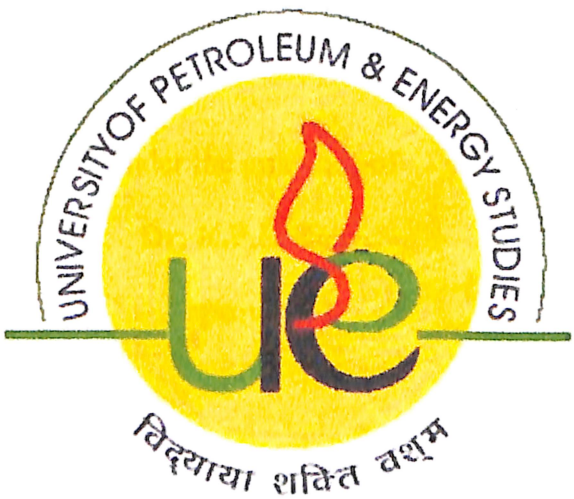
STUDY OF THE BIODEGRADABLE GREEN POLYMER

By

PRABHAKAR DEEP

SAHARSH KONNUR



College of Engineering

University of Petroleum & Energy Studies

Dehradun

May, 2010

STUDY OF THE BIODEGRADABLE GREEN POLYMER

A thesis submitted in partial fulfillment of the requirements for the

Degree of Bachelor of Technology

Applied Petroleum Engineering

By

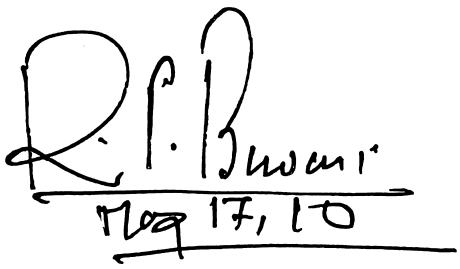
PRABHAKAR DEEP

SAHARASH KONNUR

Under the guidance of

Dr. R.P.Badoni

Approved by



.....

Dr. Shrihari

Dean

College of Engineering

University of Petroleum & Energy Studies

Dehradun

May, 2010

CERTIFICATE

This is to certify that the work contained in this thesis titled "**STUDY ON BIODEGRADABLE GREEN POLYMER**" done on bibliographical study has been carried out by **Prabhakar Deep (R010204039) and Saharsh Konnur (R040206066)**, and is authentic to the best of our knowledge.

SAHARSH KONNUR

R040206066

BTECH APPLIED
PETROLEUM ENGINEERING

PRABHAKAR DEEP

R010204039

BTECH APPLIED
PETROLEUM ENGINEERING

DR. R. P. BADONI

COLLEGE OF ENGINEERING

17th may,2010

ACKNOWLEDGEMENT

There are many people to acknowledge when a report like this is completed. My sincere thanks go to all those who are directly or indirectly involved in this project and took time out of their busy schedules to pour insights into my report.

There is one individual who needs to be highlighted, our guide, **Dr. R P Badoni** since he did too much to pave the way for what we have managed to do. His insightful feedback had been extremely important without which we would not have succeeded in my endeavor.

We are really indebted to the constant motivation provided by respected **Mr. Sachin Kumar**, who had been a torchbearer and a driving force in bringing up this work.

The University of Petroleum & Energy Studies, Dehradun must be credited for letting me do a project of my area of interest, keeping faith in us and letting it happen. Last and most assuredly not least, we are deeply indebted to many people who have helped us indirectly in this project.

CONTENTS

ABSTRACT

Polymers that are produced by biological system such as micro-organism, plants, rice straw etc. are called green polymers. For example: poly-lactic acid from fermentation process.

PLA (poly-lactic acid) is considered as a good alternative to petroleum based plastic as it is both biodegradable and had a low toxicity to humans .Until now (PLA) had been produced in two step fermentation and polymerization, which is both complex and expensive Now, through the use of a metabolically engineered strain of E coli, the team had produced poly lactic acid and their co polymers through direct fermentation. This makes the renewable production of PLA and lactate containing co polymers cheaper and more commercially viable.

1. INTRODUCTION

With the development of science and technology man had been trying to prepare new compounds to fulfill his needs and make his life comfortable. Polymers are one of the important products of the chemical industry which have a great impact on our modern life. Plastics, Synthetic fibers, synthetic rubber etc. are common examples of polymers. These polymers have multifarious uses ranging from household articles, automobiles, clothes, furniture, etc. to space aircraft and biomedical and surgical operation.

Polymers are macro-sized molecules of relatively high molecular mass. These are obtained by joining together a large number of simple molecules. Structurally, these polymers are characterized by many repeating molecular units which form linear chains, branched chains and cross-linked networks. Nature has also given us very essential polymers such as proteins, nucleic acid cellulose, etc.

The idea of producing polymers from renewable biomass has attracted much attention because of increasing concerns of environmental problems and the limited nature of fossil sources. PLA (poly-lactic acid) is considered as a good alternative to petroleum based plastic as it is both biodegradable and has a low toxicity to humans .Until now (PLA) had been produced in two step fermentation and polymerization, which is both complex and expensive Now, through the use of a metabolically engineered strain of E coli, the team has produced poly lactic acid and its co polymers through direct fermentation. This makes the renewable production of PLA and lactate containing co polymers cheaper and more commercially viable.

2. HISTORICAL DEVELOPMENT

Starting in 1811, Henri Braconnot did pioneering work in derivative cellulose compounds, perhaps the earliest important work in polymer science. The development of vulcanization later in the nineteenth century improved the durability of the natural polymer rubber, signifying the first popularized semi-synthetic polymer. In 1907, Leo Baekeland created the first completely synthetic polymer, Bakelite, by reacting phenol and formaldehyde at precisely controlled temperature and pressure. Bakelite was then publicly introduced in 1909.

Despite significant advance in synthesis and characterization of polymers, a correct understanding of polymer molecular structure did not emerge until the 1920s.Before then, scientists believed that polymers were clusters of small molecules (colloids), without definite molecular weights held together by an unknown force, a concept known as association theory. In 1922, Hermann Staudinger proposed that polymers consisted of long chain of atoms held together by covalent bonds, an idea which did not gain wide acceptance for over a decade and for which he was ultimately awarded the Nobel prize. Work by Wallace Carothers in the 1920s also demonstrated that polymers could be synthesized rationally from their constituent monomers.

An important contribution to synthetic polymer science was made by the Italian chemist GIULIO-NATTA and German chemist KARL ZIEGLER, who won the Nobel Prize in chemistry in 1963 for the development of the ZIEGLER-NATTA catalyst. Further recognition of the importance of polymers came with the award of the Nobel Prize in Chemistry in 1974 to PAUL FLORY, whose extensive work on polymers included the kinetics of step-growth polymerization and of addition polymerization , chain transfer, excluded volume , the FLORY – HUGGINS solution theory , and the FLORY convention.

3. POLYMER

Polymers are compounds of very high molecular masses formed by the combination of a large number of simple molecules (Monomers).The process by which the simple molecules (Monomers) are converted into polymers is called Polymerisation. for example,

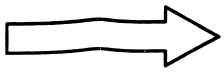
$nCH_2=CH_2$ $\longrightarrow$ $-(CH_2-CH_2-)_n$

Ethylene(monomers) polyethylene(polymer)

Polymerisation

3.1. HOMOPOLYMER

A polymer formed from one type of monomers is called Homopolymer. for example,



nCH2=CH2 $\longrightarrow$ -(CH2-CH2-)n

Ethylene(monomers) polyethylene(polymer)

Polymerisation

3.2. COPOLYMER

A polymer formed from two or more different monomers is called Copolymer. for example,

Polymerisation

$nH_2N-(CH_2)_6-NH_2 + nHOOC-(CH_2)_4-COOH \longrightarrow -(NH-(CH_2)_6-NH-CO-(CH_2)_4-)_n+nH_2O$

Hexamethylenediamine +Adipic acid Nylon-66 (Copolymer)

3.3. MONOMER ARRANGMENT IN COPOLYMER

Monomer within a copolymer may be organized along the backbone in a variety of ways.

3.4. ALTERNATING COPOLYMERS

Possess regularly alternating monomer residues.$(AB\ldots)_n$ .for example

-A-A-A-A-A-A-A-A-A-

3.5. PERIODIC COPOLYMERS

Have monomer residue types arranged in a repeating sequence. (A_nB_m) m being different from n. for example

-A-B-A-B-A-B-A-B-A-B-

3.6. STATISTICAL COPOLYMERS

Have monomer residue arranged according to a known statistical rule. A statistical copolymer in which the probability of finding a particular type of monomer residue at an particular point in the chain is independent of the type of surrounding monomer residue may be reffered to as a truly random copolymer. for example

-A-B-B-B-A-B-B-B-A-B-B-B-

3.7. BLOCK COPOLYMERS

Have two or more homopolymer subunits linked by covalent bonds Polymer with two or three blocks of two distinct chemical species (e.g., A and B) are called diblock copolymers and triblock copolymers, respectively. Polymer with three blocks, each of a different chemical species (A, B, and C) are termed triblock terpolymers. For example

-B-B-B-B-A-A-A-A-B-B-B-B-

3.8. GRAFT COPOLYMER

Graft copolymers contain side chains that have a different composition or configuration than the main chain. for example

4. CLASSIFICATION OF POLYMERS

Polymers are classified in a number of ways as described below:-

A. Based on source of availability

B. Based on structure

C. Based on molecular forces

D. Based on mode of synthesis.

4.1. BASED ON SOURCES OF AVAILABILITY

A. Natural polymers

B. Synthetic polymers

C. Semi-synthetic polymers

4.1. 1. NATURAL POLYMER

The polymer obtained from nature (plants and animals) are called Natural polymer. for examples, Starch, cellulose, proteins, nucleic acid, natural rubber.

4.1.2 SYNTHETIC POLYMERS

The polymers which are prepared in the laboratories are called Synthetic polymer. for examples, polyethylene, PVC, nylon, Teflon etc.

4.1.3 SEMI-SYNTHETIC POLYMER

These polymers are derived from naturally occurring polymers by chemical modification. for examples, vulcanized rubber, gun cotton etc.

4.2 BASED ON STRUCTURE

A. Linear polymers

B. Branched polymers

C. Cross-linked polymers

4.2.1 LINEAR POLYMER

These are polymer in which monomeric units are linked together to form linear chains. These polymers have high densities, high tensile strength and high melting points because of well packing. For examples Polyethylene, nylons, polyesters etc.

4.2.2 BRANCHED CHAIN POLYMER

These are polymer in which the monomers are joined to form long chains with side chains or branches of different lengths. These branched chain polymers are irregularly packed and therefore, they have low tensile strength and melting points then linear polymers. for examples LDPE, glycogen, starch etc.

4.2.3 CROSS-LINKED POLYMER

These are polymer in which monomer units are cross- linked together to form a three-dimensional network. These are hard, rigid and brittle because of network structure. for examples Bakelite, melamine etc.

4.3 BASED ON MOLECULAR FORCES

Depending on the intermolecular forces:

A. Elastomers
B. Fibers
C. Thermoplastics
D, Thermosetting polymers

4.3.1 ELASTOMERS

The polymers that have elastic character like rubber (weak inter-molecular forces) are called Elastomers . for examples Natural rubber.

4.3.2 FIBRES

These are the polymers which have strong intermolecular forces between the chains. These forces are either hydrogen bonds or dipole-dipole interactions. Because of strong forces, the chains are very closely packed giving them high tensile strength and less elasticity. for example nylon-66, Dacron, silk etc.

4.3.3 THERMOPLASTICS

These are the polymers which can be easily softened repeatedly when heated and hardened when cooled with little change in their properties. For example polythene , polystyrene, Teflon etc.

4.3.4 THERMOSETTING PLASTICS

These are the polymers which undergo permanent change on heating. They become hard and infusible on heating. for example Bakelite, melamine formaldehyde etc.

4.4 BASED ON MODE OF SYNTHESIS

A. Addition polymers
B. Condensation polymers

4.4.1 ADDITION POLYMERS

A polymer formed by direct addition of repeated monomers without the elimination of by product molecules is called **Addition polymer**. for example polythene, polypropylene etc.

4.4.2 CONDENSATION POLYMERS

A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water ammonia etc. is called **condensation polymers**. for example **nylon-66** etc.

5. POLYMER CHARACTERIZATION

The characterization of a polymer requires several parameters which need to be specified. This is because a polymer actually consists of a statistical distribution of chains of varying lengths, and each chain consists of monomer residues which affect its properties .A variety of lab techniques are used to determine the properties of polymers. Techniques such as **wide angle x-ray scattering, small angle x-ray scattering, and small angle neutron scattering** are used to determine the number average molecular weight average molecular weight, and polydispersity.

FTIR, RAMAN AND NMR can be used to determine composition. Thermal properties such as the glass transition temperature and melting point can be determined by **differential scanning calorimetry and dynamic mechanical analysis. Pyrolysis followed by analysis of the fragments** is one more technique for determining the possible structure of the polymer.

Thermogravimetry is a useful technique to evaluate the thermal stability of the polymer, Detailed analysis of TG curves also allow to evaluate the thermal stability of the polymer. Rheological properties are also commonly used to help determine molecular architecture (molecular weight, molecular weight distribution and branching) as well as to understand how the polymer will process , through measurements of the polymer in the melt phase. Another polymer characterization technique is **Automatic continuous online monitoring of polymerization reaction (ACOMP)** Which provides real time characterization of polymerization reaction .It can be used as an analytical method in R&D, as a tool for reaction optimization at the bench and pilot plant level and, eventually , for feedback control of full – scale reactors. **ACOMP** measures in a model- independent fashion the evolution of average molar mass and intrinsic viscosity, monomer conversion kinetics and in the case of copolymers, also the average composition drift and distribution. It is applicable in the areas of free radical and controlled radical homo-and copolymerization, polyelectrolyte synthesis, heterogeneous phase reactions, including emulsion polymerization , adaptation to batch and continuous reactors, and modification of polymers.

6. MECHANICAL PROPERTIES OF POLYMERS

The bulk properties of a polymer are those most often of end-uses interest. These are the properties that dictate how the polymer actually behaves on a macroscopic scale.

6.1 TENSILE STRENGTH

The tensile strength of a material quantifies how much stress the material will endure before suffering permanent deformation. This is very important in applications that rely upon a polymer's physical strength or durability. For example , a rubber band with a higher tensile strength will hold a greater weight before snapping. In general, tensile strength increases with polymer chain length and crosslinking of polymer chains.

6.2 YOUNG,S MODULUS OF ELASTICITY

It quantifies the elasticity of the polymer. It is defined, for small strain, as the ratio of rate of change of stress to strain. Like tensile strength, this is highly relevant in polymer application involving the physical properties of polymers, such as rubber bands. The modulus is strongly dependent on temperature.

6.3 TRANSPORT PROPERTIES

Transport properties such as diffusivity relate to how rapidly molecules move through the polymer matrix. These are very important in many application of polymers for films and membranes.

6.4 MELTING POINT

The term melting point, when applied to polymers, suggests not a solid-liquid phase transition but a transition from a crystalline or semi-crystalline phase to a solid amorphous phase. Though abbreviated as simply T_m, the property in question is more properly called the crystalline melting temperature. Among synthetic polymers, crystalline melting is only discussed with regards to thermoplastics, as thermosetting polymer will decompose at high temperatures rather then melt.

6.5 BOILING POINT

The boiling point of a polymeric material is strongly dependent on chain length. High polymers with a large degree of polymerization do not exhibit a boiling point because they decompose before reaching theoretical boiling temperature. For shorter oligomers, a boiling transition may be observed and will generally increase rapidly is increased.

6.6 GLASS TRANSITION TEPERATURE

A parameter of particular interest in synthetic polymer manufacturing is the glass transition temperature (T_g), which describes the temperature at which amorphous polymers undergo a second- order phase transition from a rubbery, viscous amorphous solids, or from a crystalline solid (depending on the degree of crystallization) to a brittle, glassy amorphous solids.

7. BIOPOLYMER

Biopolymers are eco- friendly materials because they are produced from renewable carbon sources via biological or chemical processes and after their uses, they are biologically degraded and returned to the natural environment as renewable resources, such as CO_2 and biomass.

The term Biopolymer is used to describe a variety of materials. Biopolymers fall into main two principal categories:

A. Polymers that are produced by Biological system such as micro-organism , plants and animals.
B. Polymers that are synthesized chemically but are derived from biological starting materials like amino acids, sugar, Starch etc.

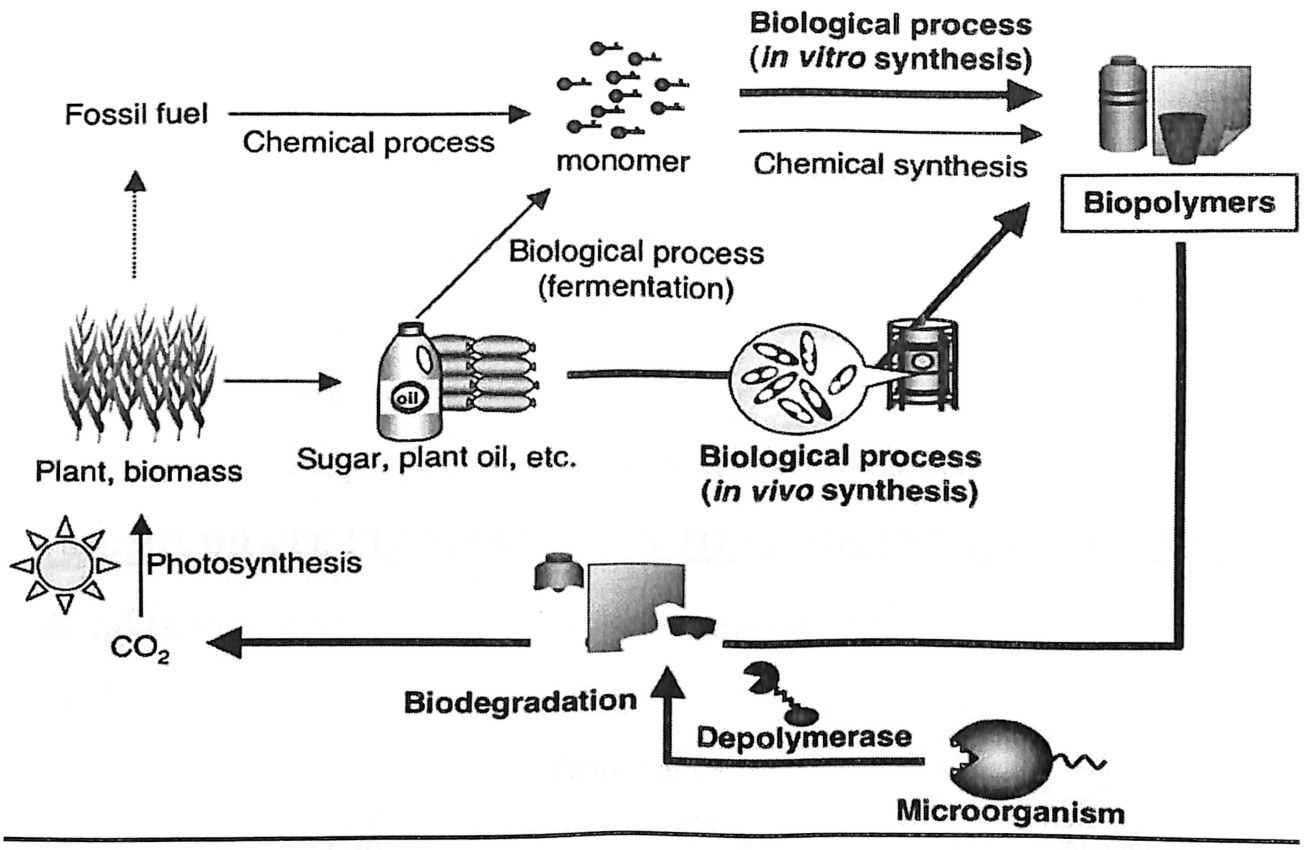


Fig-1.BIOPOLYMER RECYCLABLE ECOSYSTEM INVOLVING BIOLOGICAL OR CHEMICAL SYNTHESES AMD BIOLOGICAL DEGRADATION

8. GREEN POLYMER

Polymers that are produced by biological system such as micro-organism, plants, rice straw etc. for example: poly-lactic acid from fermentation process.

PLA (poly-lactic acid) is considered as a good alternative to petroleum based plastic as it is both biodegradable and has a low toxicity to humans .Until now (PLA) had been produced in two step fermentation and polymerization, which is both complex and expensive Now, through the use of a metabolically engineered strain of E coli, the team has produced poly lactic acid and its co polymers through direct fermentation. This makes the renewable production of PLA and lactate containing co polymers cheaper and more commercially viable.

8.1 LACTIC ACID

Lactic acid (2-hydroxy prop ionic acid) is most occurring carboxylic acid in nature. It was produced commercially by Charles E. Avery at Littleton, Massachusetts, USA in 1881.

8.1.1 LACTIC ACID SYNTHESIS

A. Chemical synthesis

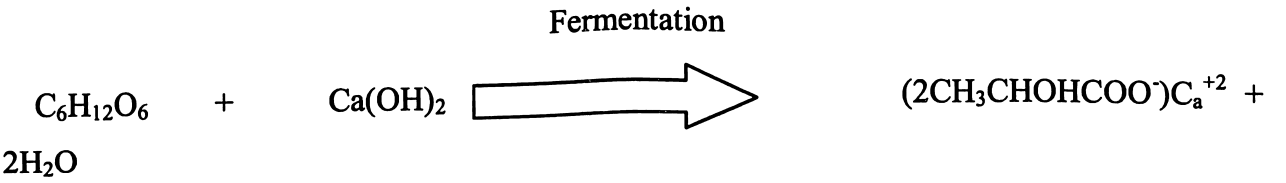
B. Carbohydrate fermentation

We are interested only in producing Green polymer from fermentation process.

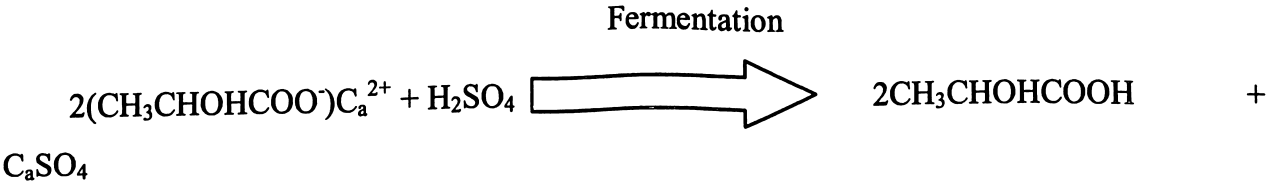
CARBOHYDRATE FERMENTATION TO PRODUCED LACTIC ACID

Carbohydrate fermentation is used to produced stereo specific acid.

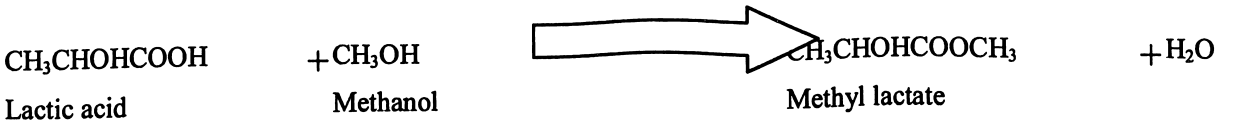
A. Fermentation and neutralization



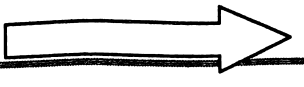
B. Hydrolysis by H2SO4



C. Esterification



D. Hydrolysis by H_2O



$CH_3CHOHCOOCH_3$	$+H_2O$		$CH_3CHOHCOOH$	+	CH_3OH
Methyl lactate			Lactic acid		Methanol

The broth containing calcium lactate is filtered to remove cells, carbon treated, evaporated and acidified with sulphuric acid to get lactic acid and calcium sulphate. The insoluble calcium sulphate is removed by filtration; lactic acid is obtained by hydrolysis, esterification, distillation and hydrolysis.

8.1.2 PROPERTIES AND USES OF LACTIC ACIDS

Lactic acid esters like ethyl/butyl lactate can be used as green solvents. They are high boiling, non-toxic and degradable components. **Poly L-lactic acid** with low degree of polymerization can help in controlled release or degradable mulch films for large-scale agricultural applications

Lactic acid is used as acidulant/ flavouring/ pH buffering agent or inhibitor of bacterial spoilage in a wide variety of processed foods. In contrast to other food acids it has a mild acidic taste. It is non-volatile odorless and is classified as GRAS (generally regarded as safe) by FDA in the US. It is a very good **preservative and pickling agent**. Addition of lactic acid aqueous solution to the packaging of poultry and fish increases their shelf life.

8.1.3 LACTIC ACID BACTERIA

Lactic acid bacteria are among the best studied microorganisms. The choice of an organism primarily depends on the carbohydrate to be fermented. Lactobacillus **delbreuckii** subspecies delbreuckii are able to ferment sucrose. Lactobacillus **delbreuckii subspecies bulgaricus** is able to use lactose. Lactobacillus helveticus is able to use both lactose and galactose. Lactobacillus **amylophylus** and Lactobacillus **amylovirus** are able to ferment starch. Lactobacillus lactis can ferment glucose, sucrose and galactose. **Lactobacillus pentosus** have been used to ferment sulfite waste liquor.

Lactobacillus has complex nutritional requirements, as they are those groups of Microorganisms that have lost their ability to synthesize their own growth factors. They cannot grow solely on carbon source and inorganic nitrogen salts. Organisms such as **Rhizopus oryzae** have less limiting nutritional requirements and can utilize starch feed stocks. They are able to produce pure L (+) lactic acid . Studies have also been carried out with **Saccharomyces cerevisiae** and **Kluyveromyces lactis** for production of pure L (+) lactic acid because of their ability to tolerate high concentration of hydrogen ion, which is desirable.

8.1.4 ENZYMES FOR LACTIC ACID FERMENTATION

Lactic acid is produced in the form of L (+) or D (-) lactic acid or as its racemic mixture. Organisms that form the L (+) form or D (-) form have two **lactate dehydrogenases** (LDH), which differ in their stereospecifity. Some Lactobacilli produce L (+) form, which on accumulation induces a racemase, which converts it into D (-) lactic acid until equilibrium is obtained.

The L- lactate dehydrogenase in L. casei have been found to be an allosteric enzyme with fructose 1,6- bisphosphate (FDP). In some cases Mn2+ acts as the cofactor. The LDH in L. casei and eukaryotes and in L. casei and vertebrates show 37% and 76% similarity respectively, but the active sites show 70% and 86% similarity respectively which shows that the essential parts of this enzyme had been conserved. In comparison to the vertebrate enzymes L. casei is found to lack 12-amino acid residues at the N- terminus, which is found to be a common characteristic of bacterial enzymes irrespective of the allosteric behaviour. L. casei also carries 7 additional amino acid residues at the C end but it is not known whether this is also characteristic of bacterial enzymes as there are no complete sequence of other bacterial enzymes available.

Fermentor for production of lactic acid

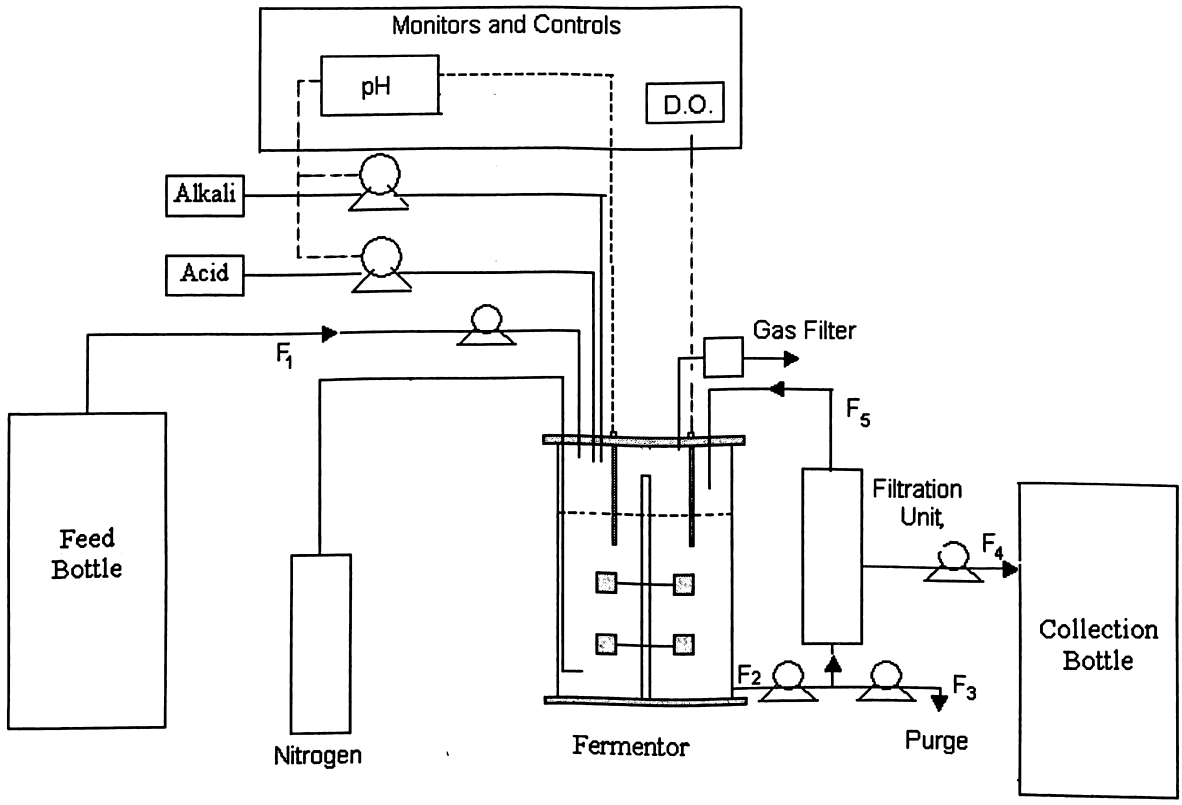


Fig.2-Sketch of the fermentor is shown with all the connection for monitoring and control of the continuous lactic acid fermentation process with continuous cell recycling.

F1: feed rate (the dilution rate was maintained by maintaining the feed rate.

F2: rate at which broth was taken out of the fermentor.

F3: rate of purging (the sample from the purge were regularly analyzed for biomass and metabolites concentrations inside the fermentor.

F4: rate at which permeate was taken out from the filtration unit

F5: rate at which biomass was recycled back to the fermentor.

Overview of lactic acid based polymers prepared by direct polycondensation or by polycondensation followed by chain extension.

Molecular size prepared in kDa	Monomer/monomers	Linking agent	Macro molecular form	Reference
Low or medium molar mass < 70 kDa	L-lactic acid	nil	Linear homopolymer	Espartero et al. 1996; Ajioka et al. 1998
High molecular size >70 kDa	L-lactic acid	HMDI	Linear homopolymer	Hiltunen et al. 1997; Woo et al. 1995
High molecular size >70 kDa	L-lactic acid	Dipentaerythriitol	Star shaped homopolymer	Kim and Kim, 1999
Low molar mass < 20 kDa	L-lactic acid with 6-hydroxycapric acid; L-lactic acid with caprolactone	Nil with 6hydroxycaproic acid, and HMDI for caprolactone monomer polymerization	Linear copolymer	Kylma et al. 1997; Kawasaki et al. 1998
High molecular size > 70 kDa	L-lactic acid with Butandiol; L-lactic acid with mandelic acid	HMDI; IPDI	Copolymers	Kylma and Seppala, 1997
High molecular size > 70 kDa	L-lactic acid with butandiol; 4 hydroxybbenzoic acid	HMDI; IPDI	Copolymers	Kylma and Seppala, 1997
High molecular size > 70 kDa	L-lactic acid with butandiol; 4 acetoxybenzoic acid	HMDI; IPDI	Copolymers	Kylma and Seppala, 1997
High molecular size > 70 kDa	L-lactic acid with butandiol; 4	HMDI; IPDI	Copolymers	Kylma and Seppala, 1997
High molecular size > 70 kDa	L-lactic acid	HMDI; IPDI	Copolymers	Kylma and Seppala, 1997

LACTIC ACID POLYMER BY POLY- CONDENSATION

Lactic acid polymers consist of mainly lactyl units, of only one stereoisoform or combinations of D and L lactyl units in various ratio. A disadvantage of polycondensation is that a low molar mass polymer is obtained. There have been studies to obtain high molar mass polymer by manipulating the equilibrium between lactic acid, water and polylactic acid in an organic solvent or a multifunctional branching agent was used to give star-shaped polymers. In the presence of bifunctional agents (dipoles and diacids) they form telechelic polymers, which can be further linked to give high molar mass polymers using linking agents like diisocynate.

LACTIC ACID POLYMER BY RING- OPENING POLYMERISATION

The ring opening polymerization route includes polycondensation of lactic acid followed by a depolymerisation into the dehydrated cyclic dimmer, lactide which can be ring opening polymerized to high molar mass polymers. The depolymerisation is conventionally done by increasing the polycondensation temperature and lowering the pressure, and distilling off the produced lactide. Solution polymerization, bulk polymerization, melt polymerization and suspension polymerization are the various methods of ring opening polymerizati. The polymerization mechanism can be cationic, anionic, coordination or free radical polymerization. It is catalyzed by compounds of transition metals: - tin, aluminium, lead, zinc, bismuth, iron and yttrium .

The synthesis of polylactic acid through polycondensation of the lactic acid monomer gave weight average molecular weights lower than 1.6 x 104,whereas ring opening polymerisation of lactides gave average molecular weights ranging from 2 x 104 to 6.8 x 105 . The monomer conversion and average molecular weights showed a maximum at a catalyst concentration of stannous octoate of 0.05%. It increases linearly with polymerisation time up to a monomer conversion of 80% to a maximum but thermal depolymerisation of resultant polylactides is observed with prolonged times at higher polymerization temperatures.

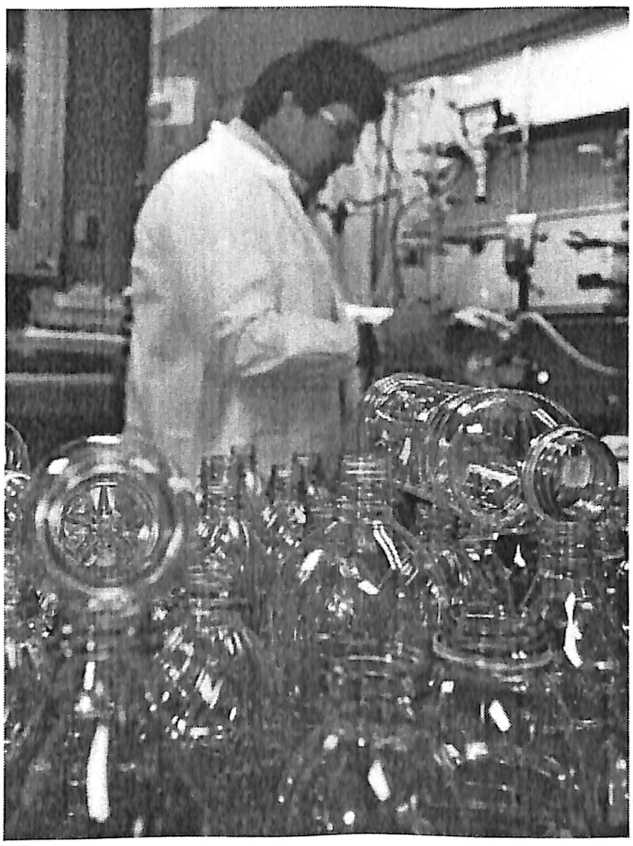
9. Economics and environmental advantages of biodegradable polymers

Organo-catalysis is a basis for a new era of green polymer chemistry whereby products are made bio-degradable like natural materials. With such a technology,disposable water bottles,for instance, would be broken down into the basic monomers needed to reform them again into new polymer bottles, creating a sustailnable cycle, according to researchers at IBM and STANFORD University.

Green polymer chemistry changes all this by quickly breaking down all plastic bottles into basic monomers, which can then be easily reassembled into pristine new polymers that are again used for drinking bottles thus forming a smarter substantial model for plastic: reusing the same materials over and over again. Orgonano-catalysis allows reuse of bothcommon pet as well as plant based plastics made from renewable sources in the environment.

Plastics today, such as the polyethylene terepthalate(PET) used in disposable drinking bottles, are not generally used in other drinking bottles but in other secondary packing materials,which

in turn will eventually turn up in the landfill. Today more than 13 billion plastics bottlea are thrown away each year and 63 pounds of plastic for every man woman and child ends up in the landfill.



Jim Hedrick, a researcher at IBM's Research facility in San Jose, Calif., works on new formulas to recycle plastic bottles for a new era of environmentally sustainable plastics.

"What we have done at IBM is develop a catalyst that can go into our material, and break it down very rapidly into the building blocks [monomers] that you can very easily build back up [into polymers]," explains Bob Allen of IBM Research. "It's what we call a chemical recycling process."

IBM is also sponsoring researvhes at king abdulaziz city for science and technology to develop a wide variety of PET-based plastics for food containers ,beverages and other liquids.the goal is to develop a wide array of PET and plant derived polymers that can create

100 percent recyc;lable plastic economy for the consumer goods, health care and electronic industries.

10. GRADING CRITERIA FOR PLASTICS MANUFACTURING

The scorecard grades the major steps in plastics manufacturing o the basis of inherent hazards of the chemicals used i manufacturing step. The manufacturing of plastic involves many steps.

- The fist step is the manufacture of [primary petrochemicals namely propene, ethylene,benzene,xylene,methanol,toluene,butadiene which along with chlorine are at y=the foundation of fossil fuel plastics.
- The second step is the conversion of primary petrochemicals into intermediate chemicals. For example "ethylbenzene" is an intermediate chemical formed from the primary petrochemicals ethylene and benzene.
- The third step is the manufacture of monomer from the intermediate chemical. For example styrene is the monomer from he chemical ehylbenzene. Monomers are the building blocks for the polymers.
- The fourth step is the manufacture of the polymer from the monomer. Individual monomer units are connected into a long chain to create a polymer. For example is the polymer from the monomer styrene is polystyrene. In the polymerisation of a monomer there is always a certain amount of unreacted monomer that becomes lodged in the polymer chain. Over time and with appropriate conditions the unreacted monomer will leak out of the product. Catalysts are used to speed up the rate at wich the monomers are linked to each other. While manufacturers reclaim and reuse the catalysts in the manufacturing process inevitably residual levels ends up in the polymer.

The plastic scorecard grades plastics based on five manufacturing attributes:

- Primary and Intermediate chemicals
- Monomers
- Catalysts
- Nanomaterials
- Additives

The chemicals used in each step of plastic manufacturing are categorised into different levels of environmental an human health performance based on assessment using Green Screen for Safer Chemicals.

The grading criteria for each of the Feedstock Production Attributes are discussed below:

The Primary and intermediate chemicals

The grade for primary and Intermediate chemicals begins at Grade C-(rather than Grade F) because these chemicals are used in closed manufacturing processes where the exposures can be minimized. That said, however the grading criteria still benefit plastics made from inherently safer primary and secondary intermediate chemicals(which greatly benefit workers and surrounding communities).

GRADE C- Any primary or intermediate chemical used in the manufacture of the plastic is Green Screen red chemical.

GRADE B- Any primary or intermediate chemical used in the manufacture of the plastic is Green Screen orange chemical.

GRADE A+ All primary or intermediate chemicals used in the manufacture of the plastic is Green Screen green chemicals.

MONOMERS

The grade for monomers begins at grade F because these residual do remain in the final plastic products and can lead to exposures during use and can lead to exposures during use and disposal and during disposal as well as during manufacture. For example the monomer Bisphenol A(used to manufacture Polycarbonate) had been restricted by governments in baby bottles.

GRADE F = Any monomer used in the manufacture of a plastic is a green screen red chemical and the plastic is used in food contact items or children's products. This grade is only relevant to final products.

GRADE D = Any monomer used in the manufacture of plastic is a Green screen red chemical. This grade is related to the inherent characteristics of the monomer.

GRADE C- = Any monomer used in the manufacture of plastic is a Green screen orange chemical and the plastic is used in food contact items or children's products. This grade is only relevant to final products.

GRADE C+ = Any monomer used in the manufacture of plastic is a Green screen orange chemical.

GRADE A+ = All monomers used in the manufacture of plastic are Green screen yellow/green chemicals.

CATALYSTS

The grade for catalysts begins at GRADE C- (rather that GRADE F) because these chemicals are generally captured and reused in the manufacturing process. That said, however, the grading criteria still benefits plastics made from inherently safer catalysts. As residual levels of catalysts do end up in products and become an issue during recycling processes.

GRADE C- Any catalyst used in the manufacture of a plastic is a Green Screen red chemical.

GRADE B- Any catalyst used in the manufacture of a plastic is a Green Screen orange chemical.

GRADE A+ All catalysts are Green Screen yellow/green chemical.

ADDITIVES

The grade for chemicals begins at grade F because additives can leak out of plastic products and lead to exposures during use and end of life management as well as during manufacture. For example the phthalate plasticisers(including DEHP) have been restricted in children's products and the polybrominated diphenyl ether(PBDE) flame retardants have been restricted from use in certain products. Nanomaterials additives that have been tested for toxicity are captured within this attribute.

GRADE F = Any additive used in the manufacture of the plastic is a green screen red chemical and the plastic is used in food contact items and children's products.

GRADE D = Any additive used in the manufacture of the plastic is a green screen red chemical.

GRADE C- = Any additive used in the manufacture of the plastic is a green screen orange chemical and the plastic is used in food contact items and children's products.

GRADE C+= Any additive used in the manufacture of the plastic is a green screen red chemical.

GRADE A+ = All additives used in the manufacture of the plastic are green screen yellow/green chemicals.

NANOMATERIALS

The grade for any nanomaterial begins at grade C+ becuse of the lack of toxicity testing data for the vast majority of nanomaterials.

GRADE C- = Product contains nanomaterials that have not been tested for toxicity concerns.

GRADE A+ = Product does not contain nanomaterials.

11. Industry Opportunities for Alternative Polymer Processing

No other group of compounds has had as great an impact on our day-to-day living as synthetic polymers. Polymers have many uses, from the foam coffee cup to the life-saving artificial heart valve. Replacement of traditional materials such as metals, wood, glass, and natural fibers with synthetic polymers and composite materials has resulted in products with lower weight, better energy efficiency, higher performance and durability, and increased design and manufacturing flexibility. Polymer synthesis is a major part of the chemical industry with annual production exceeding 30 million tons per year.

New methods for polymer processing and synthesis could reduce or eliminate the environmental problems that are associated with polymer manufacturing as well as increase energy efficiency and decrease waste generation. Utilizing alternative raw materials is one of the ways of improving material utilization and efficiency in the polymer industry.

Materials that are considered waste in one segment of the industry could become raw materials for polymer synthesis. Combining the processes of polymerization and fabrication is another area where novel techniques could decrease processing unit steps and thereby increase productivity and efficiency. Product recycling and recyclability is a potentially large area in which alternative processing and polymer synthesis could have a substantial impact.

Polymer manufacturing has traditionally involved the use of volatile organic solvents and water and has required extensive separation and containment processes to ensure that harmful materials do not enter the environment.

PROPERTIES

Important properties of biodegradable polymers are as follows:-

- The material should not evoke a sustained inflammatory or toxic response upon implantation in the body.

- The material should have acceptable shelf life.

- The degradation time of the material should match the healing or regeneration process.

- The material should have appropriate mechanical properties for the indicated application and the variation in mechanical properties with degradation should be compatible with the healing or regeneration process.

- The degradation products should be non-toxic, and able to get metabolized and cleared from the body.
- The material should have appropriate permialbility and processibility for the intended application.

Some of the inherent properties of the polymeric biomaterials that have an effect on their biocompatibility are material chemistry, molecular weight, solubility, shape and structure of the implant, hydrophilicity/hydrophobicity, lubricity, surface energy, water absorption, degradation and erosion mechanism.

12. CURRENT EFFORTS

Current efforts in biodegradable polymer synthesis have been focused on custom designing and synthesizing polymers with tailored properties for specific applications by:

(1) Developing novel synthetic polymers with unique chemistries to increase the diversity of polymer structure,

(2) Developing biosynthetic processes to form biomimetic polymer structures.

(3) Adopting combinatorial and computational approaches in biomaterial design to accelerate the discovery of novel restorbable polymers.

13. APPLICABILITY OF BIOPOLYMERS

They are being investigated in developing therapeutic devices such as temporary prosthesis, three dimensional porous structures as scaffolds for tissue engineering and for pharmacological applications.

Some of the current biomedical applications for bio degradable polymers are:-

- Large implants, such as bone screws, bone plates and contraceptive reservoirs,
- Small implants, such as staples, sutures and nano- or micro-sized drug delivery vehicles
- Plain membranes for guided tissue regeneration
- Multifilament meshes or porous structures for tissue engineering

13.1 Biodegradable polymers

Both synthetic polymers and biologically derived (or natural) polymers have been extensively investigated as biodegradable polymeric biomaterials. Biodegradation of polymeric biomaterials involves cleavage of hydrolytically or enzymatically sensitive bonds in the polymer leading to polymer erosion. Depending on the mode of degradation, polymeric biomaterials can be further classified into hydrolytically degradable polymers and enzymatically degradable polymers. Most of the naturally occurring polymers undergo enzymatic degradation. Natural polymers can be considered as the first biodegradable biomaterials used clinically. The rate of in vivo degradation of enzymatically degradable polymers however, varies significantly with the site of implantation depending on the availability and concentration of the enzymes. Chemical modification of these polymers also can significantly affect their rate of degradation. Natural polymers possess several inherent advantages such as bioactivity, the ability to present receptor-binding ligands to cells, susceptibility to cell-triggered proteolytic degradation and natural remodeling. The inherent bioactivity of these natural polymers has its own downsides.

These include a strong immunogenic response associated with most of the polymers, the complexities associated with their purification and the possibility of disease transmission. Synthetic biomaterials on the other hand are generally biologically inert, they have more predictable properties and batch-to-batch uniformity and they have the unique advantage having tailored property profiles for specific applications, devoid of many of the disadvantages of natural polymers. Hydrolytically degradable polymers are generally preferred as implants due to their minimal siteto- site and patient-to-patient variations compared to enzymatically degradable polymers. The successful performance of the first synthetic poly(-glycolic acid) based suture system during the late 1960s led to the design and development of a new array of biodegradable polymers as transient implants for orthopaedic and related medical applications. Extensive research has gone since then to custom designing biodegradable polymer systems with predictable erosion kinetics as drug/gene delivery vehicles or as scaffolds for tissue engineering. For applications that need materials with a certain level of biological activity, strategies to incorporate biological motifs onto synthetic polymers

in the form of hybrid materials have also been developed. The objective of this review is to highlight the current status of biodegradable polymers for various biomedical applications including transient implants, drug delivery vehicles and tissue engineering scaffolds. This review covers the general synthesis, biodegradation, biocompatibility and potential biomedical applications of some of the most promising polymeric biomaterials used today.

The polymeric biomaterials discussed in this review have been broadly classified into hydrolytically degradable polymers and enzymatically degradable polymers placing emphasis on the mode of degradation for the corresponding polymers.

13.1.1 Hydrolytically degradable polymers as biomaterials

Hydrolytically degradable polymers are polymers that have hydrolytically labile chemical bonds in their back bone. The functional groups susceptible to hydrolysis include esters, orthoesters, anhydrides, carbonates, amides, urethanes, ureas, etc. Two general routes are used to develop hydrolytically sensitive polymers for biomedical applications. They are step (condensation) polymerization and addition (chain) polymerization including ring opening

polymerization. Step process is used to prepare a variety of hydrolytically sensitive polymer classes, such as polyanhydrides, poly(ortho esters) and polyurethanes. Ring opening polymerization (ROP) is an extensively investigated polymerization route to develop hydrolytically sensitive polymers, including the poly(a-esters) and polyphosphazenes. Radical polymerization mostly results in the formation of non-degradable polymers; however, recent studies have demonstrated the feasibility of developing synthetic degradable polymers or cross-linked gels by radical polymerization processes. In addition, several polymers developed by microbial bioprocess are gaining significant interest as biodegradable polymers. The following sections discuss some of the most promising hydrolytically sensitive synthetic polymers developed and their biomedical applications.

13.1.1.1.1 Poly(α-esters)

Poly(a-ester)s are thermoplastic polymers with hydrolytically labile aliphatic ester linkages in their backbone. Although all polyesters are theoretically degradable as esterification is a chemically reversible process, only aliphatic polyesters with reasonably hort aliphatic chains between ester bonds can degrade over the time frame required for most of the biomedical applications. Poly(a-esters) comprise the earliest and most extensively investigated class of biodegradable polymers. The uniqueness of this class of polymers lies in its immense diversity and synthetic versatility. Poly(a-ester)s can be developed from a variety of monomers via ring opening and condensation polymerization routes depending on the monomeric units. Bacterial bioprocess routes can also be used to develop some poly(a-ester)s. Various synthetic routes for developing polyesters have been recently reviewed by Okada et al.

Among the class of poly(a-ester)s, the most extensively investigated polymers are the poly(ahydroxy acid)s, which include poly(glycolic acid) and the stereoisomeric forms of poly(lactic acid). The first synthetic suture material was successfully developed based on the glycolides in late 1960s. Several other aliphatic polyesters were developed since then as biodegradable biomaterials and are attracting significant attention as biomaterials due to their good biocompatibility and controllable degradation profiles. The class of poly(a-ester)s now include poly(a-hydroxy acids) and other ester polymers with and without oxygen atom adjacent to the a-carbon of the acid moiety.

Polyesters can be synthesized by the polycondensation of difunctional monomers such as the selfcondensation of hydroxy acids, diacids with diols, diacid chlorides with diols or by the ester interchange reaction of diesters and diols. However, since it is difficult to achieve high molecular weight polymers by the polycondensation route, it has not been extensively investigated for developing biomaterials.

ROP of cyclic lactones has developed into the most effective one pot polymerization route to develop high molecular weight homo- and copolyesters. The advantages of ROP over polycondensation route as a commercially viable process are: milder reaction conditions, shorter reaction times, the absence of reaction by-products and the ability of using even six or seven membered lactones. During ROP, specific initiator molecules such as hydroxyl containing molecules, can control the molecular weight of the polymers. The rate of polymerization can be controlled by the application of a wide-range of biocompatible catalytic systems, such as stannous octoate and 2-ethylhexanoic acid. To further improve their biocompatibility, several solvent-less polymerization routes have been developed.

13.1.1.2 Polyglycolide

Polyglycolide can be considered as one of the first biodegradable synthetic polymer investigated for biomedical applications. Polyglycolide is a highly crystalline polymer (45–55% crystallinity) and therefore exhibits a high tensile modulus with very low solubility in organic solvents. The glass transition temperature of the polymer ranges from 35 to 40 1C and the melting point is greater than 200 1C. In spite of its low solubility, this polymer has been fabricated into a variety of forms and structures. Extrusion, injection and compression molding as well as particulate leaching and solvent casting, are some of the techniques used to develop polyglycolide-based structures for biomedical applications. Due to its excellent fiber forming ability, polyglycolide was initially investigated for developing resorbable sutures. The first biodegradable synthetic suture called DEXONs that was approved by the United States (US) Food and Drug Administration (FDA) in 1969 was based on polyglycolide.

Polyglycolide shows excellent mechanical properties due to its high crystallinity. A self reinforced form composed of polyglycolide is stiffer than any other degradable polymeric system used clinically and has been shown to exhibit a modulus of approximately 12.5 GPa.

Due to its good initial mechanical properties, polyglycolides have been investigated as bone internal fixation devices (Biofixs).

Polyglycolide is a bulk degrading polymer, degrades by the non-specific scission of the ester backbone. The polymer is known to lose its strength in 1–2 months when hydrolyzed and losses mass within 6–12 months. In the body, polyglycolides are broken down into glycine which can be excreted in the urine or converted into carbon dioxide and water via the citric acid cycle.

The high rate of degradation, acidic degradation products and low solubility however, limit the biomedical applications for polyglycolide. Therefore, several copolymers containing glycolide units are being developed to overcome the inherent disadvantages of polyglycolide.

13.1.1.3 Polylactides

Unlike glycolide, lactide is a chiral molecule and exist in two optically active forms; L-lactide and D-lactide. The polymerization of these monomers leads to the formation of semi-crystalline polymers. The polymerization of racemic (D,L)-lactide and mesolactide however, results in the formation of amorphous polymers. Among these monomers, L-lactide is the naturally occurring isomer. Similar to polyglycolide, poly(L-lactide) (PLLA) is also a crystalline polymer (_37% crystallinity) and the degree of crystallinity depends on the molecular weight and polymer processing parameters. It has a glass transition temperature of 60–65 1C and a melting temperature of approximately 175 1C.

Poly(L-lactide) is a slow-degrading polymer compared to polyglycolide, has good tensile strength, low extension and a high modulus (approximately 4.8 GPa) and hence, has been considered an ideal biomaterial for load bearing applications, such as orthopaedic fixation devices. Some of the PLLA-based orthopaedic products include: the Phantom Soft Thread Soft Tissue Fixation Screws, Phantom Suture Anchors (DePuy), Full Thread Bio Interference Screws (Arthrex), BioScrews, Bio-Anchors, Meniscal Stingers (Linvatec), and the Clearfix Meniscal Darts (Innovasive Devices).

PLLA can also form high strength fibers and was FDA approved in 1971 for the development of an improved suture over DEXONs. Due to the high strength of PLLA fibers, it has been investigated as scaffolding material for developing ligament replacement or augmentation

devices to replace nondegradable fibers, such as Dacron. Some PLLA fiber-based devices are currently under investigation as long-term blood vessel conduits. An injectable form of PLLA (Sculptras) has recently been approved by the FDA for the restoration or correction of facial fat loss or lipoatrophy in people with the human immunodeficiency virus.

However, being more hydrophobic than polyglycolide, the degradation rate of PLLA is very low. It has been reported that high molecular weight PLLA can take between 2 and 5.6 years for total resorption in vivo. The rate of degradation however, depends on the degree of polymer crystallinity as well as the porosity of the matrix. Even though the polymer is known to lose its strength in approximately 6 months when hydrolyzed, no significant changes in mass will occur for a very long time. Therefore, several co-polymers of L-lactides with glycolides or DL-lactides are currently under investigation for the development of polymers with better property modulation. Thus Resomers LR708 is a 70:30 amorphous copolymer of poly(L-lactide-co- DL-lactide) and is being extensively investigated as a bioresorbable implant material. Poly(DL-lactide) (PDLLA) is an amorphous polymer due to the random distribution of L- and D-lactide units and has a glass transition temperature of 55–60 1C. Due to its amorphous nature the polymer shows much lower strength (_1.9 GPa) compared to poly(L-lactide). This polymer loses its strength within 1–2 months when hydrolyzed and undergoes a loss in mass within 12–16 months.

Being a low strength polymer with faster degradation rate compared to poly(L-lactide), it is a preferred candidate for developing drug delivery vehicles and as low strength scaffolding material for tissue regeneration.

Polylactides undergo hydrolytic degradation via the bulk erosion mechanism by the random scission of the ester backbone. It degrades into lactic acid a normal human metabolic by-product, which is broken down into water and carbon dioxide via the citric acid cycle.

13.1.1.4 Polydioxanone

Although biodegradable polylactides and glycolides have allowed for the development of versatile resorbable multifilament sutures for biomedical applications, much research has gone into developing materials that would facilitate the formation of monofilament sutures. Multifilament sutures have a higher risk of infection associated with their use and causes a

greater amount of friction when penetrating tissues. Polydioxanone (PDS) was the material of choice for the first commercially developed monofilament suture under the trade name of PDSs in the 1980s. In addition to sutures, PDS has also been investigated for several orthopaedic applications as fixation screws for small bone and osteochondral fragments (Orthosorb Absorbable Pinss). PDS is a colorless, semi crystalline polymer prepared by the ROP of p-dioxanone. The polymer exhibits a very low glass transition temperature ranging from _10 1C to 01C. Being a polyester, it undergoes degradation by the non-specific scission of the ester back bone. However, due to the high crystallinity and hydrophobicity of the polymer, it can be considered a slow to moderately degrading polymer. In the

body, PDS is broken down into glycoxylate and excreted in the urine or converted into

glycine and subsequently into carbon dioxide and water similar to polyglycolides. The

modulus of PDS is very low (approximately 1.5 GPa) compared to polyglycolides. The polymer is known to lose its strength within 1–2 months and its mass within 6–12 months by hydrolytic degradation.

13.1.1.5 Polycaprolactone

Polycaprolactone (PCL) is a semicrystalline polyester and is of great interest as it can be obtained by the ROP of a relatively cheap monomeric unit 'e-caprolactone'. The PCL is highly processible as it is soluble in a wide range of organic solvents, has a low melting point (55–60 1C) and glass transition temperature (_60 1C) while having the ability to form miscible blends with wide range of polymers. The polymer undergoes hydrolytic degradation due to the presence of hydrolytically labile aliphatic ester linkages; however, the rate of degradation is rather slow (2–3 years). Due to the slow degradation, high permeability to many drugs and non-toxicity, PCL was initially investigated as a long-term drug/vaccine delivery vehicle. The long-term contraceptive device

Due to the slow degradation rate of PCL, several co-polymeric systems containing PCL have been investigated to improve the properties of the native polymer. Co-polymers of e-caprolactone with DLlactide have yielded materials with more rapid degradation rates. Similarly, a co-polymer of ecaprolactone and glycolide resulted in fibers that ere less stiff

compared to those made of polyglycolide and are currently on the market as a monofilament suture (MONACRYLs). Another bioresorbable multiblock co-polymer composed of e-caprolactone, glycolide, lactide and poly(ethylene glycol) units has been developed as a drug delivery vehicle for small and medium sized biologically

active molecules (SynBiosyss).

13.1.1.6 Poly(trimethylene carbonate)

High molecular weight flexible poly(trimethylene carbonate) (PTMC) can be obtained by the ROP of trimethylene carbonate. Being an elastomeric aliphatic polyester with excellent flexibility and poor mechanical strength, PTMC has been investigated as a candidate implant material for soft tissue regeneration. Low molecular weight PTMC on the other hand, has been investigated as a suitable material for developing drug delivery vehicles. Unlike the previously described polyesters, PTMC undergoes surface degradation with the rate of in vivo degradation was found to be much higher than in vitro degradation. This is presumably due to the contribution of enzymatic degradation process. The low mechanical performance of the homopolymer significantly limits its applications

and consequently, several co-polymers were developed with other cyclic lactones. Thus, polyglyconates have been developed as block co-polymers of trimethylene carbonate and glycolides for use as flexible suture materials (Maxons) and orthopaedic tacks and screws (Acufexs). BioSyns is a terpolymer composed of glycolide, trimethylene carbonate and dioxane that has reduced stiffness and degrades within 3–4 months and has been used as suture materials.

Bacterial polyesters

Bacterial polyesters are naturally occurring biodegradable polyesters produced by many bacteria as their energy source. The most common polymer among this class is poly(3-hydroxybutyrate) (PHB), which was discovered in 1920 as produced by the bacteria ''Bacillus megaterium''. Since then, it was discovered that several other bacterial strains could produce

the same polymer. PHB is a semi-crystalline isotactic polymer that undergoes surface erosion by hydrolytic cleavage of the ester bonds and has a melting temperature in the range of 160–180 1C. In addition to a bacterial synthetic route, several chemical synthetic routes have been developed for PHB synthesis. Shelton et al.,

demonstrated that the ROP of optically active b-butyrolactone can result in the formation of

PHB, which is identical to the bacterial PHB. The co-polymers of PHB and 3-hydroxyvalerate P(HBHV) have similar semi-crystalline properties as PHB; however, the melting temperature is lower depending on the HV content. The polymer shows glass transition temperature in the range of _5 to 201C. Both PHB and P(HB-HV) have been found to be soluble in a wide range of solvents and can be processed into different shapes and structures, such as films, sheets, spheres and fibers. Since the homopolymer PHB is a tough, brittle polymer, the less brittle and tougher co-polymer has more potential as a biomaterial. Another unique property of P(HB-HV) is its piezoelectricity which makes it a potential candidate for orthopaedic applications since electrical stimulation is known to promote bone healing. It has also been investigated as a material for developing bone pins and plates.

The hydrolytic degradation of PHB results in the formation of D-(_)-3-hydroxy-butyric acid which is a normal constituent of blood (concentrations between 0.3 and 1.3 mM). However, PHB has a rather low degradation rate in the body compared to synthetic polyesters presumably due to its high crystallinity. The co-polymer, P(HB-HV), being less crystalline undergoes degradation at a much faster rate, however, no correlation has been found between the degradation rate and the amount of HV in the co-polymer. The mass loss of this polymer follows a zero-order release kinetics and this property along with its hydrophobic nature indicate that this polymer primarily undergoes surface erosion. This property makes it an ideal candidate for developing drug delivery vehicles that

can achieve zero-order drug release. The degradation of these polymers is slow, although not many degradation studies have been performed. As such, PHB and P(HB-HV) may be potential biodegradable candidates for long term implants.

Attempts are currently underway to increase the rate of degradation of these polymers by blending them with more hydrophilic polymers or other low molecular weight additives to increase water penetration and facilitate degradation.

Biostable polyurethanes and poly(ether urethanes) have been extensively investigated as long term medical implants, such as cardiac pacemakers and vascular grafts due to their excellent biocompatibility and mechanical properties. Based on the good biological performances of biostable polyurethanes and their synthetic versatility, attempts were made to develop biodegradable polyurethanes. Polyurethanes are generally prepared by the polycondensation reaction of diisocyanates with alcohols and/amines. However, due to the toxicity of common diisocyanates such as 4,40-methylenediphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), other biocompatible aliphatic diisocyanates have been investigated for the development of biodegradable polyurethanes. Lysine diisocyanate (LDI), and 1,4-diisocyanatobutane (BDI) are a few. Degradable poly(ester urethanes) were developed by reacting LDI with polyester diols or triols based on D,L-lactide, caprolactone and other co-polymers having a wide range of properties. In these biodegradable polyurethanes, aliphatic polyesters such as lactide/glycolide copolymers or polycaprolactones form the soft segments and polypeptides form the hard segments. Another unique feature of the peptide-based polymer systems is that active moieties such as ascorbic acid and glucose can be incorporated into the polymer which could potentially promote cell adhesion, viability and proliferation without any adverse effect. Several biodegradable injectable hydrogels systems have been developed; however, only very few studies have been performed at developing injectable materials suitable for orthopaedic applications. These materials would require the additional property of having good mechanical properties and controlled degradability. A unique injectable, two component LDI-based polyurethane system that cures in situ was recently developed for orthopaedic applications (PolyNovas). This self setting system can be administered arthroscopically in liquid form and polymerizes at physiological temperature in situ to provide appropriate bonding strength and mechanical support comparable to or superior to widely used bone cements. This material has also been shown to promote favorable cell adhesion and proliferation.

Poly(ester amide)

Due to the hydrogen bonding ability of the amide bonds and biodegradability imparted by the ester bonds, these co-polymers have good mechanical and thermal properties. The degradation of poly(ester amides) has been shown to take place by the hydrolytic cleavage of the ester bonds, leaving the amide segments more or less intact. The good mechanical properties of

poly(ester amides) derived from symmetrical bisamide-diols and succinyl chloride led to its investigation as a potential bioresorbable suture materials. Different water soluble bisamide-diols have also been prepared from glycolic acid and diaminoalkanes containing 2–12 methylene groups. Attempts were also made to increase the degradation rate of poly(ester amides) by incorporating amino acid units in the polymer backbone. CAMEOs is a poly(ester amide) blend based on leucine or phenylalanine that is currently being developed for the site specific delivery of small hydrophobic drugs and peptides.

13.1.2.Enzymatically degradable polymers as biomaterials

13.1.2.1 Proteins and Poly(amino acids)

Proteins, the major structural components of many tissues are essentially amino acid polymers arranged in a three-dimensional folded structure and are one of the most important class of biomolecules identified. Being a major component of the natural tissues, proteins and other amino acid-derived polymers have been a preferred biomaterial for sutures, haemostatic agents, scaffolds for tissue engineering and drug delivery vehicles. Furthermore, protein based biomaterials are known to under go naturally-controlled degradation processes. The human body is capable of synthesizing a wide range of proteins in which the precursor molecules pass through four major stages in becoming

functional proteins. The first step involves the formation of the primary structure where, a linear sequence of various amino acids is held together by peptide bonds. The constituent amino acids then participate in hydrogen bonding to form the secondary structure of protein. The linear primary structure arranges itself in the most stable structures— an a-helices or b-pleated sheets. These secondary structures then join together to form three-dimensional tertiary structures which in turn interact with other protein chains to form the more refined three-dimensional quaternary structure of a multi-unit protein.

13.1.2.2 Collagen

Collagen is the most abundant protein present in the human body being the major component of skin and other musculoskeletal tissues. Collagen is a rod type polymer nearly 300 nm long with a molecular weight of 300,000. There have been more than twenty two different types of

collagen identified so far in the human body, with the most common being Type I–IV. Type I collagen is the single most abundant protein present in mammals and is the most thoroughly studied protein. The Type I collagen is composed of three polypeptide subunits with similar amino acid compositions. Each polypeptide is composed of about 1050 amino acids, containing approximately 33% glycine, 25% proline and 25% hydroxyproline with a relative abundance of lysine.

Collagen undergoes enzymatic degradation within the body via enzymes, such as collagenases and metalloproteinases, to yield the corresponding amino acids. Due to their enzymatic degradability, unique physico-chemical, mechanical and biological properties collagen has been extensively investigated for biomedical applications. Collagen is mostly soluble in acidic aqueous solutions and can be processed into different forms such as sheets, tubes, sponges, foams, nanofibrous matrices, powders, fleeces, injectable viscous solutions and dispersions. Studies have also shown that the degradation rate of collagen used for biomedical applications can be significantly altered by enzymatic pre-treatment or cross-linking using various cross-linking agents. Collagen is one of the primary initiators of the coagulation cascade and its high thrombogenicity has led to its application as a haemostatic agent. Several collagen-based hemostats are currently on the market or undergoing clinical trials for multiple surgical indications. Some of these include sealant consisting of bovine collagen and bovine thrombin (Sulzer-Spines Tech) used for cardiovascular and spinal surgical procedures, CoStasiss Surgical Hemostat which is composed of bovine microfibrillar collagen, bovine thrombin combined with autologous plasma, and Floseals, a high viscosity gel haemostatic agent composed of collagen-derived particles and tropical bovine-derived thrombin. Since collagen forms the major component of the extracellular matrix and serves as a natural substrate for cell attachment, proliferation and differentiation, renewed interest in collagen as an ideal matrix material for tissue engineering and wound dressing application has occurred. Promogran, a novel spongy collagen matrix containing oxidized cellulose has been recently introduced in US and European market for treating exuding diabetic and ulcer wounds. An FDA approved bilayer skin substitute (Integras Dermal Regeneration Template), currently in the market for full thickness or deep partial thickness thermal injury, is composed of a dermal layer of crosslinked bovine collagen and glycosaminoglycan and an epidermal layer of polysiloxane. Other FDA approved collagen- based wound dressings are Biobranes and Alloderms, which

are, acellular collagen matrices obtained from chemically processed human cadavers. In addition to these acellular collagenbased products, several bioengineered skin equivalents have also been commercially developed.

Due to the high reactivity of collagen it can be cross-linked by a variety of cross-linking agents such as difunctional or multifunctional aldehydes, carbodiimides, hexamethylene-diisocyanate, polyepoxy compounds and succinimidyl ester polyethylene glycol. Cross-linking can also occur by thermal or high-energy irradiation, as well as by chemical modification, such as succinylated collagen to form collagen gels for use as carriers for drug delivery and as scaffolds for tissue engineering. Furthermore, the extent of drug release from these collagen matrices can be controlled by varying the physical properties of the gel such as porosity, density and degradation rate.

The major sources of collagen currently used for biomedical applications are bovine or porcine skin or bovine or equine Achilles tendons. One disadvantage of these collagen-based biomaterials, which is a limiting factor for the wide-spread clinical application is their mild immunogenicity imparted by the composition of the terminal region and the antigenic sites in the central helix. The immune response has been found to vary depending on the species from which collagen has been isolated, processing techniques and the site of implantation. Other concerns include, the high cost of pure collagen, variable physico-chemical and degradation properties and the risk of infectious diseases transmission due to the allogenic or xenogenic origin of the material. Several recombinant systems are currently under development to produce human sequence collagen to overcome some of the limitations of using animal-derived collagen.

13.1.2.3 Natural poly(amino acids)

Natural poly(amino acids) are biodegradable ionic polymers that differ from proteins in certain aspects. Natural poly(amino acids), such as cyanophycin, poly(e-L-lysine) and poly-g-glutamic acid are mainly composed of one type of amino acid. These molecules exhibit polydispersity and in addition to a-amide linkages, they exhibit other types of amide linkages that involve b- and g-carboxylic groups as well as e-amino groups.

Poly-g-glutamic acid (g-PGA) is an anionic, water-soluble biodegradable homo-polyamide produced by microbial fermentation and is composed of D- and L-glutamic acid units connected by amide linkages between a-amino and g-carboxylic acid groups. This biodegradable polymer was first isolated in 1937 by autoclaving capsules of Bacillus anthracis. Later, it was discovered that several other Bacillus species were capable of secreting the polymer into culture growth medium as well as nematocysts of the eukaryotic organism Hydra (Hydrozoa, Cnidaria). An investigation of the polymer composition revealed it to be a copolymer with different proportions of enantiomeric L- and D-glutamic acid. Several modified forms of g-PGA has been developed so far as drug delivery vehicles, tissue engineering scaffolds and as thermosensitive polymers. Poly(-g-glutamic acid) benzyl ester (g-PBG) was developed by Kishida et al. as a carrier vehicle for 5-fluorouracil. This polymer degrades very slowly in phosphate buffer solution (pH 7.4) and shows a diffusion-controlled release pattern that is pH dependent. The high functionality of g-PGA makes it a promising material for developing bioactive scaffolds for tissue engineering application. Matsusaki et al. demonstrated the feasibility of developing bioactive fibroblast growth factor-2 coupled biodegradable substrates using poly(-g-glutamic acid)- sulfonate (g-PGA-S) polymer. The modified polymer has several advantages over natural sulfonated polymers (e.g., heparin), such as the ability to control the content of sulfonate group, low anticoagulant activity and the ability to enhance FGF-2 activity. Thermosensitive polymers have been known to exhibit unique changes in their hydration properties following temperature changes and are considered to be nano-engineered intelligent materials for biomedical applications. Shimokuri et al., developed a thermosensitive polymer bycontrolled propylation of poly(-g-glutamic acid). Their studies showed that at appropriate levels of propyl esterification, the polymer could exhibit a hydrophobic-hydrophilic balance suitable for thermosensitivity. Being a natural polymer, g-PGA is an ideal biomaterial; however, due to its limited availability, not many studies have been performed so far. Similar to to g-PGA, poly L-lysine is of bacterial origin and is currently being investigated as scaffold material for tissue engineering and as drug delivery vehicles due to its ability to form biocompatible hydrogels. Poly(L-lysine) is known to have antibacterial, antiviral and anti tumour activity and is considered to be a potential candidate for developing drug carrier vehicles. The cytotoxicity of the polymer due to the very high positive charge limits its applications however.

13.1.2.4 Fibrin

Fibrin is a biopolymer similar to collagen that is involved in the natural blood clotting process. Fibrin is derived from fibrinogen, which is a 360kDa protein composed of three pairs of polypeptide chains. The structure can be divided into three major sections consisting of a central domain composed of fibrinopeptide E with two pairs of fibrinopeptide A and B molecules and two terminal domains of fibrinopeptide D. In the presence of the enzyme thrombin, spontaneous fibrillogenesis occurs due the cleavage of fibrinopeptide A and B to form a linear fibril. These fibrils undergo lateral association to form fibers of varying diameters ranging from 10 to 200nm depending on the environmental conditions. The fibrin clot, once formed, can undergo degradation called fibrinolysis in the body initiated by a complex cascade of enzymes present in the human body.

Fibrin is one of the earliest biopolymers used as biomaterials. This is due to the excellent biocompatibility, biodegradability, injectability and the presence of several extracellular matrix proteins, such as fibronectin, that favorably affects cell adhesion and proliferation. One of the first products developed from fibrin was a fibrin sealant. Various fibrin sealant products are being used clinically worldwide for hemostasis and tissue sealing applications in various surgical procedures. Due to its injectability and biodegradability, fibrin has also been investigated as a carrier vehicle for bioactive molecules. It has been found that proteins interact differently with fibrin clots, with certain growth factors demonstrating a strong interaction with fibrin matrices. Several cross-linking techniques are also currently under investigation to control the release profile of bioactive molecules

from the fibrin matrix. Fibrin matrices have also been found to be excellent cell carrier vehicles. Bioseeds is a fibrin-based product obtained by mixing keratinocytes with fibrin and is used to treat chronic wounds. A unique feature of fibrin-based cell carriers is that the matrix properties can be optimized for each different cell type.

13.1.2.5 Polysaccharides

Polysaccharides are macromolecules formed from many monosaccharide units joined together by glycosidic linkages. Polysaccharides are gaining renewed interest as biomaterials due to the growing body of literature pointing to their unique biological functions ranging from cell

signaling to immune recognition. This combined with new synthetic routes currently available to modify polysaccharides or synthesize oligosaccharide moieties, biodegradability and ability to fabricate appropriate structures, make them one of the most important and extensively investigated natural biomaterials.

14. CONCLUSION

Most of the biodegradable materials currently on the market are based on natural polymers such as collagen and synthetic polymers such as poly(esters). Advances in synthetic organic chemistry and novel bioprocesses are enabling the development of a wide range of novel polymeric materials as candidates for developing transient implants and drug delivery vehicles. The success of biodegradable implants lies in our ability to design or modify existing biomaterials to achieve appropriate biocompatibility, degradation and physical properties to elicit favourable biological response

15. VISION

Scientists will be able to design polymers and predict their properties, from the molecular level through the macroscopic level, relying on easy to use computational tools.

Scientists will be able to manipulate polymers precisely - from nanoscale to macroscale - for economical synthesis, processing, and manufacturing of lower cost, higher performance materials.

There will be increased acceptance of methods for disassembly and reuse, and life-cycle considerations as parts ofpolymer development.

REFERENCES

- Lee. W, et al; 2005. Biodegradable polymers
- EXPRESS Polymer Letters Vol.3, No.6 (2009) 366–375
- BIOMASS CONVERSION: FERMENTATION CHEMICALS AND FUELS
- Baniel A et al; 2005 U S patent no 67879
- Grading Criteria For Plastics Manufacturing Handbook

BIBLIOGRAPHY

- Green chemistry of Polymers
- www.wikipedia.com
- Biodegradable polymers as biomaterials
- Bioplastics Magazine
- European polymer journal