Chapter 2

BIODEGRADABLE POLYMERS

2.1 Synthetic biodegradable polymers such as aliphatic-aromatic copolyesters

2.2 Biopolymers

2.3 Synthetic biodegradable polymers that are naturally susceptible to microbial-enzyme attack
    2.3.1 Poly(lactic acid)
    2.3.2 Poly(ε-caprolactone)
    2.3.3 Polyglycolide (PGA)
    2.3.4 Poly(amino acid)
2.4 Bacterially derived polyhydroxyalkanoates

2.5 Natural biodegradable Polymers
    2.5.1 Starch and its derivatives
    2.5.2 Cellulose and its derivatives

Biodegradation of polymers have been around for almost a decade but it has only been in the last two to three years that they have started to be produced on a commercial scale. Biodegradable polymers have already found acceptance in application areas such as food packing, bags and sacks, loose-fill packaging agricultural film and many niche market applications. There is also a growing trend for brand owners and retailers to recognize the potential marketing benefits of 'green' or 'sustainable' packaging as consumers become more concerned about the development of sustainable technologies, reduction in CO2 emissions and the conservation of the earth's fossil resources. Several major world brands including Wal-Mart have been persuaded to switch from petrochemical-based plastics to biodegradable plastics in recent years. There are broadly five classes of commercially available biodegradable polymers in existence.

2.1. Synthetic biodegradable polymers such as aliphatic-aromatic copolyesters

Demand for biodegradable polymers is also benefiting from a narrowing in price differential between petrochemicals-based plastics and biopolymers. Petrochemicals-based plastic prices have gone up sharply due to a surge in crude oil prices and look like remaining at historically high levels for some time to come. At the same time, biopolymer prices have come down significantly in recent years due to better production techniques, better material sourcing by suppliers and higher production volumes.

The major classes of biopolymer, starch and starch blends, polylactic acid (PLA) and aliphatic-aromatic co-polymers, are now being used in a wide variety of niche application, particularly for manufacture of rigid and flexible packaging, bags and sacks and foodservice products. However, market volumes for biopolymers remain extremely low compared with standard petrochemical-based plastics. Polyesters have played a prominent part in the development of biodegradable polymers. One of the first products developed as a biodegradable plastic in the early 1970s was based on a polyester belonging to the polyhydroxyalkanoates (PHA) group Called polyhydroxybutyrate (PHB).

Besides the natural polyesters a number of synthetic aliphatic polyesters have also been shown to be biodegradable. From a commercial point of view the most important synthetic biodegradable aliphatic polyester was traditionally polycaprolactone (PLA).

Poly (dioxanone), a polyether-ester copolymer was obtained by the ring openig polymerization of p- dioxanone resulted in the first clinically tested monofilament synthetic suture; known as PDS (marketed by Ethicon) this material has approximately 55% crystallinity, with a glass temperature of –10 to 0 ^{o}C. The polymer should be processed at the lowest possible temperature to prevent depolymerisation back to monomer. Poly (dioxanone) has demonstrated no acute or toxic effects on implantation. The monofilament loses 50% of its initial breaking strength after three weeks and is absorbed within six months, providing an advantage over other products for slow healing wounds.

Poly (lactide-co-glycolide) is prepared using the polyglycolide and poly(*l*- lactide) properties as a starting point, it is possible to co- polymerize the two monomers to extend the range of homopolymer properties. Copolymers of glycolide with both *l*-lactide and *dl*-lactide have been developed for both device and drug delivery applications. It is important to note that there is not a linear relationship between the copolymer composition and the mechanical and degradation properties of the materials. For example, a copolymer of 50% glycolide and 50% dl-lactide degrades faster than either homopolymer. Copolymers of *l*-lactide with 25-705 glycolide are amorphous due to the disruption of the regularity of the polymer chain by the other monomer. A copolymer of 90% glycolide and 10%l-lactide was developed by Ethicon as an absorbable suture material under the trade name Vicryl. It absorbs within 3 to 4 months but has a slightly longer strength retention time.

Nowadays, various aliphatic copolyesters based on succinate, adipate, ethylene glycol and 1,4- butanediol are being produced. Companies such as NatureWorks LLC are also producing aliphatic polyesters based on natural feedstock such as lactic acid on a commercial scale.

However, most of the aliphatic polyesters presently commercially used for biodegradable materials exhibit serious disadvantages. Beside the relatively high price level, properties are often limited and exclude these materials from many examples. For example, PCL has a very low melting point of about 60^{o}C.

For conventional technical applications aromatic polyesters such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) are widely used. But these polymers are biologically inert and thus not directly applicable as biodegradable plastics. Combining both the excellent material properties of aromatic polyesters and the potential biodegrability of aliphatic polyesters has led to the development of a number of commercially available aliphatic-aromatic co-polyesters over the last decade or so.

BASF's Ecoflex is based on co- polyester from terephthalic acid and 1,4- butanediol. The content of terephthalic acid in the polymer is approximately 42-45 mol% (with regards to the dicarboxylic monomers). Modification of the basic co-polyester leads to a flexible material, which is especially suitable for film applications.

Ecoflex reportedly processes easily and has a melting point of 110-115^{o}C and other properties equal or close to those of LDPE. The F (film) version imparts high elongation and dart impact and yields clear films that weld and print easily. BASF says, masterbatches can fine-tune the feel of Ecoflex films from soft to HDPE-like stiffness. Ecoflex is said to have high toughness and good cling properties. That makes it possible for 10-micron cling films to replace vinyl in vegetable, fruit, and meat wraps. BASF claims its materials also make films with 50% lower moisture vapour transmission rate (MVTR) than other biodegradable polymers.

The biodegradation of Ecoflex film was tested under composting conditions. After 100 days in a composting environment more than 90% of the carbon in the polymer was converted to carbon dioxide. Tests also showed no toxic effects of degradation intermediates.

Eastar Bio (now owned by Novamont) is also based on co-polyester composed of terephthalic acid, adipic acid and 1,4-butanediol, but due to some special modifications the material properties are different.

Degradation of Eastar Bio was tested under composting conditions: after 210 days of composting about 80% of the polymer carbon was released as carbon dioxide.

Eastar Bio co-polyesters have a melting point of 108 ^{o}C and offer good contact clarity, adhesion, and elongation (up o 800%). They have high moisture and grease resistance, and process much like LDPE. Eastar Bio is used in lawn- and- garden bags, agricultural films, netting, and paper coatings.

DuPont's Biomax product is a standard PET with the addition of three aliphatic monomers to allow degradation to take place. Comparable to PLA, the degradation mechanism is described as an initial attack of water to the special monomers, which are sensitive to hydrolysis. Although it appears that Biomax sufficiently disintegrates under composting conditions, the process of decomposition of the material was too slow to meet accepted standards.

Biomax 6962 has 1.35 g/cc density and 195 °C melting point versus 250 °C for PET, resulting in higher service temperature capability and faster processing rates than for other biodegradable. Mechanical properties include high stiffness and 405 to 50% elongations. DuPont has targated fast-food disposal packaging, as well as yard-waste bags, diaper backing, agricultural film, flowerpots and bottles.

EnPol from Korea's Ire Chemicals are based on a group of aliphatic co-polyesters comprising adipic acid, succinic acid, 1,2-ethanediol or 1,4- butanediol. EnPol polymers meet the specifications of the US food and Drug Administration for food contact applications and the USP specifications for medical device applications.

The biodegradation of EnPol polymers was tested in a controlled laboratory-composting test and showed that within 45 days a carbon dioxide evolution of more than 90% of the carbon present in the co-polyester was detected.

Partly because of their cost, biodegradable polyesters are finding much of their market in blends. Synthetic biodegradable polyesters tend to complement one another's properties, as well as those of PLA, thermoplastic starch, and other organic materials. Eastar Bio, for instance, is flexible and tough, with good contact clarity and adhesion properties. Its deficits are relatively low stiffness, poor melt strength, and a tendency to stick in injection moulds. In contrast, Nature Works PLA tends to be brittle and has poor adhesion. Blends of the two are a logical way to increase the performance envelope of both materials.

Aliphatic polyesters like polycaprolactone (PCL) or polybutylene adipate (PBA) are readily biodegradable, but because of their melting points of 60°C are unsuitable for many applications. On the other hand, aromatic polyesters like polyethylene terephthalate (PET) or Polybutylene terephthalate (PBT) have melting points above 200°C and very good materials properties, but are not biodegradable.

The solution is a combination of incorporating aliphatic monomer (adipic acid) in the polymer chain in such a way that the material properties of the polymer would remain acceptable (e.g., melting point of the crystalline range still around 100°C), but the polymer would also be readily compostable/biodegradable. In this way it was possible to combine the degradability of aliphatic polyesters with the outstanding properties of aromatic polyesters.

Synthetic biodegradable polyesters fall into two broad categories. One is highly amorphous, imparting flexibility and clarity comparable to a conventional LDPE copolymer. A second group of semi-crystalline polyesters is more rigid, with properties similar to PET, PP, or PS.

The three most prominent global suppliers of synthetic biodegradable polymers are BASF, Novamont, which acquired Eastman Chemicals Eastar Bio product portfolio in 2005, and DuPont.

BASF's Ecoflex and Novamont's Eastar Bio Ecoflex are aliphatic-aromatic co-polyesters based on butanediol, adipic acid, and terephthalic acid. BASF's products contain long-chain branching while Eastar Bio is highly linear in structure.

BASF Ecoflex co-polyester films have a property profile similar to that of low-density polyethylene and can be produced on exiting LDPE extrusion processing lines. They have a melting point of 110-115°C, the Ecoflex f (film) version imparts high elongation and dart impact and yields clear films that weld and print easily. Ecoflex is said to have high toughness and good cling properties. That makes it possible for-10 micron cling films with 50% lower MYTR (moisture vapour transmission rate) than other biodegradable polymers.

Eastar Bio is offered in general-purpose and blow-film grades. The aliphatic-aromatic co-polyesters have a melting point of 108 °C and offer good contact clarity, adhesion, and elongation. They have high moisture and grease resistance, and process much like LDPE. Eastar Bio is used in nonwovens, lawn-and-garden bags, agriculture films, netting, and paper coating.

In the semi-crystalline category, DunPont offers a modified PET incorporating three proprietary aliphatic monomers. Biomax 6962 has 1.35g/cc density and 195 °C melting point, versus 250 °C for PET, resulting in higher service temperature capability and faster processing rates than for other biodegradables. Mechanical properties include high stiffness and 40% to 500% elongation.

Synthetic biodegradable polyesters are used mainly as specialty materials for paper coating, fibers, and garbage bags and sacks. They are also showing up in thermoformed packaging as functional adjuncts to lower-cost biodegradable materials (e.g., as moisture barrier films). Biodegradable polyesters also generally work well in blends with PLA, starch, organic wastes, and natural-fiber reinforcement such as flax.

Bags and sacks is one of the most important market sectors for Ecoflex. It can be used in the manufacture of fresh fruit and vegetable bags refuse bags and carrier bags, using either Ecoflex on its own, or an Ecoflex/starch blend.

Ecoflex co- polyesters are being used by Zerust Consumer Products in Ohio, USA, to market synthetic biodegradable clear plastics bags for lawn and leaf applications. Zerust's new Great Green Earth bags can be used to replace paper bags for organic waste disposal. Great Green Earth bags are approved by the US Biodegradable products Institute, and are certified via ASTM D6400 for their ability to biodegrade swiftly and safely during municipal and commercial composting. The Great Green Earth bags are manufactured using a proprietary technology developed by Northern Technologies International (NTI), Lino Lakes, Minn. Zerust, the consumer division of NTI, also markets food waste bags and agriculture film under the Great Green Earth brand.

In packaging, Ecoflex can be used as a coating material to make paper, cardboard or starch-based foam tougher and protect against fat, moisture and temperature variations.

These are useful properties for hamburger boxes, coffee cups, packaging for meat, fish, poultry, fruit or vegetables, food dishes and fast-food boxes.

Ecoflex is also found in agriculture films such as cover sheeting and mulch film. The film can be ploughed into the field and is degraded in the soil after use.

Eastar Bio is used in nonwovens, lawn-and-garden bags, agricultural films, netting, and paper coatings.

DunPont's Biomax is used in a number of specialty packaging applications, injection-moulded parts, coating for paper, thermoformed cups and trays, and films because of its superior barrier properties. DunPont has targeted fast-food disposal packaging, as well as yard-waste bags, diaper backing, agricultural film, flowerpots, and bottles, for particular development.

Showa's Bionelle products are used in commodity bags, agriculture films, traffic cones, and industrial trays.

boost sales of synthetic biopolymers in flexible film applications.

Synthetic biodegradable polyesters are made in modified PET polymerization facilities from petrochemical feedstocks. Unlike other petrochemical-based polymers that take a very long time to degrade after disposal, these polyesters break down rapidly to CO_2 and water in appropriate conditions where they are exposed to the combined attack of water and microbes. These products meet US, European, and Japanese composting standards, typically breaking down in twelve weeks under aerobic conditions.

2.2 Biopolymers

Biopolymers are polymers that are biodegradable. The input materials for the production of these polymers may be either renewable (based on agricultural plant or animal products) or synthetic. They are mainly based on: **Starch, Sugar , Cellulose and Synthetic materials** . Two main strategies may be followed in synthesizing biopolymer. One is to build up the polymer structure from a monomer by a process of chemical polymerization and the alternative is to take a naturally occurring polymer and chemically modify it to give it the desired properties.

Every biopolymer has its own material-specific properties, e.g. barrier properties such as oxygen permeability. The barrier properties are relevant to the choice of biopolymers for the packaging of particular products. Bioplastics have very promising prospects for use in pesticide soil pins, for packaging in-flight catering products and for packaging dairy products. Biopolymers have several economic and environmental advantages. They could also prove an asset to waste processing e.g. replacing the polyethylene used in coated papers by a biopolymer which may eliminate plastic scraps occurring in compost.

The certain starch-based and PLA biopolymers were competitive with standard thermoplastics such as PET.

- Biodegradable plastic: a biodegradable plastic is a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae.
- Composting: composting is a managed process that controls the biological decomposition of biodegradable materials into a humus-like substance called compost; the aerobic and mesophilic and thermophilic degradation of organic matter to make compost; the transformation of biologically decomposable materials through a controlled process of bio-oxidation that proceeds through mesophilic and thermophilic phases and results in the production of carbon dioxide, water, minerals and stabilized organic matter (compost or humus).

Biodegradable polymers and biopolymers can be produced by a wide variety of technologies, both from renewable resources of animal or plant origin and from fossil resources. Biodegradable polymers that are based on renewable resources include polyesters such as polylactic acid (PLA) and polyhydroxyalkanoate (PHA). Biodegradable polymers can also be made from extracts from plants and vegetables such as corn, maize, palm oil, Soya and potatoes. Biodegradable polymers can also be made from mineral oil based resources such as the aliphatic-aromatic co-polymer types. Mixtures of synthetic degradable polyesters pure plant starch, known as starch blends, are also well-established products on the market.

Biodegradable polymers are similar in terms of their chemical structure to conventional thermoplastics such as polyethylene, polypropylene and polystyrene. They can be processed using standard polymer processing methods such as film extrusion, injection moulding and blow moulding. While biodegradable polymers may be similar to petrochemical-based thermoplastics in terms of their structure, their chemical structure imbues them with technical properties that make them perform in different ways. For example, starch blends can produce film with better moisture barrier protection and higher clarity than some conventional plastics. PLA has a high water vapour transmission rate, which is beneficial for fresh food applications where it is important that the water vapour escapes quickly from the packaging. PLA also reduces fogging on the lid of the packaging.

2.3.**Synthetic biodegradable polymers that are naturally susceptible to microbial-enzyme attack**

The overview of synthetic biodegradable polymers including an examination and classification of biodegradable polymers including their chemical structure, properties and processing performance. The study (chapter) is divided into five core sections based on biodegradable polymer types. All classes of biodegradable polymers are projected to experience substantial growth during the next five years. While natural polymers are produced by living organisms, synthetic biodegradable polymers are only produced by mankind. Biodegradation reactions are the same for both, i.e., typically enzyme-catalysed and produced in aqueous media. The major category of synthetic biodegradable polymers consists of aliphatic polyester with a hydrolysable linkage along the polymer chain such as polylactic acid (PLA). Other widely available synthetic types include aliphatic/aromatic co- polyesters.

2.3.1 Poly(lactic acid)

Of the material classes with existing commercial applications, PLA will grow the fastest with a compound annul growth rate of 20.1% for the period 2007-2012. PLA demand is being driven by strong product and application development.

Polylactic acid (PLA) is biodegradable polymer derived from lactic acid. It is a highly versatile material and is made from 100% renewable resources like corn, sugar beet, wheat and other starch-reach products. Polylactic acid exhibits many properties that are equivalent to or better than many petroleum- based plastics, which makes it suitable for a variety of applications.

The starting material for polylactic acid is starch from a renewable resource such as corn. Is milled, which separates starch from the raw material. Undefined dextrose is then processed from the starch. Dextrose is turned into lactic acid using fermentation, similar to that used by beer and wine producers.

Polylactide (PLA) polymer chemistry sterms from lactide, which is the cyclic dimmer of lactic acid that exist as two optical isomers, d and l. *l*-lactide is the naturally occurring isomer, and dl-lactide is the synthetic blends of d- lactide and *l*- lactide. The homopolymer of *l*-lactide (LDPA) is a semi crystalline polymer. Poly (d*l*-lactide) (DLPLA) is an amorphous polymer exhibiting random distribution of both isomeric forms of lactic acid, and accordingly is unable to arrange into an organized crystalline structure. This material has lower tensile strength, higher elongation, and a much more rapid degradation time. PLA is about 37% crystalline, with a melting point of 175-178 0C and a glass-transition temperature of 60-65 0. The degradation time of LPLA is much slower than that of DLPLA, requiring more than two years to be completely absorbed. Copolymers of l-lactide and dl-lactide have been developed prepared to disrupt the crystallinity of l-lactide and accelerate the degradation process.

Polyalctides decompose harmlessly in the human body and have therefore long been used for medical applications, therefore, its use includes surgical implants which do not require operative removal.

Turning the lactic acid into a polymer involves a chemical process called condensation, whereby two lactic acid molecules are converted into one cyclic molecule called a lactide.

This lactide is purified through vacuum distillation. A solvent-free melt process causes the ring-shared lactide polymers to open and join end-to-end to form long chain polymer. A wide range of products that very in molecular weight and crystallinity can be produced, allowing the PLA to be modified for a variety of applications.

PLA compares well with petrochemical-based plastics used for packaging. It is clear and naturally glossy like polystyrene, it is resistant to moisture and grease, it has flavour and odour barrier characteristics similar to polyethylene terephthalate (PET). The tensile strength and modulus of elasticity of PLA is also comparable to PET.

PLA can be formulated to be either rigid or flexible and can be co-polymerized with other materials. Polylactic acid can be made with different mechanical properties suitable for specific manufacturing processes, such as injection moulding, sheet extrusion, blow moulding, thermoforming, film forming and fiber spinning using most conventional techniques and equipment.

PLA is a non-volatile, odourless polymer and is classified as GRAS (generally recognized as safe) by the us Food and Drug Administration.

Polylactic acid has been around for many decades. In 1932, Wallace Carothers, a scientist for DupPont, produced a low molecular weight product by heating lactic acid under a vacuum. In 1954, after further refinements, DuPont patented Carothers' process.

Due to high costs, the focus was initially on the manufacture of medical grade sutures, implants and controlled drug release applications. Recently, there have been advances in fermentation of glucose, which turns the glucose into lactic acid. This has dramatically lowered the cost of producing lactic acid and significantly increased interest in the polymer.

Cargill, Incorporated, was one of the first companies to extensively develop polylactic acid polymers. Cargill began researching PLA production technology in 1987. it began production of pilot plant quantities in 1992 and in 1997 formed a joint venture with Dow chemical company, Inc., creating Cargill Dow polymers LLC. The joint venture is dedicated to further commercializing PLA polymers and formally launched Nature Works PLA technology in 2001. Construction was completed on a large-scale PLA manufacturing facility in Blair, Nebraska in 2002. Cargill Dow now trades as Nature Works LLC, following the sale by Dow chemicals of its share in the joint venture to Cargill Ic. In 2005.

Polylactic acid has many potential uses, including many applications in textile and medical industries as well as the packaging industry.

The main types of Nature Works PLA that are available for packaging applications include general purpose film grades, extrusion coating, extrusion and thermoforming grades and injection stretch blow moulding.

The general-purpose film grade is; biaxially oriented', a property that gives it stability at temperatures up to 130 oC. They also offer a biaxially oriented film for high temperature applications (150 ^{o}C). According to Nature Works, these resins offer excellent optical properties; good machinability and excellent twist and dead fold characteristics. These polymers are offered in common pellet form, which should allow for rapid adoption with conventional extruders.

Grades designed for extrusion coating on paper, process easily on conventional extrusion coating equipment at a lower melt extrusion temperature than polyethylene coatings according to the company. Paper and board coated in this resin can be heat-seated on typical equipment. Potential applications for these grades include, lawn and leaf bags, hot and cold drinking cups, picnic plates, bowls straws, fried food boxes, frozen vegetable packaging, and liquid food packaging.

Clear extrusion sheet grades are designed for extrusion and thermoforming applications, and like other Nature Works' PLA polymers, use conventional processing techniques and equipment. Potential uses include dairy containers, food service ware, transparent food containers, blister packs, and cold drink cups.

PLA is available in grades suitable for manufacture of injection stretch blow moulded bottles. It is claimed these offer comparable organoleptic properties to glass and PET making it suitable for a variety of short shelf-life food and beverage bottling applications.

Nature Works LLC is also developing grades for microwavable packaging and bottles for packaging oxygen sensitive food and beverages using barrier-enhanced PLA.

Polylactic acid also has many potential uses in fibers and non-woven. It is easily converted into a variety of fiber forms using conventional melt-spinning processes. Spunbound and meltblown non-woven as well as monocomponent, bicomponent, continuous (flat and textured) and stable fibers are all easily produced.

Polylactic acid based fibres have various attributes that make attractive for many traditional applications. PLA polymers are more hydrophilic than PET, have a lower density, and have excellent crimp and crimp retention. Shrinkage of PLA materials and thermal bonding temperatures are easily controllable. These polymers tend to be stable to ultraviolet light resulting in fabrics that show little fading. They also offer low flammability and smoke generation characterization.

Major applications of PLA fibres and non-wovens include clothing and furnishing such as drapes upholstery and covers. Some interesting potential applications include household and industrial wipes, diapers, feminine hygiene products, disposable garments, and UV resistant fabrics for exterior use (awnings, ground covers).

In the field of biomedical devices, polylactic acid has become an important material, having been in use for over 25 years. Polylactic acid is biodegradable, bioresorbable polymer, i.e. it can be assimilated by a biological system. Since PLA can be assimilated by the body, it has found applications in sustained release drug delivery systems. Furthermore, its mechanical properties and absorbability make PLA polymer an ideal candidate for implants in bone or soft tissue (facial traumatology, orthopaedic surgery, ophthalmology, orthodontics', local implants for controlled release of anti-cancer drugs), and for resorbable sutures (eye surgery, conjunctional surgery of the chest and abdomen)

The mechanical, pharmaceutical and biodegradable characteristics are dependent on controllable parameters such as chemical composition and molecular weight of the polymer. The time frame for resorption of the polymer may be anything from just a few weeks to a few years, and can be regulated by use of different formulations and the addition of radicals on its chains.

PLA polymers are fully compostable in commercial composting facilities. With proper equipment, PLA can be converted back to monomer, which then can be converted back into polymers. Alternatively, PLA can be biodegraded into water, carbon dioxide and organic material. At the end of a PLA based product's life cycle, a product made from PLA can be broken down into its simplest parts so that no sign of the original product remains. Polylactides (lactic acid polymers)are made from lactic acid, which is in turn made from lactose (or milk sugar) obtained from sugar beet, potatoes, wheat, maize etc. Polylactides are water resistant and can be formed by injection moulding, blowing and vacuum forming.

2.3.2 Poly(ε-caprolactone) (PCL)

The ring –opening polymerization of ∈- caprolactone yields a semi crystalline polymer with a melting point of 59-64 °C and a glass transition temperature of – 60 °C. The polymer is regarded as tissue compatible and was originally used in the medical field s a biodegradable suture in Europe. Because the homopolymer has a degradation time of the order of two years, copolymers have been synthesized to accelerate the rate of bioabsorption. For example, copolymers of ∈-caprolactone with *dl*- lactide have yielded materials with more rapid degradation rates.

Polycaprolactone aliphatic polyesters have long been available from companies such as Solvay and Union Carbide (now Dow Performance Chemicals) for use in adhesives, compatibilisers, modifiers and films as well as medical applications These materials have low melting points and high prices (∈4.7 per kg in 2005).PCL is predominantly used as a component in polyester /starch blends such as Mater-Bi as produced by Novamont. Caprolactone limits moisture sensitivity, boosts melt strength and helps plasticise the starch.

Other types of synthetic biopolymers that have been in use for medical applications for a number of years are polyglycolide, polydioxanone and poly(lactide-co-glycolide).

2.3.3 Polyglycolide (PGA)

Polyglycolide is his simplest linear aliphatic polyester. PGA was used to develop the first totally synthetic absorbable suture, marketed as Dexon in the 1960s by Davis and Geck, Inc.Glycolide monomer is synthesized from the dimerisation of glycolic acid. Ring-opening polymerization yields high molecular- weight materials, with approximately 1-3% residual monomer present. PGA is highly crystalline (45-55%), with a high melting point (220-225 ^{o}C. Because of its high degree of crystallization, it is not soluble in most organic solvents; the exceptions are highly fluorinated organics such as hexafluoroisopropanol. PGA fibres exhibit high strength and modulus and are too stiff to be used as sutures except in the form of braided material. Sutures of PGA lose about 50% of their strength after two weeks and 100% at four weeks, and are completely absorbed in 4 to 6 months. Glycolide has been copolymerised with other monomers to reduce the stiffness of the resulting fibers.

2.3.4 Poly(amono acid)

2.4.Bacterially derived polyhydroxyalkanoates (PHA)

The starting material for Polyhydroxibutyrate is made from sucrose or starch by a process of bacterial fermentation. Varying the nutrient composition of the bacteria produces differences in the end product. This makes it possible to tune the properties of the material, e.g. its moisture resistance. The polymer can be formed by injection, extrusion, blowing and vacuum forming.

PHA, which started from virtually a zero base in 2005, is projected to grow at close to 60% per annum as commercial scale plants come on stream and better products and processes are introduced. Aliphatic polyesters such as polyhydroxyalkanoate (PHA) are also a family of easily biodegradable polymers found in nature that are beginning to commercial use.

Polyhydroxyalkanoates (PHA) is a term given to a family of aliphatic polyesters produced by microorganisms that are fully biodegradable. They offer a wide array of physical properties that can range from stiff and brittle plastics to elastomers.

An attractive feature of PHAs is the ability to produce them using renewable carbon resources. PHAs can be produced using renewable sources such as sugars and plant oils. Various waste materials are also being considered for potential carbon sources for PHA production, including whey, molasses and starch. The carbon source available to a microorganism is one of the factors (others being the PHA syntheses substrate specificity and the types of biochemical pathways available) that determine the type of PHA produced. For industrial scale production, the carbon source significantly contributes to the final cost. This makes the carbon source one of the most important components in the production of PHA and is therefore a prime for potential cost reduction.

PHAs are mainly composed of R-(-)-3-hydroxyalkanoic acid monomers. These can be broadly subdivided into two groups:

Short chain length PHAs

- Consist of 3 carbon – 5 carbon monomers (C3-C5)
- Produced by bacterium *Alcaligenes eutrophus* (plus others)

Long chain length PHAs

- Consist of 6 carbon – 14 carbon monomers (C6-C14)
- Produced by *pseudomonas oleovorans* (plus others)

Each type of PHA generally consists of 1000-10000 monomers, but most are synthesized by short chain length monomers.

There are many different types of PHA, distinctly characterized by chain length, type of functional group and degree of unsaturated bonds. A higher degree of unsaturation increases the rubber qualities of a polymer, and different functional groups change the physical and chemical properties of a polymer.

PHB (or poly-3-hydroxybutyrate (P(3HB))) is the most common type of PHA produced and is an example of a short chain length homopolymer produced by A. *eutrophus.* PHB has poor physical properties for commercial use, as it is stiff, brittle and hard to process. This has led to an increased interest to produce heteropolymers with improved qualities.

Biopol, produced by Metabolix, is a leading example of an improved poly (3-hydroxybutyrate-co-3-hydroxyvalerate), P (3HB-3HV), heteropolymer. Compared to PHB, P(3HB-3HV) is less stiff, tougher, and easier to process, making it more suitable for commercial production. It is also water resistant and impermeable to oxygen, increasing its value.

PHB is a completely biodegradable polymer and degrades through various types of bacteria and fungi to carbon dioxide and water through secreting enzymes. It can also be degraded through non- enzymatic hydrolysis. Degradation appears to be the fastest under conditions of high temperatures and mechanical distruption. PHB is also biocompatible, meaning it is a metabolite normally present in blood.

The production of biodegradable polymers using carbon as the starting material can be carried out using a 3-stage or a2- stage process.

The 3- stage process involves utilization of plant sugars derived from photo synthetically fixed CO2 as carbon sources in the fermentation of organic acids, alcohols and amino acids. These substances are then used as building blocks for the chemical synthesis of polymers. Examples of polymer using the 3- stage process include polylactic acid and polybutylene succinates.

On the other hand, the 2- stage process involves the direct conversion of plant sugars and plant oils into polymer microorganisms. At present, the biosynthesis of PHA is largely carried out through 2- stage process .Compare to the 3- stage process of polymer production, the 2 – stage process can be more cost effective provided that excellent producers of PHA are identified and the fermentation process is highly optimized. Inexpensive plant oils have been found to be an excellent carbon source for the efficient production of PHA.

There were a number of efforts to commercialize PHA, notably by ICI in the 1980s and early 1990s, and by Monsanto in the mind 1990s.However, these attempts were largely unsuccessful due to the high cost and very limited prcessability and properties. In recent years, these deficiencies have been largely overcome most notably by metabolix and by Procter and Gamble's Nodax business unit, which both specialize in PHA materials development.

The broad range of properties offered by PHA make them useful for a wide variety of applications, including:

Food packaging

Single- serves cups and other disposable foodservice items.

House ware

Appliances

Electrical and electronics

Consumer durables

Agriculture and soil stabilisation

Adhesives, paints and coatings

Automotive

Medical (bone plates and surgical sutures)

2.5.Natural biodegradable polymers

The history of man is strongly linked to a wide variety of naturally occurring polymers but in fact that these substances were polymers was not known. Naturally biodegradable polymers produced in nature are renewable. Some synthetic polymers are also renewable because they are made from renewable feedstock, for example polylactic acid is derived from agricultural feedstock. Natural polymers are produced in nature by all living organisms. Biodegradation reactions are typically enzyme-catalyzed and occur in aqueous media. Natural macromolecules containing hydrolysable linkage, such as protein, cellulose, and starch, are generally susceptible to biodegradation by the hydrolytic enzymes of microorganisms. Thus the hydrophilic/hydrophobic character of polymers greatly affects their biodegradability. It also has a great impact on their performance and durability in humid conditions. Polysaccharides such as starch are the most prevalent naturally biodegradable polymer in commercial use.

2.5.1. Starch – based polymers

Starch is a natural polymer which occurs as granules in plant tissue, from which it can easily be recovered in large quantities. It is obtained from potatoes, maize, wheat and tapioca and similar sources. Starch can be modified in such a way that it can be melted and deformed thermoplastically. The resulting material is thus suitable for conventional plastic forming processes such as injection moulding and extruding.

Starch-based polymers are projected to grow at slightly lower rates. This is mainly due to the presence of loose-fill packaging, which is relatively more mature applications sector.
This starch-based technology is unique because the modification goes beyond conventional compounding. The starch is destructurised by applying sufficient work and heat to almost completely destroy the crystallinity of amylase and amylopectine in the presence of macromolecules able to form a complex with amylase.
In nature, the availability of starch is just second to cellulose. The most important industrial sources of starch are corn, wheat, potato, tapioca and rice. In the last decade, there has been a significant reduction in the price of corn and potato starch, both in Europe and USA. The lower price and greater availability of starch associated with its very favourable environmental profit aroused a renewed interest in development of starch-based polymers based on petrochemicals.

Starch is totally biodegradable in a variety of environments and thus permits the development of totally degradable products for specific market demands. Degradation or incineration of starch-based products recycles atmospheric carbon dioxides trapped by starch-producing plants and dose not increases potential global warming.

The most relevant achievements in this sector are related to thermoplastic starch polymers resulting from the processing of native starch by chemical, thermal and mechanical means, and to its complexation to other co-polymers. The resulting materials show properties ranging from the flexibility of polyethylene to the rigidity of polystyrene, and can be soluble or insoluble in water as well as insensitive to humidity. Such properties explain the leading position of starch-based materials in the biodegradable polymer field.

Starch is unique among carbohydrates because it occurs naturally as discrete granules. This is because the short-branched amylopectin chains are able to form helical structures, which crystallize. Starch granules exhibit hydrophilic properties and strong intermolecular association via hydrogen bonding due to the hydroxyl groups on the granule surface. The melting point of native starch is higher than the thermal decomposition temperature: hence the poor thermal stability of native starch and the need for conversion to starch-based materials with a much-improved property profile.

In nature, starch is based on crystalline beads of about 15-100 microns in diameter. Crystalline starch beads in plastics can be used as filler or can be transformed into thermoplastic starch, which can either be processed alone or in combination with specific synthetic polymers. To make starch thermoplastic, its crystalline structure has to be destroyed by pressure, heat, mechanical work or use of plasticisers. Three main families of starch polymer can be used: pure starch modified starch and fermented starch polymers.

The production of starch polymers begins with the extraction of starch. Taking as an example corn; starch is extracted from the kernel by wet milling. The kernel is first softened by steeping it in a dilute acid solution, then ground coarsely to split the kernel and remove the oil-containing germ. The starch slurry is then washed in a centrifuge, dewatered and dried. Either prior, or subsequent to the drying step, the starch may be processed in a number of ways to improve its properties.

The addition of chemicals leading to alteration of the structure of starch is generally described as ‘chemical modification’. Modified starch is starch that has been treated with chemicals so that some hydroxyl groups have been replaced by for example ester or ether groups. High starch content plastics are highly hydrophilic and readily disintegrate when in contact with water. Very low levels of chemical modification can significantly improve hydrophilicity, as well as change other rheological, physical and chemical properties of starch.

Crosslinking, in which two hydroxyl groups or nighbouring starch molecules are linked chemically, is also a form of chemical modification. Crosslinking inhibits granule swelling or gelatinization and gives increased stability to acid, heat treatment and shear forces. Chemically modified starch may be used directly or palletized or otherwise dried for conversion to a final product.

Starch can also be modified by fermentation as used in the Rodenburg process. In this case the raw material is potato waste slurry originating from the food industry. The slurry mainly consists of starch, the being proteins, fats and oils, inorganic components and cellulose. The slurry is held in storage silos for about two weeks to allow for stabilisation and partial fermentation. The most important fermentation process that occurs is the conversion of a small fraction of starch to lactic acid by means of the lactic acid bacteria that are naturally present in the feedstock. The product is subsequently dried to a final water content of 10% and then extruded.

Starch-based polymers have been the most studied class of biodegradable polymer for their extrusion characteristics. Extrusion processing plays a large role in establishing the polymer properties. Starch can be made thermoplastic by using technology very similar to extrusion cooking. Starch exists as granular beads of about 15-100 micron in diameter that can be compounded with another synthetic polymer as filler. However, under special heat and shear conditions during extrusion it can be transformed into an amorphous thermoplastic by a process known as destructurising.

Starch can be destructured in the presence of more hydrophobic polymers such as aliphatic polyesters. Aliphatic polyesters with low melting point are difficult to process by conventional techniques such as film blowing and blow moulding. Films such as polycaprolactones (PCL) are tacky as extruded and have low melt strength (over 130 0c). Also, he also crystallization of the polymer causes the properties to change with time. Blending starts with aliphatic polyesters improves processability and bidegrability.

Addition of starch has a nuclearting effects, which increases the rate of crystallization. The rheology of starch/PCL blends depends on the extent of starch granule destruction and the formation of thermoplastic starch during extrution. Increasing the heat and shear intensities can reduce the melt viscosity, but hence the extrudate-swell properties of the polymer.

Starch/aliphatic polyester composition are prepared by blending starch-base component and an aliphatic polyester in a co-rotating, intermeshing twin-screw extruder. The co-rotating, self-cleaning screw on these machines prevents caking and churning of cooked starch. Temperature and pressure conditions are such that the starch is destructurised and the composition forms a thermoplastic melt. The resulting material has an interpenetrated or partially interpenetrated structure.

2.5.2. Cellulose and its derivatives

The use of cellulose for making packagin material such as cellophane is long established. The material is transparent and has good folding properties. Whether in the form of pure cellulose or of a nitrocellulose coating, the material is wholly biodegradable and can be composted by existing waste processing plant.

Water-soluble biodegradable polymers may be synthesized by modifying starch and cellulose. For example, carboxymethyl cellulose (CMC) having different degrees of carboxymethyl substitution is a family of marketed water-soluble polymers.

Hydroxyethyl cellulose (HEC) is used as thickeners in drilling fluids and as fluid-loss agents in cementing. For such polysaccharide-derived polymers, the rate or extent of product biodegradability decreases when higher levels of modification of cellulose (more than one substituent per sugar ring) are required to achieve desired performance characteristics {M. Takeo, *et al.*, *Mizu Shori Gijutsu* **38**, 57 (1997)}. Water-soluble polysaccharides are also produced by microbial fermentation. Xanthan is the most widely used microbial polysaccharide. Industrial uses of xanthan include oil recovery (viscosity control), paper manufacturing, agriculture (stimulation of plant growth), and cosmetics. Pullulan has shown a plethora of potential applications. For example, its good moisture retention and low oxygen permeability has led to its use as edible films for food packaging.

Conclusion

An important benefit of renewable feedstock, as compared with petroleum, is a reduction in the emission of fossil fuel-derived CO_2. For example, on the basis of one estimate, the volume of PLA production in 2020 will be 3.6 billion kg/year. If these polymers displace an equivalent amount of fossil fuel-based polymers, then 192 trillion of fossil-derived fuel will be saved per year, resulting in a reduction in the emission of CO_2 by 10 million tons. To avoid perturbing the ecosystem, processes must be cyclic, without creating chemical or biological imbalances. BPs from annually renewable materials allow cyclic processes that can be renewed over short time intervals (less than 1 year). The chemicals taken from nature will be returned to nature without perturbing the environment. This is a large departure from current practices. At present there is little or no current value to the manufacturer who develops such an environmentally friendly product, and BPs must therefore compete head-to-head in cost and performance with existing familiar and inexpensive products (e. g., plastic resins such as polyethylene cost about 50 cents per pound). This is extremely difficult because new processes require intensive research and large capital expenses and must be scaled-up to be economically competitive. BPs are often designed to mimic the "feel" of existing materials. It will be important when developing and marketing BPs to identify and exploit the unique attributes of the materials.