Synthetic polymers are considered to be an invaluable gift of modern sciences and technology to mankind. They have occupied a major part of our life with their wide range of applications in diverse fields such as packaging, agriculture, food, consumer products, medical appliances, building materials, industry, aerospace materials etc. However, the positive properties of these polymers such as resistance to chemical, physical and biological degradation present disposal problems when their usefulness ceases. In this respect, polymeric materials satisfying the requirement of biodegradability, biocompatibility and release of low-toxicity degradation products have become important. The design of biodegradable polymers requires application of modern approaches to obtain realistic goals. In the present work, multiple approaches are adopted to identify methods to introduce biodegradability in polymeric materials and to improve upon the performance of some existing biodegradable polymers. In the first approach, novel methods of chemical modification of existing non-biodegradable polymers are attempted, taking polyethylene as a model polymer used worldwide as a commodity plastic. Second approach adopted pertains to the design of novel biodegradable
polymers based on renewable resources such as polylactides, which are gaining importance as biodegradable polymers of great opportunities.

(A) The environmental pollution caused by the non-biodegradability of polyethylene used in packaging and agricultural applications has become a serious problem causing concern throughout the world. As, there are many inadequacies persisting for the eco-friendly applications of the existing biodegradable plastics, attempts have been made to solve these problems by incorporating biodegradability into polyethylene through modifications of their chemical structure. Polyethylene could 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.

(B) Polylactides (PLA), which are the leading candidates among the recently developed biodegradable polymers from renewable resources are gaining importance, owing to their inherent biodegradability, biocompatibility and easy availability. There are, however, some limitations such as low thermal and physical properties, low hydrophilicity and degradation rate, poor soft tissue compatibility, poor processability and high cost of production in their wide utilization. Copolymerization of lactide with appropriate comonomers and/or polymers is expected to solve some of these problems and to get new polymeric materials with unique properties for specific applications in the field. (B1) Graft copolymerization of lactide onto chitosan, an aminopolysaccharide present in the nature, might deliver graft copolymers with controlled solvation and degradation. The natural abundance of chitosan will reduce the overall cost
of the copolymer. (B2) 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. 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, since cycloaliphatic systems are nontoxic, the synthesized PEAs should be biocompatible. So, the objectives of the present work were:

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.
Chapter 1 out of five chapters gave a brief review on biodegradable polymers giving emphasis to polyethylene, polylactide, chitosan and aliphatic poly(ester amid)s.

Chapter 2 described the functionalization of LDPE under different oxidizing conditions and the modification of oxidized LDPE by the grafting of highly hydrophilic monomers such as glucose to enhance the biodegradability of LDPE. Biodegradation studies in composting conditions and in a pure soil bacterial culture *Pseudomonas sp.* was also included. In the present work, mainly three methodologies for oxidation (in solution, in melt and in solid state) were compared to study the effect of various oxidizing agents on LDPE. Oxidation of LDPE in presence of KMnO$_4$/H$_2$O/H$_2$SO$_4$ system, K$_2$Cr$_2$O$_7$/H$_2$O/H$_2$SO$_4$ system and UV irradiation resulted in the formation of -COOH groups on LDPE backbone. It was found that only ketonic carbonyl groups are formed when CAN is used as an oxidant. Grafting of glucose onto carboxyl functionalized LDPE (LDPE-COOH) was done by acid chloride method. Since this method was found to be cumbersome, grafting of glucose onto ketonic carbonyl functionalized LDPE (OxiLDPE) was done by a novel “one pot” melt phase reaction in presence of CAN in Brabender plasti-corder at high shear conditions. The present method of reactive grafting in melt avoids the use of any acid and water in the grafting reaction in presence of CAN for the first time. CAN played a dual role both as an oxidant as well as an initiator in the grafting of glucose onto LDPE. Glucose underwent a ring opening reaction to get 4-O-hydroxymethyl D- arabinose (Sugar) end-capped LDPE (Su-g-
LDPE) in presence of CAN. The ring opening of glucose during reactive grafting in presence of CAN was confirmed by FTIR spectroscopy. FTIR spectra of Su-g-LDPE showed complete vanishing of peaks corresponding to cyclic ether structure of glucose at 1235, 910 and 800 cm\(^{-1}\) and the appearance of new peaks corresponding to aliphatic ether structure at 1146 and 940 cm\(^{-1}\). The mechanical properties of Su-g-LDPE (Tensile strength: 7.82 MPa) were observed to be comparable with that of LDPE alone (Tensile strength: 8.46 MPa) at higher grafting percentages. This may be attributed to the strong intermolecular interactions such as hydrogen bonding between LDPE chains through their grafted sugar moieties at higher grafting percentages. This was further confirmed by WAXD measurements, which showed a broad peak at 2.23° 2θ (d spacing 39.6 Å) compared to that of LDPE, indicating the long range ordering in Su-g-LDPE resulted by the hydrogen bonding interactions between LDPE chains through grafted sugar moieties. Though LDPE is highly hydrophobic, Su-g-LDPE showed a water absorption of 5.2%, indicating hydrophilic nature of the grafted LDPE that was further confirmed by observing a decrease in contact angle of LDPE from
\(\Theta_s = 93^\circ\) to \(\Theta_d = 74^\circ\) after grafting. During biodegradation studies in compost soil environment a decrease in ketone carbonyl index (CI \((v_{1719}/v_{1465})\)) of Su-g-LDPE with time of degradation was observed, indicating the initiation of LDPE chain degradation. A stepwise cleavage of LDPE from the chain ends can be envisaged with microbes consuming the sugar units on the surface of Su-g-LDPE and further oxidizing the ketonic carbonyl to carboxylic acid. The microbial degradation resulted in the increase in crystallinity and decrease in viscosity of the degraded samples. SEM showed surface erosion caused by microbial degradation on Su-g-LDPE. In vitro degradation of Su-g-LDPE studied by monitoring the increase in optical density of the media indicating the growth of microbes using grafted sugar as a nutrient source. The increased hydrophilicity and sugar capped chain ends in the Su-g-LDPE might have facilitated the enhanced degradation observed in the present case. These results suggested that sugar, grafted onto LDPE provided not only a condition suitable for the growth of microorganisms but also a favorable environment for the action of microbes on polyethylene.
Chapter 3 dealt with the graft copolymerization of L-lactide (LLA) onto chitosan (CS) to solve some of the inherent problems of these renewable resource based polymers for their wide utilization in biomedical and pharmaceutical fields. The effect of hydrophobic side chains on the physicochemical properties and biodegradability of chitosan derivatives were described in detail. Chitosan/oligoL-lactide (CL) graft copolymers were synthesized in DMSO at 90°C in presence of Ti(OBu)$_4$ as ring opening catalyst. Grafting percentage and the molar composition of lactide in graft copolymer increased with increase of lactide content in the feed molar ratio. FTIR and $^1$H NMR studies showed the formation of oligoL-lactide (OLLA) as side chain in the graft copolymer. The disturbance in hydrogen bonding and crystallinity of chitosan brought about by LLA grafting resulted in the formation of amorphous copolymer. The DSC and TGA thermograms of grafted copolymers showed a higher evaporation temperature for the bound water than that in chitosan. Grafting of hydrophobic side chains resulted in the decrease of chitosan crystallinity by loosening the hydrogen bonds and increasing the number of free hydrophilic hydroxyl groups and amino groups.
of chitosan, which in turn can hold water molecules more strongly. The graft copolymers were converted to hydrogels on exposure to deionized water. This property is of special interest in biomedical applications such as wound dressing and in controlled drug delivery systems. At higher grafting percentages due to the self-assembling of longer OLLA side chains by the hydrogen bonding and dipole dipole interactions, the hydrophobic nature of the side chains became dominant, which resulted in the lower swelling of graft copolymers at higher grafting percentages. A decrease in hydrolytic degradation was observed with increase of lactide content in CL graft copolymers. *In vitro* enzymatic degradation was studied by using two types of enzymes, proteolytic enzyme papain from *Carica Papaya* and esterase enzyme lipase from *Candida Cylindracea*. Even though, CL graft copolymers were susceptible to both papain and lipase, the highly grafted chitosan was less susceptible to hydrolysis in papain medium whereas it was more prone to hydrolysis in lipase than the original chitosan and OLLA. The higher susceptibility of CL graft copolymers towards lipase compared to that of chitosan (showed no significant degradation in lipase) indicated that the chitosan segment consisting of glucosamine residues is not accessible to the lipase active site and the random distribution of OLLA side chains is at least required to be adsorbed to the active sites of the lipase. This was further
confirmed by the $^1$H NMR spectra of degraded CL-30 graft copolymer that showed almost complete vanishing of peaks corresponding to OLLA side chains grafted onto CS. As lipase is one of the main enzymes present in the human body, the higher susceptibility of CL graft copolymers towards lipase than that of chitosan and OLLA would increase its potential in biomedical field. These results indicated that the physico-chemical properties and the rate of degradation of graft copolymers as a biomaterial could be controlled by adjusting the amount of LLA in the CL graft copolymers.

Chapter 4 presented the synthesis and characterization of random multiblock poly(ester amide)s containing PLLA macromer and cycloaliphatic amide segments. Detailed in vitro biodegradation studies of PEAs using lipase from Candida Cylindracea were made. Poly(ester amide)s (PEA 1, PEA 2 & PEA 3) with different sequence length of polyamide segments were prepared from the preformed polyester segments (derived from telechelic oligomers of PLLA), 1,3-cyclohexylbis(methylamine) and sebacoylchloride by the “two-step” interfacial polycondensation method. PEA 1 and PEA 2 showed a single diffraction signal at 20.8° 2θ and a single melting transition at 166 and 164°C respectively, indicating an amide-adjacent crystallization of copolymers. In PEA 3, the diffraction signals (16.7 and 18.8° 2θ) and melting transition (101°C) characteristic of PLLA macromer were also appeared. This was attributed to the development of a crystalline structure of
the PLLA type at higher ester content, revealing the blocky nature of PEAs. The random nature of PEAs was confirmed by the appearance of single $T_g$ values. Even though the prepared PEAs were in low molecular weight (0.35 to 0.44 dL/g), they showed a thermal stability up to a temperature of 230°C. This may be attributed to the presence of strong hydrogen bond interactions between ester and amide groups and the presence of rigid cyclic ring structures in the polymer backbone. Since no evidence of thermal decomposition was observed below a temperature of 200°C, they can be processed from the melt state. All PEAs were susceptible to lipase promoted degradation and the rate of degradation increased with increase in PLLA content. Spectroscopic investigations and thermal analysis of degraded products showed the breakage of ester linkages. The results indicated that by the incorporation of cycloaliphatic amide segments onto the PLLA macromer it could be possible to synthesize PEAs having good thermal properties and biodegradability at the lower molecular weight that would increase its potential in the biomedical applications.

**Future Directions:**

The design of biodegradable polymers with tailor made physico-chemical properties and biodegradability have opened enormous research interest because of the serious problems raised by the incompatibility of the polymeric wastes with the environment. Modification of polyethylene by grafting of highly hydrophilic sugar moieties described in Chapter 2 were interesting because of the improved mechanical properties (compared to that of
LDPE/starch blend) and enhanced degradability of Su-g-LDPE that will contribute to minimize the environmental pollution caused by the non-biodegradability of polyethylene. The work could be extended to various other sugars and oligomers to obtain a comparative data on their behaviour. The “one shoot” process provides the films directly and so, the cost of production can be brought down.

Chitosan/oligoL-lactide graft copolymers given in Chapter 3 were capable of forming hydrogels in neutral water and have higher susceptibility in lipase media. The variation of these properties with lactide content in graft copolymer would increase its potential in biomedical and pharmaceutical fields. The preparation and characterization of the gels and their biomedical applications will form an interesting piece of work.

Copolymerization of PLLA with cycloaliphatic amide segments described in Chapter 4 were interesting because of their higher thermal stability at lower molecular weight and biodegradability that would expected to increase its potential in biomedical field as a better alternative to PLLA. Polymers discussed in Chapter 4 require some more modifications to improve the degradability of polyamide segments to be considered as a potential material for biomedical applications. As the degradability of polyamide segments are low due to the rigidity of cycloaliphatic structure, it would be worthwhile to study the biodegradability of PEAs by incorporating flexible hydrophilic oligo(ethylene glycol) segments or enzymatic recognition sites such as acids into the main chain.