity at composting plants (for example for packaging, disposables, foil for agricultural use, *etc.*). The development (*Anonymous* 2000*a*) in the chemical sector (solvents, glues, coatings, *etc.*) will also become an important encouragement for the application of degradable raw materials.

New biotechnological processes have direct implications for society (*Anonymous* 1998; Weterings *et al.* 1997) but there are significant ethical issues of great public and personal concern to sustain the social development (Gerngross and Slater 1999). In this issue the wide use of BDP plays an important role. First, BDP can prevent or reduce any impact of industrial waste on the environment, thus providing a high level of environmental protection. Second, the use of BDP protects the soil and ensures that the application of biologically treated biowaste enhances soil carbon level. Third, the use of BDP ensures the functioning of the internal market and helps in avoiding obstacles to trade and distortion and restriction of competition within and outside the EU (*Anonymous* 2000*b*).

2 BIODEGRADABLE POLYMERS OBTAINED BY CHEMICAL SYNTHESIS

Okada (2002) in his recent review described the progress in the field of commercially available BDP. According to him, chemically synthesized BDP can be classified into three groups:

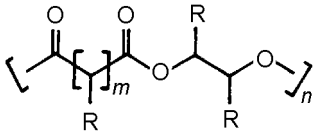
(*1*) polyesters
(*2*) polymers containing both ester and other heteroatom-containing linkages in the main chain
(*3*) polyamino acids

Lindblad *et al.* (2002) presented in their review a number of aliphatic polyesters obtained from renewable resources, which have shown interesting application as biomedical materials and degradable plastics. Polymers with heteroatom linkages such as polyamino acids are very important in medical applications (Park and Park 1996) and as catalysts (Bentley *et al.* 1997). However, polyamino acids are too expensive to be a good substitution of common plastic materials.

2.1 Polyglycolic acid (PGA)

PGA is produced by *Dupont* as an aliphatic–aromatic copolymer, either under the trade name Biomax® or in form of aramid fibers with the name Kevlar®. It combines the excellent material properties of aromatic PET (polyethylene terephthalate), and the biodegradability of aliphatic polyesters.

This BDP is prepared by a polycondensation reaction of glycol and aliphatic dicarboxylic acids. Both components can be obtained from renewable resources, *e.g.*, glycol from glycerol and suitable organic acids by fermentation, as documented by Varadarajan and Miller (1999). The final material is soft and has a good touch. Melting points are relatively high for a degradable material (≈200 °C). Depending on the application,



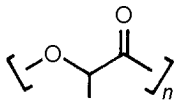
polyglycolic acid

up to three aliphatic monomers are incorporated into the PET structure. The monomers create weak spots in the polymeric chains, thereby making them susceptible to degradation through hydrolysis. Applications include disposal bags, diapers and eating utensils. PGA can be used to create geo-textiles and plant pots, and it is suitable for thermoformed blown bottles and injection molded objects.

The production price is only marginal in comparison with the costs of production of PET itself because PGA can be manufactured with existing equipment using existing bulk monomers. Currently available degradable materials can cost twice as much. The material can be recycled, incinerated or land filled, but is intended mainly for disposal composting and in-soil degradation. If properly disposed, it degrades in eight weeks (Shimao 2001). The large polymer molecules are cleaved by moisture into smaller units, which are then consumed by naturally occurring microbes and converted to carbon dioxide and water.

2.2 Polylactic acid (PLA)

PLA is not a new polymer. In 1932, Carothers (*see*, *e.g.*, Mark and Stafford 1940) produced a low molar-mass product by heating lactic acid *in vacuo*. Subsequent work by *DuPont* and *Ethicon* has focused on the manufacture of medical grade sutures, implants and controlled drug release applications. The flexibility of PLA has attracted big companies such as *Chronopol*, which currently operates a 1 Gg (*i.e.* 1000 ton) per year PLA facility in Colorado and has plans for 50 Gg per year in the future. Other companies have also entered into the PLA hunt, but *Chronopol* has developed a new technology that should reduce the costs of PLA from 2–3 USD/kg to 1 USD/kg. *Fiberweb* (France) disclosed nonwoven webs and laminates made of 100 % PLA in 1997 and introduced a range of melt-blown and spun laid PLA fabrics under the Deposa™ brand name. However, *Cargill Dow LLC*, the global leader in commercialization of PLA, and *Mitsui Chemicals*, a leading Japanese chemical company, have announced collaboration on the further business development of PLA – a polymer made from annually renewable resources, and have signed an agreement to accelerate the market development for PLA in the Pacific zone.



polylactic acid

PLA production and use are well documented in the literature. We have found more than 550 of papers devoted to PLA production and use on *Web of Science*. Generally, PLA is based on lactic acid that uses dextrose from corn or sugar beet as a feedstock for fermentation. Lactic acid is the basic monomer for PLA production. The improvement of continuous lactic acid fermentation (Melzoch *et al.* 1996) is a big challenge for bioengineers as documented in the latest paper of Kwon *et al.* (2001). Recently, Drumright *et al.* (2000) summarized the biotechnological aspects of PLA production.

Generally, there are two major routes to produce polylactic acid from the lactic acid monomer (Lunt 1998). The first route involves condensation–water removal by the use of solvent under high vacuum and temperature. This approach was used by Carothers (Mark and Stafford 1940) and is still used by *Mitsui Toatsu Chemicals* to produce a low to intermediate molar mass polymer. This polymer can be used as such, or coupled to isocyanates, epoxides or peroxides to produce a wide range of molar masses. An alternative method is to remove water under milder conditions, without solvent, to produce a cyclic intermediate dimer, referred to as lactide. In the year 2002, *Cargill Dow* launched a 300-million-USD effort to begin mass-producing its new plastic based on PLA under the trade name NatureWorks™.

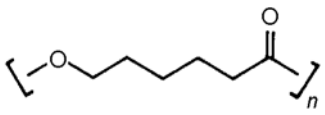
This intermediate is readily purified by vacuum distillation. Ring opening polymerization of the dimer is accomplished under heat, again without the need for solvent. By controlling the purity of the dimer it is possible to produce a wide range of molar masses (Kolstad 1996). With adjustable Young's modulus between 350 and 2800 MPa, melting 150 °C and degradation time 18–24 month, PLA is a good material for production of clothing, carpet tiles, interior and outdoor furnishing, geotextiles, bags, filtration systems, *etc.* Agrawal and Ray (2001) published a review on the advanced use of PLA in tissue biomedical engineering.

Kimura *et al.* (2002) investigated the primary biodegradability of PLA using hydrolysis tests at various composting temperatures and pH. They demonstrated that composting is a useful method for PLA biodegradation. This is in agreement with results of Karjomaa *et al.* (1998), who studied the biotic degradation of PLA oligomers at 25 and 58 °C in an aquatic aerobic biodegradation test for six months.

2.3 Polycaprolactone (PCL)

PCL is a biodegradable thermoplastic polymer obtained by chemical synthesis from crude oil. *Solvay Group*, the world's largest producer of PCL (Capa®), prepares its monomer using a unique process, which utilizes in the first step a high-strength aqueous hydrogen peroxide agent (87 %, *W*/*W*) and acetic acid to produce peracetic acid. This is used in the second step to oxidize cyclohexanone by a Bayer–Villiger reaction to caprolactone. The polymer is produced by a ring opening addition and polymerization reaction rather

than by the condensation polymerization reaction normally used for polyester production. This specialized *Solvay* process yields a high-purity, highly reactive caprolactone monomer, which is ideally suited for consistent polymer production. PCL has good water, oil, solvent, and chlorine resistance. It has a low mp (58–60 °C) and low viscosity, and is easy to process.



polycaprolactone

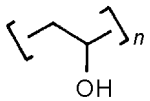
PCL is used mainly in thermoplastic polyurethanes, resins for surface coatings, adhesives and synthetic leather and fabrics. It also serves to make stiffeners for shoes and orthopedic splints, and fully biodegradable compostable bags, sutures, and fibers. The low melting point makes the material suited for composting as a means of disposal, due to the temperature during composting which routinely exceeds 60 °C. Degradation time is very short. In Sweden there has been an attempt to produce PCL bags, but they degraded before reaching the customers. Sanchez *et al.* (2000) described the biodegradation of PCL at 50 °C by a thermotolerant *Aspergillus* sp. The material was degraded and assimilated after 6 d and degradation products were identified as succinic, butyric, valeric and caproic acids.

Although the polymer is now being prepared from fossil resources, it may also be prepared from renewable resources *via* chemical treatment of saccharides. In the first step, the saccharides could be converted to ethanol and acetic acid by fermentation. In the second step, ethanol can be converted to cyclohexanone by use of chromic acid. Naturally, such product is expensive and is therefore mixed with large amounts of other natural materials to obtain a good biodegradable material at a low price. Recently, Ishiaku *et al.* (2002) and Duquesne *et al.* (2001) summarized three different strategies that can be used for preparing starch–PCL blends with desired mechanical parameters. Yang *et al.* (2001) used natural chitin as blend material (up to 60 %, *W/W*) to design a novel thermo-resistant plastic material. Zhong and Sun (2001) evaluated the thermal dependence of material strength and water resistance of PCL–soy protein isolate blends with 10, 20, 30, 40, and 50 % PCL (SPI–PCL) alone or with the addition of 0.5, 1, 2 and 5 % methylenebiphenyl-4,4′-diisocyanate. Zhang *et al.* (2000) observed an increase in biodegradation of cellulose derivatives such as cellulose acetate, ethylcellulose and hydroxyethylcellulose acetate when PCL was used as a blending material. Nitz *et al.* (2001) studied the properties of PCL composites with wood and lignin. The addition of maleinanhydride improved mechanical properties of PCL blend material during reactive extrusion.

Due to its low melting point, biocompatibility and high biodegradability, PCL has an important biomedical use. Gough *et al.* (2002) described the application of PCL fibers for incorporation into a PCL matrix for craniofacial bone repair. Hattori *et al.* (2001) pointed out that PCL was successfully proven as a new and inexpensive technique for bone fixation. The PCL fiber was fixed tightly by melting and the strength of this thread was higher than that of a stainless-steel wire with the same cross-sectional area. Shen *et al.* (2000) described the results of the application of PCL-biodegradable composites for regulation of drug release in an organism. Calandrelli *et al.* (2000) summarized the current state of art of preparation and characterization of composites based on biodegradable polymers for "*in vivo*" application.

2.4 Polyvinyl alcohol (PVA)

PVA exists only as a polymer, monomer has not yet been isolated. It is manufactured from vinyl acetate monomer in a multistep process when the monomer is polymerized into polyvinyl acetate and then hydrolyzed to polyvinyl alcohol. The most suitable renewable base material is ethanol. Over 400 Gg (*i.e.* 4×10^5 ton) of PVA are produced each year, in many grades, for use in diverse applications. Other details can be found in a comprehensive monograph of Finch (1992) that provides a critical and authoritative review of 20 years of research and developments of the PVA technology. PVA combines high tensile strength with ease of film formation and shows excellent adhesive and bonding characteristics. It may be partially hydrolyzed and thus have better adhesion to hydrophobic surfaces, its water resistance being increased with increasing hydrolysis. The super-hydrolyzed grades of PVA should be used when maximum water resistance and humidity resistance are desired.



polyvinyl alcohol

PVA has a wide use in production of adhesives or paper coatings, ceramics, in reprography and photography, in medicine and biotechnology and in manufacturing of biodegradable polymer films.

As shown by Shimao (2001), the biodegradability of PVA in the nature was extensively studied. Kawai (1995) describes the mechanism of metabolic degradation of PVA by microorganisms. Usually, PVA

biodegrades in microbial active environments within 5–6 weeks. Huang *et al.* (2002) has found that the fungus *Phanerochaete chrysosporium* degraded 73 % of PVA in a water environment within 5 d.

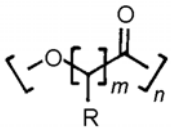
When compared with other BDP, the market of PVA is huge. According to the web server **www.chemindustry.com** there are many suppliers of PVA as is apparent from the following list of PVA trade names: Akwa Tears, Alcotex, Alvyl, Aracet, Cipoviol, Celvol, Elvanol, Ethenol, Gelvatol, Gohsenol, Ivalon, Kuralon, Kurare, Lemol, Liquifilm, Mowiol, Polydesis, Polysizer, Polyvinol, Polyviol, Poval, Resistoflex, Rhodoviol, Sno Tears, Solvar, Sumitex, Vibatex, Vinacol, Vinalak, Vinarol, Vinarole, Vinavilol, Vinol, Vinylon. However, the list is not yet complete because new and high production capacities are now opening in the Republic of Korea, India and Southeast Asia. Consumption of PVA in the United States, Western Europe and Japan increased at an overall rate of almost 2 % annually between 1992 and 2000.

3 BIODEGRADABLE POLYMERS PRODUCED THROUGH FERMENTATION BY MICROORGANISMS

Many microorganisms overproduce polyesters and neutral polysaccharides if they have access to a carbon source. Both groups of compounds are easy biodegradable and they can be produced from renewable resources. Polyesters, which are more important for the production of BDP, consist of simple carbon chain monomers. About 90 polyesters are identified as intracellular storage compounds performing different properties (Jendrossek *et al.* 1996).

3.1 Polyesters

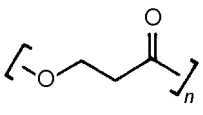
Polyhydroxyalkanoates (PHA) are linear polyesters produced in nature by bacterial fermentation (Byrom 1987; Katoh *et al.* 1999) from renewable natural sources such as sugar or lipids (Anderson and Dawes 1990). Large chemical companies such as *Imperial Chemical Industries* developed ways to produce PHA. In the case of PHA, however, the bacterium *Ralstonia eutropha* (Yu *et al.* 2002) converts sugar directly into plastic. Usually, PHA naturally accumulates within the microbes as granules that can constitute up to 90 % of a single cell mass. Recently, Jian *et al.* (2002) described the kinetics of PHA granule formation in a batch submersed culture. At about the same time, Tohyama *et al.* (2002) extended the quantitative description of process kinetic to a mixed culture in a fed-batch process (Du *et al.* 2001).



PHA

The PHA plastics have a wide range of industrially useful properties (Lee 1996) which will allow them to be used in both performance and commodity applications. At one end of the property range, the plastics are semi-crystalline with properties similar to polypropylene. At the other end of the range, the PHA are elastomeric – similar to natural rubber. The PHA plastics can be extruded into films, molded or coated onto other substrates, using conventional processing equipment. In addition, the PHA can be prepared either in a latex form, or as dry powders ready for melt processing. Typical PHA products are expected to encompass everyday items such as packaging materials, lawn and leaf bags, disposable diapers, fast food service ware, single-use medical devices, paints, as well as performance materials, which take advantage of superior properties inherent to the PHA.

Poly-3-hydroxybutyrate (PHB) is an energy reserve polyester naturally accumulated by a wide variety of microorganisms; it is accumulated amongst others (*e.g.*, *Azotobacter chroococcum*, Parshad *et al.* 2001; *Bacillus mycoides*, Thakur *et al*. 2001) by the bacteria *Ralstonia eutropha* (*Alcaligenes eutrophus*) in storage granules (Poirier 1999). Recently, Poirier (2002) summarized the progress in application of autoretransgenic plants for the synthesis of PHB.



PHB

PHB-like copolymer called PHBV [poly(hydroxybutyrate–valerate)] is less stiff and tougher, and is used as packaging material. Since April 1996, *Monsanto Company* has the sole rights for the production of PHBV under the trade name Biopol^{TM} (*Anonymous* 2000*c*).

PHA and PHB can be either thermoplastic or elastomeric materials, with melting points ranging from 40 to 180 °C. The most common type of PHA is PHB; it has properties similar to those of polypropylene. However, it is stiffer and more brittle. It is biocompatible and therefore can be implanted in the body without causing inflammations. The producer claims that it is nontoxic. The current price is very high compared to other oil-derived polymers. Gerngross and Slater (1999) discovered that making 1 kg of PHB from genetically modified corn plants would require about 300 % more energy than that needed to manufacture an equal amount of fossil fuel-based polyethylene

(29 MJ). Thus, the benefit of using corn instead of oil as a raw material could not offset this substantially higher energy demand. On the other hand, Choi and Lee (1997) demonstrated that the economic feasibility of PHB fermentation is comparable with petrochemical processes when cheap or waste substrates are used (Wong and Lee 1998; Yu and Si 2001) and unconventional microorganisms applied (Kofroňová *et al.* 1994; Pal *et al.* 1998). Recently, Du *et al.* (2001*a*,*b*) described a sophisticated two-stage culture process that has a chance to improve the economical effectiveness of the fermentation process.

The PHA and PHB are biodegraded in microbially active environments within 5–6 weeks (Shimao 2001). The action of some enzymes produced by microorganisms degrades plastic material, which is then absorbed through the cell wall and metabolized. It is normally broken down to carbon dioxide and water when degraded under aerobic conditions. In the absence of oxygen the degradation is faster, and methane is also produced.

Ramakrishna *et al.* (2001) summarized and compared the biomedical applications of polyesters and related BDP for development of implant/medical devices, sutures, bone plates, joint replacements, ligaments, vascular grafts, intraocular lenses, *etc.*

3.2 Neutral polysaccharides

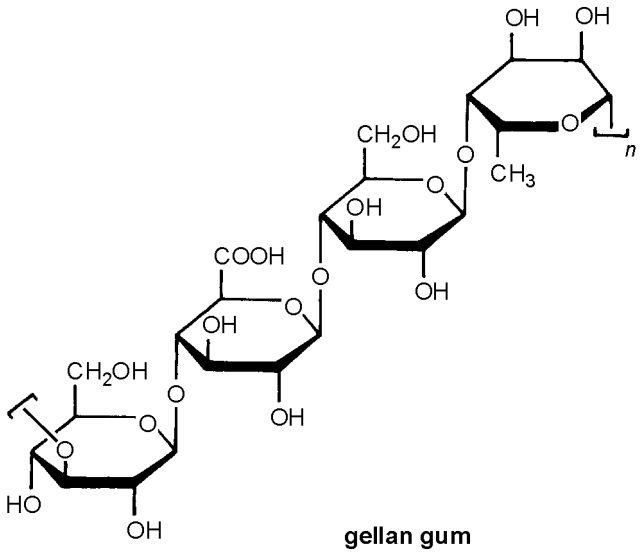
The use of microbial polysaccharides in the food, pharmaceutical and chemical industries has increased steadily during the past decade. They are natural gelling polysaccharides suitable for new biomedical applications (Murano 2000).

Crescenzi (1995) published a frequently cited survey on research activities in Europe in the field of saccharide polymers of microbial origin. The most important neutral polysaccharides produced by bacteria are xanthan, dextran and gellan. Commercially significant fungal polysaccharides are pullulan and glucan. Xanthan, a natural biopolymer produced by the culture fermentation of *Xanthomonas campestris*, is mostly applied as a gelling agent in food and pharmaceutical industry. Dextran is the generic name of a large family of microbial polysaccharides. It is produced by fermentation or enzymic conversion of the feedstock sucrose by *Leuconostoc mesenteroides* (Karthikeyan *et al.* 1996), *Saccharomyces cerevisiae*, *Lactobacillus plantarum*, and *Lactobacillus sanfrancisco* (*Anonymous* 2000*d*), which are currently used in food processing (Zasypkin 1997). However, both dextran and xanthan are commercially unimportant for industrial production of BDP.

3.2.1 Gellan gum

Gellan gum is an extracellular polysaccharide produced by *Sphingomonas* sp. (Pollock 1993); it is the newest member of the microbial polysaccharides (Giavasis *et al.* 2000) to be developed commercially. Chemically it consists of a tetrasaccharide unit, *viz.* D-glucose, D-glucuronic acid, D-glucose and L-rhamnose, and forms a transparent gel which is heat-resistant in the presence of divalent cations. Based on this character, gellan gum can make a processable material which has been regarded as unsuitable for food processsing as summarized by Kasapis (1995). However, there are new applications (Banik *et al.* 2000) for the production of biodegradable plastics that use the excellent properties of gellan gum (Manna *et al.* 1996). Hashimoto *et al.* (1999) described the enzymic machinery for the assimilation and depolymerization of gellan gum in bacteria. As for the other neutral polysaccharides, full biodegradation was observed in three days.

Gellan gum was developed and produced by the *Kelco Biopolymers* (*Division of Merck*) under the trade names Kelcogel® and Gelrite®. This polymer has applications in the food industry as a gelling agent in frostings, glazes, icings, jams and media for tissue cell cultures.



gellan gum

3.2.2 Pullulan

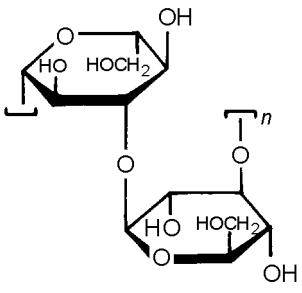
Pullulan is a polysaccharide of α-D-glucose that is a co-polymer of maltotriose (1,4-bonding) and isomaltose (1,6-bonding) with an additional 1,3-branching. It has adhesive properties and can be used

to form fibers, compression moldings, and strong, oxygen-impermeable films. Pullulan and its derivatives have numerous potential food (Xu *et al.* 2001), pharmaceutical and industrial applications (Shih 1996). The material is produced as a water soluble, extracellular polysaccharide by certain strains of the polymorphic fungus *Aureobasidium pullulans*. Seviour *et al.* (1992) summarized and evaluated the ability of microorganisms to produce exopolysaccharides, considering their chemical diversity, and examined factors that affect their production. The current state of art in pullulan chemistry and biotechnology is described by Steinbüchel *et al.* (2002). A promising chemical modification of pullulan has also been accomplished by acetylation (Jeong *et al.* 1999). Recently, Muzzarelli *et al.* (2002) published data on the biodegradation of pullulan and its derivatives. At neutral pH values and 25 and 37 °C, full biodegradation was observed in 3 d.

Commercial production of pullulan began in 1976 by *Hayashibara* (Japan). One of pullulan-based products is a film for foodstuffs that have low gas barrier properties to preserve aroma properties. The product is oil-resistant and easily biodegradable. Other suppliers market pullulan-based product as food additives or components for cosmetic products.

3.2.3 Laminarin and curdlan

Laminarin (1,3-β-D-glucan) is a polysaccharide which is a cell-wall constituent of many microorganisms like bacteria, fungi or algae (Augustin 1998). Mostly, it is extracted from the cell walls of baker's yeast, which are a by-product in the production of alcoholic beverages (Osumi 1998). The preparation of zymosan, a soluble form of yeast glucan, is known since 1940 (Holan *et al.* 1980).



laminarin

Curdlan is an extracellular bacterial 1,3-β-D-glucan, which was discovered by Harada *et al.* (Kanzawa *et al.* 1987) and given its name because of its ability to "curdle" when heated. Curdlan is produced by *Alcaligenes* sp. and *Agrobacterium* sp. (Nakata *et al.* 1998). Lee and Park (2001) described in details an optimal control strategy of curdlan production with feedback control of the pH profile. Nfiura *et al.* (1996) described the biodegradation of 1,3-β-D-glucan *in vivo* and found that it varied from 1 h to 1 d depending on the molar mass of the polymer.

Among the vendors of chemicals, *ABAC GmbH* (Switzerland) and *Biopolymer Engineering* (USA), are the largest suppliers of medical-grade yeast glucan that can be orally administered to stimulate the immune system. Karinen and Bergelin (1993) patented the preparation of glucan-enriched alimentary fibers, which are now an important product on the market of cholesterol-controlling functional foods (Cho and Dreher 2001). Recently, *Nurture Inc.* (USA) patented (Potter *et al.* 1999) the technique of glucan film preparation.

Takeda Chemical Industries Ltd. (Japan), transferred the production of curdlan to an industrial scale in 1989, and curdlan was approved and commercialized for food usage in Korea, Taiwan, and Japan. In 1996, Pureglucan®, the trade name of curdlan, was launched in the US market as a formulation aid, processing aid, stabilizer, and thickener or texture modifier for food use (Spicer *et al.* 1999). No evidence of any toxicity nor carcinogenicity of Pureglucan® has been observed. Now, curdlan is mostly used in the food industry. However, recent development in the field made possible its use for the production of special biodegradable plastic for medical applications.

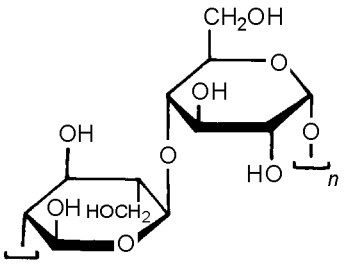
4 BIODEGRADABLE POLYMERS FROM CHEMICALLY MODIFIED NATURAL PRODUCTS

Finding new uses for agricultural commodities is an important area of research. New uses and markets for agricultural materials are needed to address the current slump in commodity prices. One application area being investigated is the replacement of petroleum-based materials with natural materials such as cellulose, chitin, agricultural products such as starch, proteins from wheat and soybeans, milk, *etc.* The successful replacement of petroleum-based materials will open new value-added markets for agricultural commodities and lessen the dependence of national economy on foreign crude oil and gas. As shown above, many agricultural products can be used as blends with one or more additional materials. The main components of this material are storage and structural polysaccharides. Storage polysaccharides include starch and glycogen whereas structural polysaccharides include cellulose, chitin and glucan (these polysaccharides differ in the types of linkages between monomers).

4.1 Starch

Starch is a major plant storage form of glucose. It consists of two components: amylose, in which the glucose units are 1,4-α-D-linked together in straight chains, and amylopectin (colored by elemental iodine), in which the glucose chains are highly branched. Principally, there are three ways how starch can be used for BDP's production. The first one is the preparation of starch composites (de Graaf and Janssen 2000; Ken and Sun 2000) with other plastics with a low amount of starch to enhance the biodegradability of traditional oil-based polymer materials. The second mode of starch application is the preparation of starch composites with starch content being more than half by mass. This material, so-called plastified starch, exhibits mechanical properties similar to conventional plastics but at a lower price (Bastiolli 1998*a*,*b*, 2001). The third way of starch BDP's preparation uses the extrusion processing of mixtures of granular starch in the presence of soy protein (Otaigabe *et al.* 1999), glycerol, alginate, lignin, humic substances, urea, sucrose, ammonium chloride *etc*. as plasticizers (Glenn and Hsu 1997; Glenn *et al*. 2001).

Generally, starch and synthetic plastics are incompatible in that they do not mix easily, leading to a non-homogeneous product. To overcome this problem, starch has to be chemically blended with synthetic polymers. It allows to reduce the price of synthetic plastics and to increase the biodegradability of the final product (Burgesscassler *et al.* 1991; Imam *et al.* 1992; Breslin and Swanson 1993; Wool *et al.* 2000).



starch

As explained below, starch can be applied in four different technological modes that result in diverse groups of products.

4.1.1 Starch composites with low amount of starch (≈10–20 %)

Starch is used as a biodegradable additive or replacement material in traditional oil-based commodity plastics. If starch is added to petroleum derived polymers (*e.g.*, polyethylene), it enhances the disintegration of the blend in nature, but not its biodegradability. Generally, it is supposed that starch can accelerate the disintegration or fragmentation of the synthetic polymer chains. Microbes consume the starch, thereby creating pores in the material, which weaken it and enable it to break apart. Disintegration of starch–plastic blends is not the same as biodegradation.

Their breakdown, also under optimal conditions, is quite slow. A series of papers (Hebeish *et al.* 1988, 1991, 1992, 1996, 1997) describe a technique for preparation of starch composites with different copolymers. Usually, the starch composites were prepared by copolymerization with maize starch using $KMnO_4$–citric acid as a redox initiator system. Wool *et al.* (2000) studied the kinetics of biodegradation of polyethylene–starch composites. The microbial invasion was detected with scanning electron microscopy. It was found that enzymic diffusion is an overall rate-controlling step. This is in accordance with the data of Burgesscassler *et al.* (1991) and Imam *et al.* (1993). Lopezllorca and Valiente (1993) used scanning electron microscopy to monitor the biodegradation of starch–plastic films prepared as a starch composite with PHA. Amylase tests on an agar medium were positive for nearly all the isolates. Aquino *et al.* (2001) described the pattern of starch degradation by thermophilic fungi at a temperature typical for fast composting.

In 1993 PLA–starch blends were commercialized by *Novon* under the trade name Ecostar®. Now, Novon sells a new generation of a modified starch blend with autooxidants under the trade name ECO-3®. This product contains 10–20 % of starch and is recommended as an additive to traditional plastics. It was confirmed that samples of low-density polyethylene film containing 20 % ECO-3® showed a 95 % reduction in elongation after being buried in soil for 18 months. *Novon International* and *Novon Polymer China* is now the successful producer and vendor of other new starch composites under the trade names Poly-Novon® and Degra-Novon®. In Europe, the most important vendor of starch-based additives for production BDP with a low content of starch is the multinational *Amylum Group*. It produces and markets a broad set of starch based ingredients for a wide range of food and especially non-food applications such as BDP.

4.1.2 Starch composites with medium amount of starch (≈40–60 %)

This sort of starch composites is also called plastified starch materials. They exhibit mechanical properties similar to conventional plastics such as polypropylene, and are generally resistant to oils and alcohols; however, they degrade when exposed to hot water. Properties of these materials can be varied as the content of starch and other materials changes. They are fully biodegradable and compostable, and they can replace traditional plastics in food service, food packaging, personal health care, *etc.*

Usually, their basic compound is corn starch (40–60 %), a renewable natural material. The rest is performance-enhancing additives and other biodegradable materials. When disposed in biologically active environments such as compost facilities and wastewater treatments systems, they display degradation characteristics similar to leaves, wood chips and paper. Most conventional plastic processes used for starch composite treatment are blow or injection molding, extrusion and thermoforming.

Imam *et al.* (1992) studied the biodegradation of plastic films containing corn starch (40 % dry mass) in combination with polyethylene. The spectroscopic analysis of the starch–plastic films indicated that up to about 40 % of starch in the films disappeared after a 60-d exposure. There is no doubt that starch composites containing about half mass fraction of both granular and gelatinized starch biodegrade faster than those with low starch content. Most basic research studies concerning plastified starch materials were performed by Bastiolli *et al.* (1995*a*,*b*) from *Novamont*. The present situation and future perspectives are described by Bastiolli (1998*a*,*b*, 2001). In the scientific world *Novamont* is recognized as a pioneer in the field of biodegradable materials; 41 articles and participation to international meetings, 27 patents and patent applications and 4 awards testify to its scientific contribution. This company was created within the *Montedison Group* at the end of the 80-ties as a research and development company with the aim to control the market between chemistry and environment using agricultural products. The core business activity of *Novamont* is placed in the field of biodegradable thermoplastic materials, commercialized worldwide with the trademark Mater-Bi® (Bastiolli 1998a). Now, *Novamont* is the largest supplier of plastified starch materials in Europe. Mainly derived from corn, wheat and potato starch, Mater-Bi® products are thermoplastic materials, which can be processed with the same machines traditionally used to process conventional plastics. Recently, *Novamont* and *Goodyear*, the world's largest manufacturer of tires, have announced the discovery of technology that makes the production of an environmentally friendly and biodegradable tire possible.

A new generation of starch-based materials that have a starch content ranging from 40 to nearly 70 % was announced in USA. *Agri-Tech Industries* commercialized a material that contained up to 50 % (*W*/*W*) starch and is targeting its applications such as personal hygiene and disposable medical products.

The starch composite of *Supol* Ex is marketed as a more ecological alternative to the above products containing conventional plastics. Manufacture of this bioplastic material is based on a patented procedure using 100 % sustainable raw materials (starch 50 %, plant oil, resin and small amount of other additives). The material produced by *Supol* can be treated by injection molding. In contrast to Mater-Bi®, the final products based on *Supol* Ex series are not water-resistant. Similar product as *Supol* seems to be Vegemat® produced by the French company *Vivadur*. The material contains 40–50 % starch, 30–40 % proteins, 5–10 % lipids, and 5–10 % natural additives. Vegemat® is obtained by transforming all the aerial parts of corn with neither separation nor purification of constituent parts and without the addition of a plastic of petrochemical origin. Thermoplastic granulate of Vegemat® can be shaped by injection molding without particular adaptation of the industrial tool. The final material is a rigid plastic and can be treated as wood. Similarly as *Supol* Ex, Vegemat® is not water-resistant and biodegrades usually in 8 weeks.

4.1.3 Starch composites with high amount of starch (≈90 %)

Bioplastics with high amount of starch are usually referred to as thermoplastic starch. They are stable in oils and fats; however, depending on the type, they can vary from stable to unstable in hot or cold water. They can be processed by traditional techniques for plastics. These materials contain most (>90 %) of starch that can be obtained from renewable natural sources. Coloring and flame retardant additives are possible. Depending on the grade, thermoplastic starch can degrade completely within 5 d in aqueous aerobic testing and in 45 d in controlled compost, or can decompose in water. Among other final products, starch-based tubes, degradable compost bags, agricultural mulch films are commercialized. Most conventional plastic processes are blow and injection molding, extrusion and thermoforming.

In the last two decades more then 90 research papers were dedicated to thermoplastic starch. Approximately half of the research data was addressed to optimization of the extrusion process. According to *Web of Science* the most cited paper of Wiedemann and Strobel (1991) described the preparation of thermoplastic starch as a combined process consisting of extrusion cooking and plastic compounding. The quality of the product is determined largely by the degree of mechanical shear, temperature and water content. Later, Poutanen and Forssell (1996) discussed the influences of water and other plasticizers on the physical properties of starch. A new technique in the extrusion of thermoplastic starch laminated sheets was examined by Wang *et al.* (2000) and Averous and Fringant (2001).

The second large group of research papers dealt with biodegradation of thermoplastic starch. Vikman *et al.* (1995, 1999) consolidate the opinions on testing methods for assaying the biodegradability of starch-based materials. The authors recommended to use the excess of *Bacillus licheniformis* α-amylase and

Aspergillus niger glucoamylase at 37 °C. The degree of degradation can be monitored by measuring the dissolved saccharides or by the mass loss of the samples. Shin *et al.* (2000) reported about the relationship between mechanical properties and biodegradability of thermoplastic starch–polycaprolactone blends, confirming that the degree of biodegradation of starch composites is proportional to starch content and the material degrades in 6 weeks during composting. Similar results were obtained by Martin *et al.* (2001) for mechanical properties of multilayer films based on thermoplastic wheat starch.

Among the vendors of BDP with a high amount of starch, *Biotec GmbH* with Bioplast® and *Novon International* with Novon® play an important role on the market. Bioplast® is manufactured by compounding and melting starch and other completely biodegradable ingredients and then processed to granules; they can be processed on only slightly modified machines for thermoplastic resins and used same way as traditional synthetic plastics.

The biodegradation of granules and final products requires special conditions. The details are given by Lorcks (1998) and Schroter (1998). The most cited papers describing the details on Novon® are papers of Park *et al*. (1993) and George *et al.* (1994).

4.1.4 Foamed starch

Foamed starch is an antistatic, insulating and shock-absorbing material containing 100 % of starch. It is fully biodegradable and compostable and can replace polystyrene foam as biodegradable packaging material or can be pressed into starch-based sheets for thin-walled products, such as trays, disposable dishes, *etc.*

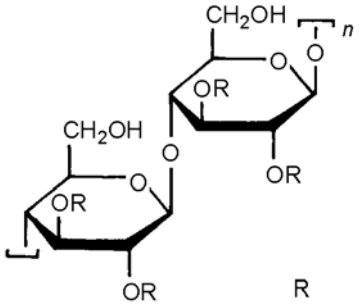
Foamed starch can be environmentally friendly blown into a foamed material using water steam or a compression–explosion process (Glenn and Orts 2001). Miladinov and Hanna (2001) described an alternative process that permitted to control the final product properties by the temperature and ethanol additive to acetylated starch foam.

The porous structure (Shogren *et al.* 1998) of starch foam allows disposing of food packaging and serving articles after use by composting. Composting tests confirm degradation within a few weeks without accumulation of residues (Tiefenbacher 1993). As mentioned above, the acetylation of starch allows controlling the biodegradability of final products (Fringant *et al.* 1998). The spectrum of microorganisms that can degrade foamed starch products is broad. As shown by Šimůnek *et al.* (2001), all bacteria that were isolated from the digestive tract of different mammals fully degrade starch substrates. This means that the materials based on foamed starch may also be biodegraded in standard wastewater cleaning plants.

There are few important producers of foamed starch BDP. *National Starch & Chemical* produces and sells in 20 countries a loose-fill packaging material under the trade name Eco-foam®. *Norel Unisource* (USA) produces foamed starch loose-fill under the trade name Envirofill®. Among other important producers and vendors of foamed starch material are *Biotec GmbH* with Biopur®, *Novon Polymers* (China) and *SudStarke* (Denmark).

4.2 Cellulose

Cellulose is one of the most abundant biopolymers on earth. It is the major constituent of plant cell walls, and more than half of the organic carbon on earth is found in cellulose. It is composed of unbranched, linear chains of D-glucose molecules, linked to one another by 1,4-β-D glycosidic bonds, which no vertebrate has the capacity to digest enzymically. Herbivores subsist largely on cellulose, not because they can digest it themselves, but because their digestive tracts contain microbes that produce cellulose-hydrolyzing cellulases; various cellulase types are also synthesized by fungi (*see*, *e.g.*, Kolarova and Augustín 2001; Gomes *et al*. 2001; Witkovska and Maj 2002). When compared with starch, cellulose is relatively resistant to biodegradation. Because each cellulose molecule is an unbranched polymer of 10^3–10^6 D-glucose units, cellulose-containing materials from various sources are all the same at the molecular level. The aerobic biodegradation of organic polymeric test materials is investigated in aquatic test systems based on respirometry and the evolution of carbon dioxide (Pagga *et al.* 1995, 2001). Lednická *et al.* (2000), in search for bacterial cultures, which are able to rapidly degrade cellulose plant fibers, characterized >70 bacterial strains that were grouped into 3 clusters (*viz. Cellulomonas* spp., *Cellvibrio*



spp. and *Pseudomonas* spp.). These bacteria degrade several flax, broom and cotton fibers very rapidly in a standardized *in vitro* test, causing mass losses of 40–86 % within 13 d of incubation. The anaerobic degradation of cellulose is much slower than the aerobic one. Clarkson and Xiao (2000) published the results of anaerobic bioconversion of newsprint and office paper. The bioconversion of paper was nearly complete within 20 d but continued for ≈165 d with methane yield efficiency ranging from 71 to 85 % of potential chemical oxygen demand. An obligatory step in cellulose degradation by anaerobic bacteria is the adhesion of the bacterium to the polysaccharide. In many anaerobic bacteria the adhesion protein, and the enzymes required for polysaccharide hydrolysis, are organized into a complex and interesting structure called cellulosome (Schwarz 2001). This mechanism and other details on anaerobic biodegradation of cellulose were described in a comprehensive review of Leschine (1995) and in the book of Robyt (1998). In this journal a fundamental study on anaerobic decomposition of cellulose was published by Suchardová *et al.* (1986).

The very substantial, but so far little exploited category of cellulose-based materials, which has lead to some of the very first industrial polymer products such as celluloid and cellophane, still offers numerous new possibilities for polymeric materials.

Now, basically two main groups of cellulose-materials can be distinguished (Simon *et al.* 1998): cellulose composites suitable only for treatment in conventional processes, and thermoplastically processsable cellulose derivatives such as esters which can be used for extrusion and molding.

4.2.1 Cellulosic biocomposites

When embedding natural cellulose containing fibers in a BDP polymeric matrix, we obtain a new generation of fiber reinforced materials (Chand *et al.* 1988), the so-called biocomposites (Hermann *et al.* 1998). Whereas traditional compounds consist of very stable components which are very difficult to decompose, biocomposites are made completely from biologically renewable resources. This offers additional possibilities of a convenient removal after the end of the lifetime, *i.e.* biodegradation, composting or carbon dioxide neutral combustion (Riedl and Nickel 2001). Mohanty *et al.* (2000) published a critical overview (with 250 references) that is focused on the use of renewable raw materials for production of cheap cellulose-based biocomposites. Another review (George *et al.* 2001) compares the techniques of natural fiber modifycation for production of reinforced plastic composites. Among more than 400 papers dedicated to the development of biocomposites, the most cited is an experimental paper of Bledzki *et al.* (1996), which is dedicated to the suitable modification of natural fibers with silan or stearic acid to decrease moisture absorption. The authors have shown that this property influences both mechanical strength and low specific density.

As shown by Mohanty *et al.* (2000), huge amount of research work is being done to combine natural materials containing cellulose with materials such as glass, metals, plastics, inorganics, and synthetic fibers to produce new materials that are tailored for end-use requirements. A wide distribution of such low-cost materials and high performance composites on the market was attained for wood and similar lignocellulosic biocomposites (Callum and Hill 2000). Since 1998, *Dow Polyurethanes* produces a new generation of biocomposite wood-replacement panels made from wheat straw and *Dow*'s polyurethane resin. *Phenix Biocomposites* is an important vendor of Environ® biocomposite panels which are a decorative interior material that respects the environment by using recycled paper products, a soy-based resin system, and color additives. *Neste Resins Corporation* produced powdered formaldehyde-based resins have been used for essentially all wood adhesive applications either as powders or as liquid resins reconstituted from powders.

In Europe, the research is coordinated by the *Scientific Center of Excellence – The BioComposites Center* established in 1989 at the *University of Wales* (Bangor). The Center is self-financing and is staffed by an interdisciplinary team of wood, polymer and material scientists, biologists, chemists and physicists, with many years of experience of research into industrial utilization of wood and plant fibers and plant polymers. Under the name Fasal®, *Austel* markets injection molding granules of renewable raw materials. It is a thermoplastic granulated material which contains about 50 % wood, *e.g.*, waste wood or weak wood in chip form or as sawdust. A similar product is sold by the German company *LignoPol* under the name Lignopol®, which is based on composites comprising lignin and natural fibers plus additives, also from natural sources. *Tecnaro GmbH* develops, produces and markets Arboform®, a sustainable thermoplastic material, with a current capacity of 300 Mg (*i.e.* 300 tons) annual output. The product is made from 100 % renewable raw materials (lignin and cellulose) and is mainly used for injection molded wood applications. The Treeplast® product is a *Craft* project of six companies, funded by the *European Commission*. The stan-

dard version of Treeplast® is absolutely natural renewable and biodegradable. It is made from wood chips (50 %), with crushed corn and natural resin and does not contain other plastics.

4.2.2 Cellulose acetate

Cellulose acetate is an amorphous thermoplastic and translucent material belonging to the cellulose esters family. Since 1905, when Camille and Henri Dreyfus developed a commercial process to manufacture cellulose acetate, it is obtained by introducing acetyl groups into cellulose (as cotton or wood fibers) to produce a tough plastic material. It is especially suitable for non-flammable "safety film" and other coatings applications requiring high melting point, toughness, clarity, and good resistance to UV light, chemicals, oils, and greases. Edgar *et al.* (2001) published a review containing 300 references where they examined the possible cellulose ester application with particular focus on biodegradable plastics, composites, laminates, optical films, and separation membranes.

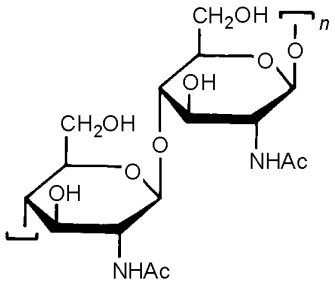
In the last decade, the biodegradability of cellulose acetate products was extensively studied (for review *see* Shiraishi and Yoshioka 2000). The most cited paper of Buchanan *et al.* (1993) described in details the mechanism of aerobic biodegradation of cellulose acetates. While cellulose monoacetate films required 10–12 d for extensive degradation, most of 80 % cellulose diacetate films were able to degrade in 4–5 d. Films prepared from cellulose triacetate remained essentially unchanged after 28 d in an *in vitro* assay. The cited work demonstrated that cellulose acetate fibers and films are potentially biodegradable and that the rate of biodegradation can be controlled by the degree of acetylation. Gartiser *et al.* (1998) compared several test methods for the determination of the anaerobic biodegradability of cellulose acetate and demonstrated that it can be degraded to methane. Sakai *et al.* (1996) have found that bacteria isolated from soil preferentially degrade the cellulose part of the cellulose acetate molecule under aerobic conditions.

According to the *Federal Trade Commission*, the market for cellulose acetate is highly concentrated. Three companies currently produce cellulose acetate in the *United States*: (*1*) *Eastman Chemical Company*; (*2*) *Primester*, a joint venture, the shares of which are owned by *Eastman* and *Rhodia*, a specialty chemicals company subsidiary; (*3*) *Celanese Ltd*., until recently a wholly-owned subsidiary of *Hoechst*. *Celanese* controls approximately 46 % of US production capacity, *Eastman* owns approximately 44 %, and *Primester* holds the remaining 10 %.

4.3 Chitin and chitosan

Chitin (poly-*N*-acetyl-D-glucosamine, 2-acetamido-2-deoxy-1,4-β-D-glucan) is one of the three most abundant polysaccharides in nature. It ranks second to cellulose as the most plentiful organic compound on earth. Chitosan, known as soluble chitin, is a natural product obtained from deacetylated chitin.

Usually, chitin is extracted from shells of crustaceans and cell walls of fungi. It is biodegradable, nontoxic and readily biocompatible. The ability to degrade chitin was detected in *Actinomycetes*, especially the *Streptomyces* spp. (Itoh *et al.* 2002; Schrempf 2000) living in soil (Hanzlíková and Jandera 1993) and in other bacterial species (Hashimoto *et al.* 2000), *Vibrio* spp. (Salyers *et al.* 1996) and *Clostridium* spp. (Kopečný and Hodrová 2000; Šimůnek *et al*. 2002). On the *Web of Science* more than 2500 papers are dedicated to the degradation of chitin or production of chitin-degrading enzymes as summarized by Felse and Panda (2000). The most cited paper is the review of Flach *et al.* (1992), which deals with developments in molecular and physiological aspects of chitinases from plants, fungi, bacteria, insects and fish. Šimůnek *et al.* (2001) analyzed the anaerobic chitinolytic bacteria that were isolated from the digestive tract of different mammals.



chitin

Data on the kinetics of chitin degradation can be found in the literature only sporadically. Boyer (1994) measured potential rates of chitin degradation and its mineralization. Under aerobic conditions in water environment 88–93 % of particulate chitin was mineralized to CO_2 within a few days. The highest degradation (≈30 % of chitin) was observed after 1 d. The process of two-phase composting of a chitin-rich substrate from shrimp shells was described by Roy *et al.* (1997). The monitoring of chitin degradation was performed according to Gooday (1990). Struszczyk (2002*c*) published a comprehensive review on biodegradation and bioactivity of chitin and its derivatives.

Usually, chitin is extracted from crab chum. During a pre-treatment phase, dilute solution of sodium hydroxide (pH 13.5) dissolves any remaining flesh and prevents further microbial activity or shell

degradation. The crushed shells are conveyed into a reactor, where they are treated with hydrochloric acid to gasify the minerals. In the third stage of the process, the material is washed before entering another NaOH solution with a slightly elevated temperature to liquefy proteins and produce chitin. On a dry mass basis, there is 12 % yield in the process of extracting chitin from crab chum.

Chitosan is produced from chitin. It is washed and put through boiling lye to remove acetate from the molecule. After hydrolysis, the resulting chitosan is washed, dried, ground, weighed and packed for sale. Rao *et al.* (2000) described the critical factors of the process where the three stages of the classical process are replaced by lactic fermentation of shrimp shells. Other details can be found in a recent comprehensive review (Struszczyk 2002*a*) and in the handbook edited by Muzzarelli and Peter (1997).

Goosen (1997) published a book dedicated to the application of chitin and chitosan. Now, chitin and chitosan are applied (Kumar 2000) in the textile industry, in medicine (Singla and Chawla 2001) and in food production (Jeon *et al.* 2000). Generally, chitosan beds, films or fibers can be obtained in a wet way by pumping high-viscous chitosan salt (acetate, malate, chloride, citrate, *etc.*) into a basic solution (Struszczyk 2002*b*).

According to the *Web of Science*, more than 50 review papers were published on chitin or chitosan applications. A review by Kumar *et al.* (2002) summarizes the present state (418 references) of art regarding the synthetic methods and characterization of nanoparticles, the suitability of polymeric systems for various drugs, drug loading and drug release properties of various systems such as nanoparticles, hydrogels, microspheres, films, membranes, tablets, *etc.* Hutmacher *et al.* (2001) described the application of chitosan-based plastics for tissue engineering. Jenkins and Hudson (2001) evaluated the recent state of art (178 references) in the field of preparation of biodegradable polymers with chitin or chitosan blends. Vikhoreva *et al.* (1999) summarized the properties of water-soluble derivates of chitin for fiber production. The most cited review in this field (Rathke and Hudson 1994) covers in 244 references the traditional approach to chitosan fibers and films fabrication. There are more than 50 large chitin and chitosan suppliers. In the USA *Biopolymer Engineering* with ChitoPure® is one of the world's premier manufacturers of chitosan products. Its trade competitors on the Atlantic coast are *Primex*, *Iceland* with ChitoClear® and *Groupe RT* (Canada) with Kitomer®. Important suppliers of chitin in the Pacific region are *Kate International* (India), *Sonat Co.* (Russia) and *Taizhou Candorly Sea Biochemical & Health Products Co.*, *Dalian Xindie Chitin Co.*, both from China. In continental Europe, the largest merchant of chitin and chitosan is *Sigma Chemicals*.

4.4 Soy-based plastics

The raw, hulled soy beans contain, depending upon variety, approximately 18 % oil, 38 % protein, 30 % saccharides, and 14 % moisture and ash. The saccharide component is normally about 15 % of soluble saccharides and 15 % of starch. Since 1940, when Henry Ford presented in public the strength of a car body made of a soybean-based material, this material is taken as highly prospective for production of soybean–formaldehyde-based thermoset composite from renewable resources. The papers of Paetau *et al*. (1994*a*,*b*) reported on the comeback of soy-based plastic in the USA.

Spence *et al.* (1996) summarized the data on aerobic degradation of protein–starch plastics. Park *et al.* (2000) published an extensive study on soy protein films during composting; they found that the samples degraded with 50 % mass loss in about 10 d and with up to 95 % mass loss in 30 d.

There are four main ways how to prepare soy-protein plastic materials. Current research and development is focused on commercializing of the following soy products: (*1*) soy–phenol–resorcinol–formaldehyde; (*2*) an improved waterproof product to replace phenol–formaldehyde (Rhim and Weller 2000); (*3*) a foaming glue for plywood (Park and Hettiarachchy 1999; Lodha and Netravali 2002); (*4*) an improved water-resistant product to replace urea–formaldehyde materials (Otaigbe *et al.* 1999). The mechanical properties and morphology of soy-plastic materials were described by Sue *et al.* (1997). Soy plastics can possess significantly higher Young's module (4.4 GPa) than those of petrochemical plastics and show good potential as an alternative for replacing petrochemical, nonbiodegradable plastics for engineering applications. Otaigbe and Adams (1997) published an innovative approach to improve the resistance of soy protein plastics to water by polyphosphate fillers.

When compared with starch biocomposites the commercialization of soy-protein plastics is limited to the USA. A commercial production facility for soy-based adhesives was started-up by *Heartland Resource Technologies* (Iowa). *Urethane Soy System Company* (Illinois) is now producing soy-based polyols for rigid and flexible urethane foams under the name SoyOyl®. *Dow Chemical* developed soy-based biodegradable material BioBalance® which is used in carpet backings.

5 PERSPECTIVES AND CONCLUSIONS

The development of biodegradable plastics is best viewed in the context of diminishing of crude oil reserves. In future years, it will be largely driven to derive more carbon for chemical processes from renewable resources and to preserve the ecosystem. As shown above there are three technological approaches to the production of BDP. Industrial chemistry can use the know-how of petrochemistry to produce suitable replacement of conventional plastics. Fermentation industry supported by developments of genetic engineering can yield microbes that more efficiently convert inexpensive raw materials to polyesters and neutral polysaccharides. The construction of new overproducing microbial strains will be facilitated by using genetic methods. These powerful technologies will allow designing industrially feasible cost-effective biological routes to a wide range of chemicals, including monomers and polymers. Now the technical background of food industry permits to develop an environmentally friendly products based on starch and composite materials. On the basis of economic and environmental considerations, the commercialization of BDP continues and shows increasing markets of products that have a relatively short-use lifetime. The number of research papers concerning BDP is an endless belt of knowledge, implicating new projects that end in building up of new manufacturing capacities.

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