CHAPTER 1

INTRODUCTION

1.1. Relevance of Biodegradable Polymers

Lord Alexander Todd (Nobel laureate in Chemistry, 1957) once said that polymers are the biggest contribution of chemistry to mankind\(^1\). They have become indispensable to our life with their wide range of applications in diverse fields such as packaging, agriculture, consumer products, medical appliances, building materials, industry, aerospace materials etc. However, the resistance of synthetic polymers to chemical, physical and biological degradation has become a serious concern when used in areas such as surgery, pharmacology, agriculture and the environment, and as a consequence time-resistant polymeric wastes are becoming less and less acceptable\(^2\). Naturally, the necessity for polymeric materials satisfying the conditions of biodegradability, biocompatibility and release of low-toxicity degradation products, as an alternative to these existing polymers is apparent.

The severe environmental problems, including the increasing difficulties of waste disposal and the deepening threat of global warming (due to carbon dioxide released during incineration) caused by the non-biodegradability of polyethylene (used in packaging and agriculture field) have raised concerns all over the world. We must confront them in order to build a new society and
economy free of plastic pollution in the 21st century. The use of biodegradable counterparts as an alternative to non-biodegradable polymers is, therefore, evoking considerable interest lately. Unfortunately, the degradable polymers available until recently have inferior physical properties in terms of strength and dimensional stability and most of them are very expensive and are technically difficult to process. As a result, attempts have been made to solve these problems by including biodegradability into polymers in everyday use through slight modifications of their structure. Polyethylene can be made to an environmentally friendly polymer by introducing sugar moieties that will increase the hydrophilicity and the number of active sites for the microbial attack on polyethylene backbone.

In recent years, biodegradable polymers from renewable resources have attracted much interest for environmental and medical applications because of their desirable properties of biodegradability, biocompatibility and natural abundance. Polylactides (PLA) is the leading candidate among these biopolymers. Due to its high capital cost and slow degradation rate as compared to the waste accumulation rate, the focus of PLA has been mainly on the biomedical field. However, certain limitations of PLA such as low hydrophilicity and degradation rate, poor soft tissue compatibility, low thermal and physical properties, lack of processability limits their wide utilization. These limitations of PLA along with its increased use in medicine generated more research interest for new materials by copolymerization of PLA with suitable monomers and/or polymers, so that some of the problems associated
with them can be solved for wider applications. A controlled solvation and degradation could be achieved by graft copolymerization of lactide onto chitosan, an amino polysaccharide present in the nature. The local toxicity due to the acid byproducts of PLA can be neutralized by the alkalescence of chitosan to get better biocompatibility. Copolymerization of PLA with cycloaliphatic amide segments would be expected to compliment the defects of PLA by the formation of intramolecular and intermolecular hydrogen bonds between ester and amide groups. Cycloaliphatic monomers are expected to be a better alternative to aliphatic counter parts as they are biocompatible and their incorporation increases the thermal and physical properties of copolymers at lower molecular weight in poly(ester amide)s.

1.2. What is Biodegradation?

There are a number of definitions on biodegradation, which depend on the field of application of the polymers (biomedical area or natural environment)\(^3\)\(^-\)\(^5\). Van der Zee\(^6\) and Seal\(^7\) reviewed all of the definitions found in different standards. The definition given by Albertsson and Karlsson appears to give a broad outlook on biodegradation. According to them, biodegradation can be defined as an event that takes place through the action of enzymes and/or chemical decomposition associated with living organisms and their secretion products. It is also necessary to consider abiotic reactions like photodegradation, oxidation and hydrolysis, which may alter the polymer before or during biodegradation because of environmental factors\(^8\)\(^,\)\(^9\).
1.3. Categories of Biodegradable Polymers

Biodegradable polymers can be divided into three categories based on the origin of the raw materials and the process used in their manufacture\textsuperscript{3,10-15}.

1.3.1. Natural Biodegradable Polymers

The natural polymers or polymers from renewable resources fall in four broad groups:

- Polysaccharides (starch, cellulose, lignin, chitin and chitosan)
- Proteins (wool, silk, collagen, gelatin and casein)
- Bacterial polyesters (polyhydroxyalkanoates (PHAs))
- Others (lignin, shellac, natural rubber etc.)

1.3.2. Synthetic Biodegradable Polymers

Polymers produced from feed stocks derived from petrochemical or biological resources such as polyesters\textsuperscript{16,17}, polycaprolactone (PCL), polyamides, polyurethanes, polyureas, polyanhydrides, poly(vinyl alcohol) (PVA), poly(vinyl esters) etc. generally fall in this classification. The higher cost of production is the main barrier for the wide utilization of these polymers.

1.3.3. Biodegradable Polymer Blends

The blending of biodegradable polymers from renewable and non-renewable resources is a method of reducing the overall cost of the material and offers a method of modifying both properties and degradation rates\textsuperscript{18,19}. Melt processability, humidity resistance and mechanical properties of starch can be improved by blending starch with synthetic polymers such as PVA\textsuperscript{20}. 
PLA\textsuperscript{21}, PCL, PHAs etc. to make these materials suitable for the production of biodegradable films, injection-molded items and foams\textsuperscript{4}.

1.4. Factors Affecting Biodegradation

Factors on which the biodegradation of a polymer depends are\textsuperscript{3,22};

1.4.1. Polymer Characteristics

\begin{itemize}
  \item Chemical structure
  
  Polymers containing hydrolysable linkages along the chain or easily oxidisable functional groups on the chain are susceptible to biodegradation by microorganisms and hydrolytic enzymes. Most of the biodegradable polymers, therefore, have easily hydrolysable linkages. Furthermore the polymer chains must be flexible enough to fit into the active sites of the enzymes\textsuperscript{23}.

  \item Degree of hydrophilicity
  
  Polymers containing hydrophilic segments (such as PVA, poly(acrylic acid), polyether) are seemed to be more biodegradable than hydrophobic polymers of comparable molecular weight. The biodegradability of a polymer could be promoted by increasing the hydrophilicity of the polymer by chemical modifications. Hydrophilicity in a polymer not only helps in better penetration of microorganism in the polymer but also induces the production of necessary enzymes within the microorganism relatively more easily compared to hydrophobic polymer.

  \item Stereochemistry
  
  Stereochemistry has a role in biodegradation of polymers. Huang et al. reported that when the poly(ester-urea)s synthesized from D-, L-, and D,L-
phenylalanines subjected to enzyme catalyzed degradation, the pure L-isomer was degraded much faster than the D,L-isomers$^{24}$.

- **Degree and type of branching**

  The main factors affecting the enzymatic degradation of synthetic polymers are the steric configuration of the polymer itself and the nature of the substituents adjacent to the susceptible bond. Branching of the molecular chain inhibits biodegradation.

- **Crystallinity**

  Crystalline regions of a polymer are difficult to penetrate and are inaccessible to microbes as well as to abiotic agents. Amorphous regions are selectively degraded prior to the degradation of the crystalline regions in synthetic polymers as well as in biopolymers. The size, shape and number of crystallites have a pronounced effect on the chain mobility of the amorphous regions and thus affect the rate of degradation.

- **Molecular size**

  Initiation process of biodegradation takes place due to the presence of end groups in the form of unsaturation, hydroperoxide or any other functional groups in the polymer structure. High molecular weight polymer has lesser concentration of these chain end functionality and thus is more resistant to biodegradation. However, biopolymers (such as cellulose or starch) as well as some synthetic polymers (e.g. polycaprolactone) are readily biodegradable despite the long chain structure. Degradation of these polymers depends on the
presence of hydrolysable linkages and hydrophilic functional groups present in
their chemical structure.

1.4.2. Environmental Factors

In biological environment, certain factors such as temperature, moisture,
salts, pH and oxygen are essential for the biodegradation process. The most
significant element is the moisture factor.

1.5. Mode of Biodegradation

1.5.1. Microorganisms

The term microorganism covers a heterogeneous group of living beings
(e.g. bacteria and fungi), which have a microscopic size and are, for the most
part, unicellular. The degradative action of microorganisms is chiefly a result
of the production of enzymes, which breakdown nonliving substrates in order
to obtain nutrient materials present in polymer compositions. Certain
environmental conditions such as optimal ambient temperature, the presence of
nutrient materials and high humidity are essential for optimum growth and
degradative activity of microorganisms.

1.5.2. Enzymes

Enzymes are essentially biological catalysts, with the same action as
chemical catalysts. The activity of enzymes is closely related to the
conformational structure, which creates certain regions at the surface forming
an active site. At the active site the interaction between the enzyme and
substrate takes place leading to chemical reaction, giving a particular product.
The active sites are specific for a given substrate or a series of substrates. For
optimal activity certain enzymes must associate with cofactors that can be metal ions (e.g. Na, K, Mg, Ca and Zn) or organic cofactors such as NAD\(^{+}\), NADP\(^{+}\), FAD\(^{+}\) and ATP called coenzymes\(^{3,5}\).

Different enzymes have different actions, some enzymes change the substrate through a free radical mechanism while others follow alternative chemical routes typically of biological oxidation and biological hydrolysis (Figure 1.1)\(^{3}\).

Figure 1.1. Biological oxidation and hydrolysis by enzymes.
• **Biological oxidation**

  Certain enzymes react directly with oxygen (e.g. cytochromoxidase) (Figure 1.1. eq. 1). In many cases oxygen is directly incorporated into the substrate (e.g. hydroxylases or oxygenases) (Figure 1.1. eq. 2). In another type of biological oxidation the oxygen molecule function as a hydrogen acceptor (i.e. electron acceptor) (e.g. oxidases) (Figure 1.1. eq. 3 & 4).

• **Biological hydrolysis**

  Several different hydrolysis reactions occur in biological organisms. Proteolytic enzymes (proteases) catalyze the hydrolysis of peptide bonds (Figure 1.1. eq. 5) and also the related hydrolysis of an ester bond (Figure 1.1. eq. 6).

1.6. Chemistry of Biodegradation

  Biodegradation is the only degradation pathway that is able to completely remove a polymer or its degradation products from the environment. Biodegradation takes place in two stages (Figure 1.2): The first stage is the depolymerization of the macromolecules into shorter chains. This step normally occurs outside the organism due to the size of the polymer chain and the insoluble nature of many polymers. Extra-cellular enzymes (endo or exo-enzymes) and abiotic reactions are responsible for the polymeric chain cleavage. During this phase the contact area between the polymer and the microorganisms increases.

  The second step corresponds to the mineralization. Once sufficient small size oligomeric fragments are formed, they are transported into cells where
they are bioassimilated by the microorganisms and then mineralized\textsuperscript{5,26}. Biodegradation takes place in two different conditions depending upon the presence of oxygen; aerobic biodegradation (in the presence of oxygen) and anaerobic biodegradation (in the absence of oxygen). Complete biodegradation or mineralization occurs when no residue remains, i.e., when the original product is completely converted into gaseous products and salts.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1_2.png}
\caption{Diagrammatic representation of the chemistry of biodegradation.}
\end{figure}

1.7. The Way of Polymer Degradation

Polymer degradation in natural environment occurs in two stages. The first stage is mainly abiotic and the second stage is purely biotic\textsuperscript{25,27}. 
1.7.1. Abiotic Degradation

As microbes cannot act upon high molecular weight polymers, they have to be fragmented into smaller chains before microbial degradation. The environmental factors, causing chemical degradation of polymers under natural conditions are given below\textsuperscript{25,27}.

a) Thermal degradation

All polymers can be degraded by the influence of heat, whether present at the service temperature or applied during polymer processing. When heated to the extent of bond rupture, polymer degradation results from the production of free radicals, which causes either random scission to smaller molecules of varying chain length (e.g. polyethylene) or depolymerization of the polymer to monomer or monomers (e.g. polymethylmethacrylate (PMMA)). Thermal degradation of polymers like poly(vinyl chloride) (PVC) is caused by elimination of side groups, resulting in the formation of polyenes followed by chain scission, aromatization and char formation.

b) Photo-oxidative degradation

Chemical bonds in polymers can be broken by the highest energy UV waves of the solar spectrum, leading to their photodegradation\textsuperscript{28,29}. Photo-oxidative degradation is a radical-based auto-oxidative process as given in Figure 1.3\textsuperscript{30}. Chromophoric species such as carbonyl groups, hydroperoxides, unsaturation, metallic impurities such as iron and titanium, polynuclear aromatic compounds (PNA) such as anthracene, phenanthrene and naphthalene are responsible for the UV absorption\textsuperscript{31}. They are incorporated into polymers
during processing or introduced intentionally into the polymer structures either by copolymerization or by mixing with polymers.

![Auto-oxidative mechanism for all polymers](image)

**Figure 1.3. Auto-oxidative mechanism for all polymers (R- polymer chain, H- most labile hydrogen, X° - any radical, k_i- reaction rate).**

c) **Hydrolytic degradation or Bioerosion**

Hydrolysis is the most important mode of degradation of biodegradable polymers especially synthetic polymers\(^{11,32}\). Depending on the erosion mechanism degradable polymers are classified into surface (or heterogeneous) and bulk (or homogeneous) eroding materials as illustrated in Figure 1.4\(^{33}\). The way a polymer matrix erodes depends on the diffusivity of water inside the matrix (\(V_{Dif}\)), the degradation rate of the polymer’s functional groups (\(V_{Deg}\)) and the matrix dimensions. When \(V_{Deg} > V_{Dif}\); the surface erosion dominates.
when $V_{\text{Deg}} < V_{\text{Diff}}$, the bulk erosion dominates. Since bulk erosion is not confined to the surface of the device, the size of a device will remain constant for a considerable portion of time during its application. Surface eroding polymers lose material from the surface only. They get smaller but keep their original geometric shape and bulk integrity. There are several factors that influence the velocity of this degradation: the type of chemical bond, pH, copolymer composition, chain stiffness, formation of crystalline domains and water uptake are the most important. Hydrolysis can be catalyzed by acid or basic compounds and by enzymes$^{33-35}$.

![Figure 1.4. Schematic illustration of the changes a polymer matrix undergoes during surface erosion and bulk erosion.](image)

d) **Degradation due to environmental stress cracking (ESC)**

ESC is defined as the catastrophic failure of a material at a stress much lower than its ultimate strength, due to combined effects of stress and environment. The stress-cracking agents that occurred in the environment are detergents, alcohols, oils, solvents, chemicals and vapors of polar liquids.
e) **Chemical degradation**

Chemical degradation of corrosive gases and liquids can affect most polymers, except PTFE (polytetrafluoroethylene) and PEEK (polyether ether ketone). Ozone, atmospheric pollutants (such as nitric and sulfuric oxides) and acids like sulfuric, nitric and hydrochloric will attack and degrade most polymers.

f) **Mechano-chemical degradation**

Owing to their length, polymers have the ability to convert mechanical energy applied in shear into main-chain bond energy resulting in bond scission. When polymers are subjected to shear, during processing in a screw extruder, macro alkyl radicals are formed that lead to accelerated oxidation.

g) **Radiation-induced degradation**

Transfer of energy by gamma ray or electron beam irradiation onto polymer backbone results in severe degradation of the polymer. Irradiation produces free radicals, which, depending on the chemistry of the polymer, initiates degradation (e.g. polyethylene, polypropylene).

h) **Degradation due to weathering**

All plastics subjected to long-term exposure to weather degrade to different extent, depending on their composition. “Weathering” implies the action of individual; or a combination of various environmental factors on polymers: heat, light, ionizing radiation, oxygen, ozone, humidity, rain, wind, dust, bacteria, and chemical pollutants (SO\textsubscript{2} and nitric oxides etc.).
1.7.2. Biotic Degradation

In this stage the low molecular weight products formed by the abiotic degradation are consumed by microorganisms, leaving CO₂, water, and other harmless substances at the end of the metabolic process.

1.8. Test Methods and Standards for Biodegradable Polymers

American Standard Testing Methods (ASTM) and the Indian Standard Organization (ISO) have proposed several test methods to assess the biodegradability and compostability of polymers\textsuperscript{3,5,36,37}. The Biodegradable Products Institute (BPI) and the U.S. Composting Council (USCC) have launched a labeling program so that consumers can recognize and choose certified compostable products.

The use of this compostable logo signifies that the plastic products meet the ASTM D6400-99 specification for compostable plastics, as defined by the BPI

1.9. Applications of Biodegradable Polymers

For economic reasons, even for health and safety reasons, biodegradable plastic products are establishing themselves as viable alternatives in a number of important niche markets. Some of these lie in the fields of medicine, textiles,
hygiene and agriculture, as well as some specific packaging applications.

Few of the commercially available biodegradable polymers are listed in Table 1.1.

Table 1.1. Commercially available biodegradable polymers

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Composition</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dexon &amp; Medifit</td>
<td>Polyglycolic acid</td>
<td>Absorbable sutures</td>
</tr>
<tr>
<td>Vicryl</td>
<td>PLLA (8%-co-PGA (92%)</td>
<td>Absorbable sutures</td>
</tr>
<tr>
<td>PDS II</td>
<td>Poly(p-dioxanone)</td>
<td>Absorbable sutures</td>
</tr>
<tr>
<td>Lactomer</td>
<td>Poly(LLA/GA 70/30)</td>
<td>Ligating clips &amp; bone pins</td>
</tr>
<tr>
<td>Monocryl</td>
<td>Poly(GA-co-ε-CL)</td>
<td>Absorbable sutures</td>
</tr>
<tr>
<td>Maxon</td>
<td>Poly(GA-co-trimethylene carbonate)</td>
<td>Absorbable sutures</td>
</tr>
<tr>
<td>Lupron Depot</td>
<td>PLA/PLGA</td>
<td>Absorbable sutures</td>
</tr>
<tr>
<td>Zoladex</td>
<td>PLA/PLGA</td>
<td>Drug delivery products</td>
</tr>
<tr>
<td>Biopol</td>
<td>Poly(3-HB-co-3-HV)</td>
<td>Packaging &amp; Agriculture</td>
</tr>
<tr>
<td>Tone &amp; Enviroplastic-C</td>
<td>Poly(ε-caprolactone)</td>
<td>Agricultural planting Container</td>
</tr>
<tr>
<td>Bionolle</td>
<td>Poly(Butylene succinate)</td>
<td>Agriculture &amp; Packaging</td>
</tr>
<tr>
<td></td>
<td>Poly(ethylene succinate)</td>
<td>Agriculture &amp; Packaging</td>
</tr>
<tr>
<td>Aqua-NOVON &amp; Vinex</td>
<td>Starch/PVOH</td>
<td>Agricultural mulch film</td>
</tr>
<tr>
<td>BIOCETA</td>
<td>Cellulose acetate</td>
<td>Agricultural mulch film</td>
</tr>
<tr>
<td>Biomax</td>
<td>PET modified</td>
<td>Disposable items, bottles</td>
</tr>
<tr>
<td>Cereplast</td>
<td>Corn &amp; potato starch</td>
<td>Biodegradable utensils</td>
</tr>
<tr>
<td>Mater-Bi</td>
<td>Starch &amp; Vegetable oil</td>
<td>Disposable items, packaging, personal care &amp; hygiene</td>
</tr>
</tbody>
</table>
The task of making commercially available synthetic polymers "environmentally friendly", which is one of the main goals to be achieved in the field of biodegradable polymers, appears to be surmounted by lots of technical difficulties. It would, therefore, be interesting to discuss initially the cases of highly hydrophobic polymers such as polyethylene, which are the main causes for the environmental problems of the present world.

1.10. Biodegradation of Polyethylene

Plastics, made from petrochemical feed stocks are portrayed by the "green" lobby as ecologically undesirable, because they are made from fossil carbon resources and it is assumed that they are very resistant to biodegradation in the environment. It is ironical that the very physical property of durability, that have made the polyolefin so commercially successful in packaging and other agricultural applications, is a disadvantage, when the material appears in the waste stream\textsuperscript{39,40}. The environmental impact of persistent plastic wastes is growing more global concern, and alternative disposal methods are limited. Incineration may generate toxic air pollution, and satisfactory landfill sites are limited. Recycling is, at present, only viable for high cost, low volume specialty plastics\textsuperscript{41,42}. The high cost or the lack of commercially acceptable performance of fully biodegradable polymers available until recently has meant that they have never replaced traditional non-degradable plastics in the mass market\textsuperscript{43,44}. Hence, it is increasingly felt that the best solution for rectifying the
environmental pollution caused by the non-biodegradability of existing commercial plastics would be making them biodegradable.

1.10.1. Historical Perspective

The potential degradability and ultimate biodegradability of polyethylene (PE) have been started to consider in the early 1970s as specific attributes for applications in packaging and agricultural market segment. Since that time several techniques in which starch is used as a biodegradable additive have been patented\textsuperscript{45-54}. In 1978, Griffin had first presented the idea of using native or modified starch such as thermoplastic starch and plasticized starch as filler in polyethylene in order to increase the biodegradability of the resulting material\textsuperscript{55}. The incompatibility between starch and LDPE affected the mechanical properties of the blend negatively\textsuperscript{56,57}. Later Dennenberg et al.\textsuperscript{58}, Henderson et al.\textsuperscript{59} and Fanta and Doane\textsuperscript{60} have made extensive studies on the modification of starch with vinyl monomers to increase the compatibility between starch and LDPE. A percolation threshold concentration of 31.17% was established by Peanasky et al. for the continues accessibility of starch in PE–starch blends\textsuperscript{61}. Later, Goheen and Wool came to a similar conclusion in the biodegradation of PE–starch blends in soil over a period of eight months\textsuperscript{62}.

Several teams have reviewed the progresses made in the synthesis of biodegradable polyethylene\textsuperscript{3,63-66}. In a series of works, Bikiaris et al. used ethylene-co-acrylic acid (EAA) as compatibilizer in LDPE/plasticized starch (PLST) blends\textsuperscript{67-69}. They reported that EAA increases the thermal oxidative degradation of LDPE, where as PLST inhibits it. Later, the same group has
prepared LDPE/PLST blend containing PE-g-MAH copolymer as a compatibilizer\textsuperscript{70,71}. Even though, compatibilized blends have retained the tensile strength of LDPE to a great extent at high amounts of starch (up to 30 wt %), the biodegradation rate showed a decrease compared to their uncompatibilized counterparts. So far, PE-g-MAH was considered as the most effective compatibilizer between starch and polyethylene and only very small amount of MAH is needed to attain a large improvement in mechanical properties\textsuperscript{72-77}. Sastry et al. synthesized films of polyethylene–starch blends containing vegetable oil as a compatibilizer\textsuperscript{78}. Kiatkamjornwong et al. used cassava starch-g-poly(acrylic acid) prepared by \(\gamma\)-ray irradiation, which was further modified by esterification and etherification with poly(ethylene glycol) 4000 and propylene oxide respectively, for a biodegradable LDPE sheet\textsuperscript{79}.

The thermo-oxidative ageing studies done by Sharma et al. revealed that the incorporation of pro-oxidant, which consisted of metal salts (Manganese stearate) and unsaturated elastomer (SBR and ENR-50), enhanced the degradation rate of sago starch filled LLDPE composites\textsuperscript{80}. Where as Khabbaz et al. reported that starch have an inhibiting effect on the thermal degradation of LDPE containing pro-oxidant and photosensitizers\textsuperscript{31,81}. Abd El-Rehim et al. observed an accelerating effect in biodegradation of LDPE/starch blend subjected to soil burial treatment after UV-irradiation\textsuperscript{82}. These studies indicated that an exposure of the material to sunlight is necessary to stimulate the photo-oxidative action on PE, which further reduces the application scope of these polymers. Whereas, the temperature at landfill sites are suitable for the thermo-
oxidative degradation of PE, that attracts many researchers to carry out biodegradation of thermally oxidized PE to evaluate their ultimate biodegradation (e.g. mineralization) in soil\textsuperscript{39,83-87}. They observed bioassimilation of PE films after its thermo-oxidative degradation into low molar mass products. More recently, Raghavan et al.\textsuperscript{88} prepared starch/PE/poly(lactic acid) composites and Sedlarik et al.\textsuperscript{89} prepared lactose-filled composites of metallocene linear low-density polyethylene.

This brief history on the synthesis and properties of biodegradable polyethylene reveals that the existing techniques are not a satisfactory solution for the environmental problems arising from the non-biodegradability of polyethylene. Even though, in almost all reported works starch was considered as the best additive for the pre-biotic degradation of PE, it raises secondary environmental problems after starch degradation. Polyethylene modifications with monosaccharides, disaccharides and other hydrophilic molecules are actively pursued to eliminate the drawbacks of starch and minimize the environmental problems.

1.10.2. Polyethylene Modifications to Facilitate Biodegradation

The methods adopted to facilitate polyethylene disintegration and subsequent biodegradation are as follows\textsuperscript{3}:

i) Insertion of week links into vinyl polymer

Particular emphasis on this approach of insertion of ‘weak links’ on non biodegradable polymers has been placed on two types of polymer modifications: namely the insertion of functional groups in the main chain,
especially ester groups (Figure 1.5), which can be cleaved by chemical hydrolysis, and the insertion of functional groups in or on the main chain that can undergo photochemical chain-cleavage reactions, typically carbonyl groups (Figure 1.6). On irradiation with ultraviolet light, the activated ketone groups present can take part in two different types of free radical bond-breaking reactions referred to as Norrish I and Norrish II reactions (Figure 1.7).

Figure 1.5. Insertion of ester group into vinyl polymer.

Figure 1.6. Insertion of ketone group into vinyl polymer.
ii) Compounding of polymer with pro-oxidants and photosensitizers

The thermal (\(\Delta\)) and/or photolytic (\(\text{hu}\)) pre-biotic treatment, which constitutes the major route for promoting the eventual biodegradation of polyethylene, could be enhanced by using pro-oxidant additives\(^{68,69}\). The prooxidants most generally used for this purpose are divalent transition metal salts of higher aliphatic acids such as stearic acid, unsaturated elastomers as autooxidizable substances and transition metal complexes such as dithiocarbonates as photosensitizers or photoinitiators\(^{80,90,91}\). During photo- and thermo-oxidative degradation, the material degrades by a free radical chain reaction, involving the formation of hydroperoxides, carbonyl groups and finally to low molecular mass oxidation products such as carboxylic acids, alcohols, ketones, esters and low molecular mass hydrocarbons (Figure 1.3)\(^{92}\). Peroxidation and
carbonyl group formation also lead to hydrophilic surface modification friendly to microorganisms, that are thus able to bioassimilate the low molar mass oxidation products\textsuperscript{93,94}. Transition metals catalyze the hydroperoxide decomposition step of the oxidation mechanism according to the reactions given in Figure 1.8\textsuperscript{69,95}.

\[
\begin{align*}
\text{ROOH} & \rightarrow \text{Me}^{n+} \rightarrow \text{RO} \cdot + \text{Me}^{(n+1)+} + \text{OH} \\
\text{ROOH} & \rightarrow \text{Me}^{(n+1)+} \rightarrow \text{ROO} \cdot + \text{Me}^{n+} + \text{H}^+ \\
2\text{ROOH} & \rightarrow \text{Me}^{n+} / \text{Me}^{(n+1)+} \rightarrow \text{RO} \cdot + \text{ROO} \cdot + \text{H}_2\text{O}
\end{align*}
\]

\textbf{Figure 1.8. Reaction of metal catalysts with hydroperoxides.}

Unsaturated compounds, which are very prone to oxidation, generate free radicals much more readily than saturated groups. These free radicals catalyze the initiation step of LDPE degradation by transforming LDPE from RH into free radical R\textsuperscript{−}69.

\textbf{iii) Blends of biodegradable and non-biodegradable polymers}

The most frequently adopted approach to degradability design of LDPE has been the introduction of pro-degradant additives such as starch and cellulose into synthetic polymers\textsuperscript{3}. When these blends are deposited in the environment, various microorganisms consume the biodegradable component, leaving the polymer in a form full of holes. This form enables easier disintegration of the polymer into small pieces and also increases the total surface area accessible to microorganisms. Recent studies on this blends have
shown that even after starch consumption molecular weight of the polymer remain unaffected that will further evoke environmental problems.

1.10.3. Chemistry of Polyethylene Biodegradation

Biodegradation of polyethylene involve a complex interaction of abiotic and biotic mediated oxidative processes. The carboxylic acids formed by the abiotic reactions undergo \( \beta \)-oxidation, where two carbon fragments are removed from the carboxylic molecule by reaction with coenzyme A, leaving behind a still activated acid. The activated acid repeatedly participates in the same process until the whole chain is split into two carbon fragments (Figure 1.9). The two carbon fragments enter the citric acid cycle, from which carbon dioxide and water are released.

![Figure 1.9. Biotic conversion of carboxylic acids (\( \beta \)-oxidation)](image-url)
An analysis of the existing biodegradable plastics from polyethylene as discussed above indicates inadequacies in terms of technology, cost of production and extent of degradability. It appears that a comprehensive approach is required to attain the realistic goals in the development of biodegradable polymers. In this connection, it would be interesting to look for biodegradable polymers from renewable resources.

1.11. Polylactide and Its Copolymers

1.11.1. Polylactide a Dominating Biopolymer

Polylactides (PLA) are considered as the most versatile material among biodegradable polymers because of its inherent biodegradability, biocompatibility and the easy availability from renewable agricultural sources\textsuperscript{102}. These attributes make them a leading candidate in biomedical and pharmaceutical industries as a resorbable implant material, wound closure, bone fixation devices and a vehicle for controlled drug delivery\textsuperscript{103-105}. It is also used as an environment friendly plastic, although their market is still limited due to its higher cost and slow degradation rate as compared to the waste accumulation rate\textsuperscript{106,107}. However, their clinical applications are sometimes affected by the high hydrophobic and consequent poor water uptake, which results in a slow hydrolytic degradation rate\textsuperscript{35,108}. Another potential disadvantage is the complications resulting from the accumulation of lactic acid produced in the process of PLA degradation, and its poor processability\textsuperscript{109,110}. Ultra high molecular weight is required for processing PLA into strong fibers. PLA is belonging to the group of thermally less stable polymers and have poor
physical properties and high cost of production\textsuperscript{111}. Copolymerization of lactide with other comonomers and/or polymers is used to modify the properties of PLA and to control its degradation behaviour suitable for the specific applications in the field.

1.11.2. PLA based Copolymers: A Literature Review

In 1932, Carothers demonstrated the synthesis of poly(L-lactide) (PLLA) by ring opening polymerization of lactide\textsuperscript{112}. Since that time PLA has been used as a bioabsorbable material in the medical and pharmaceutical fields\textsuperscript{113-116}. However, the application scope of PLA is limited because of the certain weaknesses mentioned above. Copolymerization of L-lactide with other monomers has been recognized as an important tool to modify PLLA suitable for specific applications in the field. The frequently employed comonomers are D-lactide\textsuperscript{117}, meso-lactide\textsuperscript{118-121}, glycolide\textsuperscript{122-125}, caprolactone (\epsilon-CL)\textsuperscript{126} and trimethylene carbonate (TMC)\textsuperscript{127}. Grijpma and Pennings have done a detailed study on the synthesis, thermal properties and hydrolytic degradation of these copolymers\textsuperscript{127}. Glycolide copolymers are much more hydrophilic than PLLA, while \epsilon-CL and TMC reduce the glass transition temperature of the L-lactide copolymer. All comonomers decrease the crystallinity of the polylactide and provide optimal mechanical properties to the materials.

Another approach for increasing the hydrophilicity and degradation rate of polylactide was the copolymerization with other polymers such as polyethylene glycol\textsuperscript{128-135} and chitosan\textsuperscript{136-140}. In 1998, Kim et al. prepared biodegradable nanospheres composed of methoxy poly(ethylene glycol) and
D,L-lactide block copolymers as novel drug carriers. In 2001, Otsuka et al. gave a review article regarding the self assembly of poly(ethylene glycol)-PLA block copolymers for biomedical applications.

Albertsson et al. prepared a pH sensitive physically cross linked hydrogel by grafting D,L-lactic acid onto amino groups in chitosan without using a catalyst. Later Dutta et al. reported that the molecular mechanism of gelation involves interaction between chitosan and lactic acid. Yao et al. reported the in vitro fibroblast static cultivation on a cytocompatible poly (chitosan-g-L-lactic acid) film and the cell growth rate on the copolymer film was found to be much faster than that of the chitosan film. In another work, Liu et al. have reported the synthesis of a brush like copolymer of polylactide grafted onto chitosan. Later, Wu et al. studied the amphiphilic properties of a graft copolymer of water-soluble chitosan and polylactide prepared by using triethyl amine as catalyst. In 2005, Peesan et al. prepared hexanoyl chitosan/PLA blend films and in 2006, Wan et al. prepared a biodegradable polylactide/chitosan blend film. The biodegradability of these chitosan/polylactide graft copolymers was, however, not studied in these works.

The introduction of functional groups in polylactide for the modification of its properties has been investigated since 1990s. Barrera et al. synthesized a copolymer of poly(lactic acid-co-lysine) containing lysine residues. The free amino group in the lysine residue was used to chemically attach a biologically active peptide GRGDY. Gonsalves et al. and Ouchi et al. reported the
introduction of hydroxyl and carboxylic acid groups on the surface of polylactide by copolymerization with the amino acids and aspartic acid (P(Lac-Asp)), respectively. Recently, Wang and coworkers synthesized a series of polylactide- polyurethanes (PLAUs) having the property of shape-recovery temperature near to the body temperature from poly(L-lactide) diols, hexamethylene diisocyanate and 1,4-butanediol\textsuperscript{151}.

In 1992 Simone et al.\textsuperscript{152} and Castaldo et al.\textsuperscript{153} introduced the idea of random multiblock PEAs containing poly(L-lactide ) blocks as hydrolytically degradable segments. They reported that the presence of amide functions in the polymer chain might lead to better physical properties than aliphatic polyesters usually have. Qian et al. reported a decrease in the degradation rate of PEAs with increase of amide content, macromolecular weight and thickness of the test samples, and increase with incubation temperature and pH of the degradation medium\textsuperscript{154-158}. Angelo et al. prepared poly(ether-ester-amide)s based on poly(L,L-lactide) macromer for the delivery of bioactive compounds\textsuperscript{159}. They reported that an enhancement of biodegradability of PEAs could be achieved by the incorporation of flexible hydrophilic oligo(ethylene glycol) segments into the main chain.

1.1.3. Synthetic Methods of PLA

Lactic acid polymers are most commonly prepared by ring opening polymerization (ROP) of lactides by means of cationic, anionic, enzymatic and co-ordination insertion mechanisms\textsuperscript{102,160,161}. Extremely strong acids or carbenium ion donors are capable of initiating a cationic polymerization of
lactides. The anionic polymerization of lactides is initiated by alkali metal alkoxides, phenoxides and carboxylates. Racemization is an unavoidable side reaction of both cationic and anionic polymerizations.

Co-ordination insertion mechanism is based on metal alkoxides having a covalent metal-oxygen bond and the character of weak Lewis acids. The lactide plays temporarily the role of a ligand co-ordinated with the metal atom via the carbonyl O-atom (Figure 1.10). This co-ordination enhances the electrophilicity of the CO-group and the nucleophilicity of OR-group, so that an "insertion" of the lactone into the metal-oxygen bond may occur. Typical initiators of this mechanism are the alkoxides of Mg, Al, Zn, Sn, Zr and Ti. An advantage of the covalent initiators is the easy control of the molecular weights via the monomer/initiator ratio. Furthermore, the risk of side reactions is much lower compared to ionic initiators, so that much higher molecular weights can be obtained. Moreover, the covalent nature of these initiators significantly reduces the risk of racemization even at high temperatures.

Enzymatic polymerization is an eco-friendly process of polymer synthesis and is based on using easily renewable resources as starting materials. Enzyme catalyzed polymerizations have several advantages over conventional chemical methods: (a) mild reaction conditions, i.e., temperature, pressure, pH and absence of organic solvents, (b) high enantio and regioselectivity and (c) recyclability of catalysts.
1.11.4. Properties of PLA

The presence of asymmetric carbon atoms generates structural particularities, which make lactic acid-derived polymers rather special when compared with other polymers. Because of the chirality of the lactyl unit, lactide exists in three diastereoisomeric forms, i.e. L-lactide, D-lactide and meso-lactide, the latter containing a L-lactyl unit and a D-lactyl one in the ring. An equimolar ratio of L- and D-lactide is referred to as racemic D,L-lactide\(^{35}\). The thermal, mechanical and biodegradation properties of lactic acid polymers are known to depend on the choice and distribution of stereoisomers within the polymer chains. High purity L- and D-lactides form stereoregular isotactic poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA), respectively. These are

Figure 1.10. Ring opening polymerization of lactides.
semicrystalline polymers with a high melting point \( T_m \sim 180^\circ C \) and a glass transition temperature in the range of 55-60\(^\circ\)C. PLLA can be used as a hard and tough engineering plastic for a broad variety of applications, for instance, in medicine for the internal fixation of bone fractures. The meso- and D,L-lactide, on the other hand, form atactic poly(D,L-lactide) (PDLLA), which are amorphous. It can be used for the production of transparent films, glues and for drug delivery applications. The presence of \(-CH_3\) side groups imparts a hydrophobic nature to PLLA. The steric shielding effect of the ester groups by methyl substituents, reduces the hydrolytic degradation rate of PLLA on comparing with that of other polylactones\(^1\).

1.11.5. Mechanism of Degradation of PLA

The mechanism of hydrolytic degradation of PLA polymers is quite unusual. In general, a bulk erosion mechanism has been considered as the main degradation pathway for PLA and its copolymers such as PLGA; random chain scission on the linkage of ester bonds in the polymer backbone proceeds homogeneously throughout the device\(^1^0^3\). Recently, it was reported that massive devices (>1mm thick) of PDLA, PLA and PLGA degrade via a heterogeneous mechanism i.e. the degradation proceeds more rapidly in the center than at the surface. This was attributed to the autocatalytic action of the carboxylic acid end groups of degrading products which were trapped in the matrix\(^1^6^2,1^6^3\). If the surrounding tissues cannot eliminate the acid by products of a rapidly degrading implant, then an inflammatory or toxic response may result\(^3^5,1^6^4\).
Recently, there has been an increasing number of reports on the enzymatic hydrolysis of PLA\textsuperscript{165-169}. Enzymatic hydrolysis of PLA proceeds mainly via the surface erosion mechanism and the surface area of polymeric materials would have a great influence on the enzymatic degradation. Abiotic hydrolysis is the initial stage of microbial degradation of PLA in nature. The released degradation products could be consumed by microorganisms\textsuperscript{106,170}.

Although PLA has many admirable properties, it is shown that it has serious disadvantages that can be overcome by materials copolymerization techniques. In this connection copolymerization with chitosan and cycloaliphatic amides appears to be gaining promise.

1.12. Chitosan as a Biomaterial

There is a growing interest in utilizing renewable resources as a functional biopolymer in a broad range of scientific areas such as biomedical, agricultural, food, cosmetics, wastewater management and environmental field\textsuperscript{101}. Among them, chitosan, a unique amino polysaccharide has attained great interest because of its special structure, properties and its inexpensive abundant resources\textsuperscript{171-175}. The specific properties of chitosan such as biocompatibility, biodegradability, bioactivity, low immunogenicity and multifunctionality increase its potential as a beneficial material for various applications in biomedical field\textsuperscript{176-188}. Although, the area of possible applications is broad, a break-through has not yet been achieved. This is related to the insufficient property-profiles of chitosan: insolubility in water and most organic solvents, slow \textit{in vivo} degradation and the unsatisfactory mechanical
and processing properties. Intensive research and a concentration of effort will be needed to improve the properties of the biopolymer in bioplastic and biomedical applications. Chemical derivatisation of chitosan with various types of branches was reported as one of the strategies for tailor-made applications of chitosan in biomedical field.

1.12.1. Structure and Properties of Chitosan

Chitosan is a linear amino polysaccharide composed of β-(1,4)-linked 2-amino-2-deoxy-D-glucopyranose (GlcN, D-unit) and 2-acetamido-2-deoxy-D-glucopyranose (GlcNAc, A-unit). This polycationic biopolymer is generally obtained by alkaline deacetylation of chitin (β-(1-4)-linked 2-acetamido-2-deoxy-D-glucopyranose (GlcNAc)), which is the main component of the exoskeleton of crustaceans, such as crabs and shrimps. Chitin, in fact, is the second abundant polysaccharide next to cellulose, making chitosan a plentiful and relatively inexpensive product. The main parameters influencing the characteristics of chitosan are its molecular weight and its degree of acetylation (DA). Moreover, DA influences the physicochemical properties and biological properties of chitosan. Chitosan can be digested in vivo by lysozomal enzymes according to the amount of N-acetyl groups and their distribution in the backbone. The aminosugars resulted from the degradation of chitosan can be incorporated into glycosaminoglycans and glycoproteins metabolic pathways, or excreted. It is a haemostatic agent, which presents antithrombogenic properties. Since chitosan provided bacteriostatic and fungistatic activities it appears to be a good candidate for wound dressing.
and for soft tissue regeneration\textsuperscript{198-200}. Chitosan in hydrogel form have been considered to be advantageous in their application as a wound dressing material, in controlled drug delivery systems and in tissue engineering\textsuperscript{179,201-204}. Since chitosan has a capacity of forming film it has been suggested as a biopolymer of choice for the development of contact lens (soft and hard contact lenses) and artificial kidney membranes\textsuperscript{183}. Chitosan is insoluble in neutral water and soluble in dilute acids when the degree of acetylation is lower than 0.5 (pKa value is 6.5) and it behaves as a cationic polyelectrolyte\textsuperscript{205-207}.

1.12.2. Chemical Modifications of Chitosan

Chemical derivatisation of chitosan with hydrophilic moieties such as carboxymethylation\textsuperscript{208,209}, quaternarization\textsuperscript{210}, acetylation\textsuperscript{211} etc. was reported as one of the methods to improve the solubility of chitosan in water. Since the chemical modifications change the fundamental skeleton of chitosan, the modified chitosan loose the original physicochemical and biochemical activities. Thus, as an alternative strategy to improve the water solubility but at the same time keeping the fundamental skeleton of chitosan intact, the covalent conjugation of hydrophilic polymers such as polyethylene glycol is preferable\textsuperscript{212-217}.

Introduction of carbohydrate branches onto chitosan as a branched polysaccharide analogue is another interesting modification to induce new chemical and biological functions\textsuperscript{192,218,219}. Since the specific recognition of cell, virus, and bacteria by sugars has been discovered, this modification has generally been used to introduce cell-specific sugars into chitosan.
In order to solve the problem of insolubility in organic solvents, some chemical modifications to introduce hydrophobic nature to chitosan such as phthaloylation, tosylation and acylation reactions were done\textsuperscript{193,220}. The introduction of hydrophobic branches generally endows the polymers with a better soluble range than chitosan itself, and also with other new physico-chemical properties such as the formation of some polymeric assemblies including gels, polymeric vesicles, Langmuir–Blodgett films and liquid crystals. Recently, there has been a growing interest in grafting vinyl monomers onto chitosan for biomedical applications\textsuperscript{221,222}. The enzymatic approaches to modification of chitin and chitosan is interesting, owing to its specificity and environmental impact compared with chemical modifications\textsuperscript{184,194}.

1.13. Significance of Aliphatic Poly(ester amide)s

Aliphatic poly(ester amide)s (PEAs) has been the object of extensive investigation during the last few decades as an emerging class of biodegradable condensation copolymers. Aliphatic polyesters have poor thermal, mechanical and processing properties. Aliphatic polyamides, on the other hand, have better thermal and mechanical properties than aliphatic polyesters, but their degradation rate is too low to classify them as biodegradable polymers\textsuperscript{223,224}. Therefore, by combining the favorable properties of these two classes of polymers, it could be possible to produce new polymeric materials possessing not only good biodegradability but also good materials and processing properties. Another advantage of PEAs over other biodegradable polymers is
that they can be suitably tailored to the needs of their applications by varying the nature of the monomers and/or their composition and architecture\textsuperscript{225}. Recently, cycloaliphatic systems are considered as a better alternative to aliphatic counterparts in poly(ester amide)s\textsuperscript{226-229}. This is because the conformational restrictions arising from the rigidity of cyclic ring structures largely influence the thermal and physical properties of the copolymers than their homopolymers.

1.13.1. Structure -Property Relation of Poly(ester amide)s

Poly(ester amide)s are a class of biodegradable condensation polymers having regular enchainment of ester and amide groups as the integral part of polymer chain\textsuperscript{230}. According to the distribution law of ester and amide groups along the chain, PEAs can be grouped into three fundamental classes: alternating copolymers, random copolymers and block or segmented copolymers\textsuperscript{231-233}. Two types of hydrogen bonds are involved in PEAs, amide-amide and amide-ester hydrogen bonds\textsuperscript{234}. Hydrogen bonding has a strong influence on the biodegradability of PEAs: increased hydrogen bonding leads to lower biodegradability\textsuperscript{235}. Meanwhile, the chemical structure, crystallinity degree, chain flexibility and a balance of hydrophilic and hydrophobic properties also affect the enzymatic degradation of PEAs. The ester component, in fact, reduces the crystallinity of polyamide segments and increases the chain flexibility of PEAs needed to fit into the active sites of the enzymes. Since amide groups are polar, their incorporation into the ester main chain leads to an increase of hydrophilicity\textsuperscript{236}. The enhanced hydrophilicity increases the amount
of water sorption in the amorphous region followed by degradation. The hydrolytic degradation rate of PEAs are determined by ester moiety content, since $\lambda_{\text{ester}}$ is much larger than $\lambda_{\text{amide}}$ (Figure 1.11)\textsuperscript{34,158}. So the chemical composition must have a great effect on the biodegradation of these copolymers\textsuperscript{237-239}.

![Figure 1.11. Hydrolytic degradation of PEAs.](image)

Enhanced degradability of poly(ester amide)s could be achieved by incorporating into the chain both hydrophilic, flexible segments consisting of short sequences of ethylene glycol groups and/or linkages built up by $\alpha$-amino acid sequences, that can be degraded by specific enzymes\textsuperscript{240}. Therefore, the combination of good physical properties, biocompatibility and controlled degradability makes PEAs a valuable material for biomedical applications as absorbable sutures or temporary implants and drug delivery systems\textsuperscript{241-248}.

### 1.14. Scope and Objectives of the Present Work

It can be noted from the preceding discussions that the biodegradable polymers for short time applications have attracted much interest all over the world in different sectors such as surgery, pharmacology, agriculture and the
environment. The reason behind this growing interest is the incompatibility of the polymeric waste with the environment where they are disposed after the usage. The recovery of polymeric waste as a solution to this problem is not easy or feasible, like in surgery for obvious reasons, or in the environment in the case of litter. The development of novel biodegradable polymers satisfying the requirement of degradability, compatibility with the disposed environment and the release of low-toxicity degradation products are the ultimate solution to these issues. An analysis of the existing biodegradable plastics indicates inadequacies in terms of either technology or cost of production especially in the case of applications in environmental pollution. So, there is a need to look for novel methods for introducing biodegradability in existing polymers for use in the environmental areas. Alternately, one can consider modifying suitably the natural polymers obtained from the renewable resources, by tailoring their properties by altering the composition and structure with a view to solving some of the existing problems associated with them for the synthesize of new biodegradable polymers. The present work, therefore, has adopted a dual strategy of (1) modification of polyethylene, a commodity plastic largely used in packaging materials, using a novel technique for anchoring mono/disaccharides, which being carbohydrates can act as a nutrient source for microorganisms to enhance biodegradation and (2) design of copolymers based on polylactide, using either chitosan or cycloaliphatic amide segments, which are gaining importance as a polymer of great opportunities.
The mass production and consumption of polyethylene for the various applications in packaging and agricultural fields, has resulted in mounding global concerns over the environmental consequences of such materials, when they enter the waste stream after their intended uses. The degradable polymers available until recently have inferior physical properties in terms of strength and dimensional stability and most of them are very expensive and are technically difficult to process. These inadequacies persisting for the eco-friendly applications of the existing biodegradable plastics indicate the need for novel approaches for the design of the material. So, the strategy employed here for minimizing the environmental pollution of polyethylene was to increase its biodegradability by oxidation and grafting of simple sugars such as monosaccharides onto polyethylene chain ends. The increased hydrophilicity and the easy accessibility of chain ends will attract microbes towards polyethylene, leading to fast degradation. Anchoring of simple sugars instead of starch on polyethylene can reduce the negative effects on physical properties observed in the case of polysaccharide grafting.

The world scenario of biodegradable polymers shows that the polymeric materials generated from renewable resources are growing in interest due to their inherent biodegradability, biocompatibility and easy availability. Among these biopolymers, polylactides are the leading candidates for various applications in biomedical field and in the environment. Due to the high capital cost and slow degradation rate as compared to the waste accumulation rate, the focus of PLA has been mainly on the biomedical field. However, certain
limitations of PLA such as low hydrophilicity and degradation rate, poor soft tissue compatibility, low thermal and physical properties, lack of processability, high cost of production limits their wide utilization. These limitations of PLA along with its increased use in medicine generated the necessity in search for new materials by copolymerization with suitable monomers and/or polymers, so that some of the problems associated with them can be solved for wider applications. Graft copolymerization of lactide onto chitosan was one of the strategies adopted to explore their full potential and control the functions suitable for the applications in biomedical and pharmaceutical fields. The interest in chitosan stems from the fact that they are the only amino polysaccharide present in the nature. Further more, they are biocompatible, biodegradable, have antimicrobial activity, low immunogenecity and more over low production cost. Controlled solvation and degradation could be achieved by controlling the ratio of chitosan:L-lactide in the graft copolymer to obtain an optimum hydrophobic-hydrophilic balance. In addition, the alkaleness of chitosan can neutralize the acidic degradation products of polylactide, so that the local toxicity due to the acid byproducts can thus be alleviated to get better biocompatibility. Again a controlled degradability of chitosan by various enzymes present in the human body could be achieved after lactide grafting. Another strategy employed for the synthesis of a new biodegradable copolymer based on PLA was: copolymerization with cycloaliphatic amide segments, so that the resulting poly(ester amide)s would be expected to compliment the defects of PLA by the formation of
intramolecular and intermolecular hydrogen bonds between ester and amide groups. The combination of the favorable properties of both classes of materials may lead to new materials that combine good end-use and processing properties and biodegradability. The advantage of cycloaliphatic structures are that the incorporation of these rings in the amide segments increases the thermal properties of PEAs even at relatively low molecular weight than that of its linear aliphatic counter parts. Again, as cycloaliphatic systems are nontoxic the synthesized PEAs should be biocompatible.

Accordingly the objectives of the present work can be formulated as:

(1) Effect of different oxidizing agents on the functionalization of polyethylene.

(2) Synthesis and biodegradation studies of polyethylene modified with sugar grafting, using ceric ammonium nitrate as an oxidant and initiator by a "one pot" melt phase reaction in Brabender plasti-corder.

(3) Synthesis and characterization of chitosan/oligoL-lactide graft copolymers and study of the effect of hydrophobic side chains on their physico-chemical properties and biodegradability.

(4) Synthesis and biodegradation studies of random multiblock poly(ester amide)s containing poly(L-lactide) macromer and cycloaliphatic amide segments.
1.6. References

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