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Recent Advances in Biodegradable Polymers

Sunil Dhamaniya[a], Virendrakumar Gupta[a,*] and Rucha Kakatkar[b]

[a]*Polymer Synthesis & Catalysis, Reliance Research & Development Centre, Reliance Industries Limited, Ghansoli 400701, Navi Mumbai, India*

[b]*Department of Fibres & Textile Processing Technology, Institute of Chemical Technology, Mumbai, India*

Abstract: Biodegradable polymers are important as an alternative to conventional non-degradable polymers for sustainable eco-system. The recent trends indicate that the new developments in biodegradable polymers focus on novel polymer systems that can cater the need of biomedical and packaging applications in-terms of performance and economics. The new interest is rapidly moving toward reducing carbon footprint through utilization of carbon dioxide and developing new methods of manufacturing such as 3D printing for specific purposes. This review focus on the present state-of-art and recent developments in biodegradable polymers covering their sources, synthetic methodologies, salient properties, degradation patterns, polymer blends and nanocomposites. As well as biodegradable polymers as a 3D printing material and the use of carbon dioxide as a renewable raw material for biomedical and packaging applications.

Keywords: Biodegradable polymers, polymer blends, 3D printing, carbon dioxide, renewable resources.

1. INTRODUCTION

Conventional plastics have a variety of applications in different forms and have always been the focus of major industrial and research areas. In the present scenario, these non-degradable conventional polymers have become a serious environmental concern because of their high durability. One of the main challenges of polymer research is to substitute existing non-degradable polymers with degradable polymers having comparable mechanical properties. Poly(lactide) (PLA) is certainly the most promising biodegradable polymer today, has become a commercial reality and is produced at world-scale plants. Its mechanical properties and cost-performance balance have made it suitable for applications like packaging, agriculture and disposable molded articles. Biodegradable polymers can provide a solution to managing packaging waste, textile waste and also holds great promise in biomedical and pharmaceutical applications, since they combine the features of biocompatibility and biodegradability. For example, aliphatic polyesters, such as polylactic acid (PLA), poly(glycolide) (PGA), poly (β-hydroxy butyrate) (PHB), poly(ε-capolactone) etc. are extensively used in biomedical and pharmaceutical applications. The diversity of the application of biodegradable polymers gives the impetus for development of a wide range of new biomaterials [1-12].

As an alternative to conventional non-degradable polymers the interest has increased in developing and exploring more suitable biodegradable polymers. Firstly, non-biodegradable polymers are not environment benign. Secondly, governmental regulations and consumer appeal to eco-friendly materials have encouraged the use of biodegradable polymers. The biodegradable polymers could be sourced from nature or laboratory. The natural based biodegradable polymers such as cellulose, starch, chitin, chitosan, find applications in various fields due to their biocompatibility, lower cost, sustainability, availability and biodegradability [13-20].

The chemical synthesis of biodegradable polymers is an attractive approach to prepare novel biopolymers. Synthetic biopolymers have advantage over naturally produced biopolymers because chemical modification of later is difficult and former can be easily tailored. Apart from this, biodegradable polymers based on renewable resources have equal importance. Nowadays, the most of the commodity polymers have emerged from fossil fuels. However, these reserves are limited and will deplete in near future. In this contrast, synthetic polymers based on renewable resources have ample scope for sustainable development [9-12].

This review focus on recent developments in biodegradable polymers covering their sources, synthetic methodologies and salient properties. Moreover, the review covers the major attention points in the development of biodegradable polymers either as exploiting monomer which are available in abundance or targeting the application which are entirely novel in terms of futuristic manufacturing. Recently, the research focus has shifted to synthesizing polymers or modifying the existing polymers to reduce the carbon footprints of the

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*Address correspondence to this author at the Polymer Synthesis & Catalysis, Reliance Research & Development Centre, Reliance Industries Limited, Ghansoli 400701, Navi Mumbai, India; Tel: +912279650368;
E-mail: Virendrakumar.gupta@ril.com

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polymers in the form of their final product or application. Various methods have been devised to achieve this object. In accordance to this, CO_2, an abundantly available gas as well as a pollutant, has been considered one of the prime monomers used for producing biodegradable polycarbonates which find applications in scaffolds, grafts and other tissue engineering uses and also in producing packaging materials [21-29].

3D printing is a form of additive manufacturing based on methods such as selective laser sintering, stereo-lithography and Fused Deposition Modelling. PLA has been extensively used as a filament for 3D printing. 3D printing has a major application in the formation of scaffolds and in other tissue engineering applications where it can be synthesized as per the requirement of the patient which makes it advantageous as compared to conventional manufacturing process. The review also focus on the latest developments in bionanocomposites having application in biomedical filed and novel biodegradable polymers blends for medical as well as packaging applications. The recent development in polymers biodegradation and applications have also been documented [30-34].

2. SOURCES OF BIODEGRADABLE POLYMERS

2.1. Natural Biodegradable Polymers

Natural polymers find applications in various fields due to their biocompatibility, lower cost, sustainability, availability and biodegradability. Natural polymer sources can be broadly classified into polysaccharides and protein sources. This review mainly covers the two easily available sources, namely, starch and cellulose. Starch and cellulose are crystalline in nature and hence, they need to be modified using various chemicals to make them easy to process [11-12]. They can further be combined with other synthetic biodegradable polymers in order to overcome their individual drawbacks and prepare multi-functional biodegradable polymer blends or composites [14, 20, 35].

2.1.1. Starch Based Biodegradable Polymers

Nishat *et al*. prepared starch based polymer complexes utilizing transition elements such as Zn(II), Mn(II), Cu(II), Co(II), and Ni(II). Pure starch has poor mechanical properties and this limitation can be overcome by crosslinking starch using agents like glutaraldehyde. This crosslinked starch is further reacted with transition metals to form coordination bonds in the composite. Thus the complex formed will exhibit enhanced mechanical strength, thermal stability and other mechanical properties. Thus, as the crosslinking or the coordination bonds increased, the biodegradability decreased, however, the thermal stability of the composite increased. The synthesized composites have applications in waste water treatment, biomedical field and drug delivery devices [13]. In continuation with the previous work, Nishat *et al*. modified the polymeric starch using thiourea which aids in the formation of transition metal complexes. The incorporation of metal ions in the polymer matrix increased the thermal stability of the matrix. It was observed that complexes containing Cu (II) exhibited highest antibacterial properties amongst all the other starch-metal complexes. Thus, the synthesized polymer complexes can be used for bioplastic manufacturing and waste water treatment [36].

Moreover, biodegradable films derived from cassava starch could be used for food packaging and transportation applications as reported by Souza *et al*. Since, pure cassava starch exhibits high brittleness, plasticizers such as sugars and glycerol are added to the films. The plasticizers enhance the film flexibility and prevent cracks in the film. However, the addition of plasticizer leads to increase in the permeability of the films above the optimum level. To overcome the high permeability limitation, easily available, inexpensive nanoclay particles are added to the film. The biodegradable films can be used in food packaging and transportation application [37]. Thiol-ene click reaction was carried out between ally starch (AS) and thiol starch (St-SH) reported by Li *et al*. to give a novel starch based hydrogel. It was demonstrated that the mechanical properties of the hydrogel could be varied by the thiolene molar ratio. It was shown that the degradation process of the hydrogel took place by two mechanisms combined, namely, surface erosion and diffusion mechanisms. Thus, the synthesized hydrogel is most suitable for tissue engineering and other biomedical applications [38].

On the other hand, tetraethylhydrosilicates (TEOS) incorporated in the carioca starch based film using in situ condensation technique to improve the mechanical properties and to reduce the overall hydrophilicity of the film were prepared by Lima *et al*. This improvement in the properties can be because of migration of silica to the boundaries of the film and due to the interaction between starch and TEOS. It was demonstrated that incorporation of 40% TEOS in the film gave optimum film properties [14]. Mendes *et al*. synthesized polymer blends containing thermoplastic cornstarch (TPS) matrix and thermoplastic chitosan (TPC) as the reinforcement using melt extrusion technique. Chitosan decreased the tensile strength, however, it enhanced the thermal stability of the matrix. It was observed that an optimum of 5 to 10wt % of chitosan gave a plasticizing effect to the matrix, thus, further enhancing its properties and making them suitable for applications in packaging [15].

Whereas, Golacki *et al*. used thermoplastic starch derived from potato along with plant glycerol and incorporated two additives in the film, namely, polyvinyl alcohol and keratin separately to study the final film properties. These additives perform the function of a plasticizer in the film thereby enhancing the mechanical properties of the film. In the first stage of production, a starch pellet was prepared by mixing the components and in the second stage of production, the film was blown from the previously formed starch pellet [16]. Dual modified films which are used in packaging applications were prepared by Biduski *et al*. These films were synthesized from sorghum starch and further modified the film using either or both of acid and oxidation modification to improve the film properties. Acid modification was carried out using an optimum of 3% lactic acid, whereas oxidation modification was done in the presence of 1.5% active chlorine. In the case of modification using both the techniques, acid modification was carried out first followed by further oxidation. It was demonstrated that upon oxidation treatment in the form of single or dual treatment, the film mechanical properties improved to a much greater extent as compared to single acid treatment. Also, increasing the amount of sorghum starch gave enhanced properties to the film [39].

Arolkar *et al*. prepared biocomposite films from corn starch and poly (ε-caprolactone) (CPSCL) and further modified them using air-plasma treatment. The modified films exhibited enhanced biodegradability, surface roughness, hydrophilicity and adhesion between the two film components as compared to the original biocomposite films. It was demonstrated that films when subjected to 2 minutes of air plasma treatment gave optimum mechanical as well as barrier properties. Thus, depending on the need, air plasma treatment for different time periods can be given to the film for suitable use as packaging material [40]. On the other hand, starch/PBAT blend biodegradable films could be prepared by adopting two techniques based on blown extrusion method as reported by Brandelero *et al*. PBAT was added to the starch polymer in order to give strength to the film. In the first technique, starch and plasticizer (glycerol) pellets were extruded with PBAT pellets to give the films. In the second technique, starch granules were extruded with plasticizer (glycerol) pellets and PBAT pellets to produce the film. It was demonstrated that for starch concentration upto 50%, first technique was used for synthesis, whereas for starch concentration above 50%, second technique was used for synthesis to give optimum mechanical and structural properties [41].

2.1.2. Cellulose Based Biodegradable Polymers

Norain *et al*. synthesized biocomposite films based on regenerated cellulose (RC) matrix and lignocellulosic biomass fillers such as coconut shells (CS) fillers. It was observed that 3wt% CS gave optimum strength properties to the biocomposite. The tensile strength and other mechanical properties of the biocomposite film could be further improved by chemically treating the cellulose with butyl methacrylate acid (BMA). Also, incorporation of BMA in the film aided in formation of a uniform dispersion and increased the adhesion between CS and the RC matrix [17]. Liyana *et al*. synthesized a novel biocomposite film based on regenerated cellulose derived from lignocellulosic material using the casting technique. Oil palm empty fruit bunch (OPEFB) and microcrystalline cellulose (MCC) were dissolved in N-dimethylacetamide/lithium chloride. (DMAc/LiCl) solution and regenerated to produce the regenerated cellulose. It was demonstrated that 2wt% of OPEFB gave optimum mechanical properties and dispersion properties to the film due to the uniform dissolution and dispersion of OPEFB fibers in the OPEFB matrix [18]. Mostafa *et al*. synthesized bioplastics using inexpensive raw materials such as cotton linters and flax fibers. The bioplastics were in the form of cellulose acetates produced by acetylation reaction of the raw materials using sulphuric acid. The prepared bioplastics had chemical resistance comparable to the petroleum based polymers such as polypropylene and polyethylene. Thus, these bioplastics can be a suitable substitute for petroleum based polymers because of biodegradability, cost efficiency, safe-to-use properties. It was observed that flax fibers gave a higher yield as compared to the cotton linters. The synthesized bioplastics find application in biomedical field and food packaging [19].

Mahecha *et al*. synthesized novel biodegradable nanofibers from fibrous residues. These residues were obtained from various extraction processes and pre-treatments applied on achira rhizomes to obtain starch as the product. Processes used for the extraction included use of chlorine bleach, mechanical treatment under high pressure, acid of different concentrations and hydrolysis. It was observed that the nanofibers produced from mechanical treatments led to development of electronegative surface charges on the nanofibers, thus, giving good dispersion and mechanical properties. Sulfuric acid treatment lead to formation of highly crystalline nanofibers. These fibers exhibited low water permeability properties. Thus, depending on the pre-treatments, nanofibers with specific requirements can be obtained [42]. Barari *et al*. synthesized novel bionanocomposites using bio-based epoxy resin as the matrix and anisotropic and isotropic nanocellulose fibers (CNF) as reinforcement using modified liquid composite molding technique. The epoxy resin is subjected to thermosetting reaction to produce a net shaped matrix for the composite. Silane treatment was further given to nanocellulose to improve the mechanical properties of the bionanocomposites. The composites prepared from anisotropic CNFs demonstrated better properties than those synthesized using isotropic CNFs [43]. Balakrishnan *et al*. synthesized nanocomposites from potato starch and cellulose nanofibers derived from pineapple leaves using the casting technique. Glycerol was added to the system as a plasticizer giving flexibility to the starch matrix. By the addition of glycerol, the starch and cellulose interaction also increases, since, the cellulose fillers have a tendency to move towards glycerol rich starch phase in the composite. The prepared biocomposites can used for packaging purposes [44].

2.1.3. Starch and Cellulose Based Biodegradable Polymers

Pelisaari *et al*. synthesized inexpensive novel nanocomposites with banana starch as the polymer matrix and cellulose nanofibers derived from easily available banana fibers as the reinforcement using solution casting method. The extraction process for cellulose nanofibers should not include extreme mechanical treatments which may cause defects in the nanofibers and subsequently in the nanocomposite. Extraction using chemical treatments followed by an optimum of 5 passages through the high pressure homogenizer is found to be the most suitable treatment for nanofibers extraction. Since both the matrix and reinforcements were obtained from banana fibers, they were chemically similar and thus, the prepared nanocomposites demonstrated good mechanical properties and thermal stability. The synthesized nanocomposites can suitable for food packaging applications [20].

Thermocavity foam molding technique was adopted by Zhang *et al*. to prepare open cell membrane structured bionanocomposites over modified starch and plant fibers to. In order to improve the properties and compatibility of the composite, additives such as thermoplastic starch (TPS), oxidized starch (OS) and thermoplastic oxidized starch (TPOS) were incorporated in the composite Glycerol or modified glycol were used as the plasticizer to prepare TPS whereas, hydroxyl peroxide and copper sulphate were used as the oxidizing agent and catalyst respectively for synthesis of OS. Both the plasticizer and oxidizing agent were used for preparing TPOS. It was demonstrated that with the incorporation of TPOS, the re-crystallization of starch reduced, tensile strength and mechanical properties of the composite increased substantially due to the hydrogen bond formation between the starch and the fibers [45]. Cellulose/PHB bionanocomposites which are used in packaging materials in food and agricultural field were prepared by Seoane *et al*. The author synthesized bilayer bionanocomposites using cellulose cardboard in fiber form and PHB in solution form using compression moulding and solution casting technique. It was demonstrated that pressed composite gave a better performance and exhibited enhanced properties as compared to composite produced from solution casting technique. PHB being expensive, its amount was optimized to 15 wt% for compression moulding and 10 wt% for solution casting technique to give good films [35].

2.2. Synthetic Biodegradable Polymer

Biodegradable polymers can be synthesized by conventional methods, such as polycondensation and ring opening polymerization of lactones or lactides. Enzyme catalyzed polymerization has also attracted a great deal of interest as this is in contrast with conventional method a high regiospecificity as well as high stereospecificity can be achieved by enzyme catalyzed polymerizations [7].

2.2.1. Step Growth Polymerization

Step-growth polymerization of various diacids and diols traces back to pioneer work of Carothers in the 1930s [46]. This is the traditional synthetic route to aliphatic polyesters that usually proceeds by the reaction between two different functional groups, for example, isocyanate and hydroxyl groups, or hydroxyl and carboxyl groups. Diesters or diacids and their derivatives are used for the synthesis of aliphatic polyesters in step-growth polymerization.

2.2.1.1. Step Growth Polymerization/Polycondensation: Method and Catalyst Systems

Step-growth polymerization reactions for polyesters are commonly referred to as polycondensation since they form small molecules such as water or methanol as byproduct. Generally, it is difficult to achieve high molecular weights in step polymerization reactions, since a very high conversions (>98-99%) is required for this. Since esterification reactions are equilibrium processes, therefore, achieving high conversions are very challenging. The polycondensation reactions are carried out in a driven system, accomplished by the use of high temperature, high vacuum, and high pressure of inert gas to remove the byproduct [47-50].

The other drawback of polycondensation is the high polydispersity index of synthesized polymers. The value of polydispersity index for polycondensation is generally >2 and depends on the extent of reaction. In general, a bulk polycondensation reaction accomplish with a two-step procedure, esterification and polycondensation. Esterification is the first step of bulk polycondensation that complete with an oligomeric product. In this step monomers are heated at moderate temperatures without the application of vacuum. Esterification is considered to be accomplished after the collection of almost the theoretical amount of byproducts such as water and methanol, which can be removed by distillation from the reaction mixture. Esterification is followed by the polycondensation and in this step, oligomers prepared from the former step are subjected to heat at high temperature with the application of vacuum. The high molecular weight polymers are achieved in polycondensation step. The progress of reaction can be monitored by the change in viscosity, which gradually increases to an extent where stirring of reaction mixture cease [47-50].

Many disadvantages of the bulk polycondensation can be overcome by the solution polycondensation method. Thermal control is easier in solution polycondensation because the solvent assists in the transfer of the heat of polymerization. Additionally, solvent acts as a diluent and allows easier stirring, since the viscosity of the reaction is low even at higher molecular weight. On the other hand, solvent may cause other complexities, such as chain transfer to solvent and impurities because of residual solvent. Solution polycondensation is carried out in presence of proton traps such as, tertiary amines and pyridine, molecular sieves to facilitate the removal of byproducts [48-50].

Different metal acetates are employed to catalyze the polycondensation reactions for example zinc acetate [$(CH_3COO)_2Zn$], manganese acetate [$(CH_3COO)_2Mn$] and lead acetate [$(CH_3COO)_2Pb$]. For a polycondensation reaction, the temperature, pressure and solution concentration depends on the nature of catalyst. Titanium-based catalyst [$KTiO_x$, $Ti(OC_4H_9)_4$], tin based catalyst [$(But)_2SnO$] and antimony based catalyst [Sb_2O_3] are also reported as the efficient catalyst systems for the polycondensation of polyesters [50-53].

2.2.1.2. Functionalized Polymers from Step-Growth Polymerization

Various classes of functional polymers such as polyesters, polycarbonates, polyaminoacids, polyamides etc. have been synthesized by step-growth polymerization. Polyaminoacids or polypeptides are biodegradable and biocompatible polymers comprehensively reviewed by Deming [54]. Yu *et al*. have synthesized a nonionic water soluble polypeptide having mono and diethyleneglycol functionalities using polycondensation reaction [55]. Guo *et al*. have introduced copolymers with functional groups like chloro, azido, allyl or propargyl in poly(g-benzyl-L-glutamate) [PBLG] based copolymers through ester exchange reactions [56]. Dhamaniya et. al. reported on a novel class of functional aliphatic polyesters derived from natural resources, namely, tartaric acid derivatives. These functional polyesters could have applications in controlled drug delivery and synthesized through polycondensation methodology via a protection and deprotection of functional groups that resulted in hydroxyl functionalized polymers [57-58].

2.2.1.3. Biodegradable Polymers Based on Renewable Cyclic Sugar Diol Monomers

1,4:3,6-Dianhydrohexitols have been served as a potential bio-based renewable monomer for the synthesis of variety of biodegradable polymers, such as polyesters, poly(ester anhydride)s, poly (ester amide)s, poly(ester carbonate)s, polyurethane etc. 1,4:3,6-dianhydrohexitols sugar diols exist in three different isomeric forms i.e. isosorbide, isomannide and isoidide (Figure **1**). Among the three isomers, isosorbide is commercially produced, however impurities of its isomers as well as high cost restrict its polymers to be commercialized [12, 59].

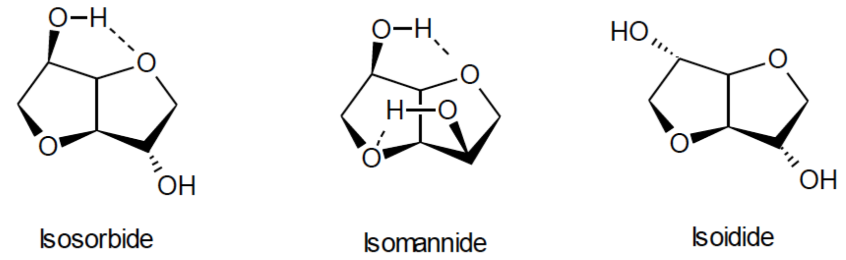


Figure 1: Different isomeric forms of 1,4:3,6-dianhydrohexitols sugar diols [12,59].

1,4:3,6-dianhydrohexitols based different polymers can be synthesized by step-growth polymerization or solution polycondensation method. For polymer synthesis acid chlorides are an attractive choice because of its high reactivity, since 1,4:3,6-dianhydrohexitols based sugar diols have secondary hydroxyl groups that make it less reactive. As a monomer 1,4:3,6-dianhydrohexitols based sugar diols have interesting properties like non-toxicity and high rigidity that encourage its incorporation in biodegradable polymers to enhance the thermo-mechanical properties [12].

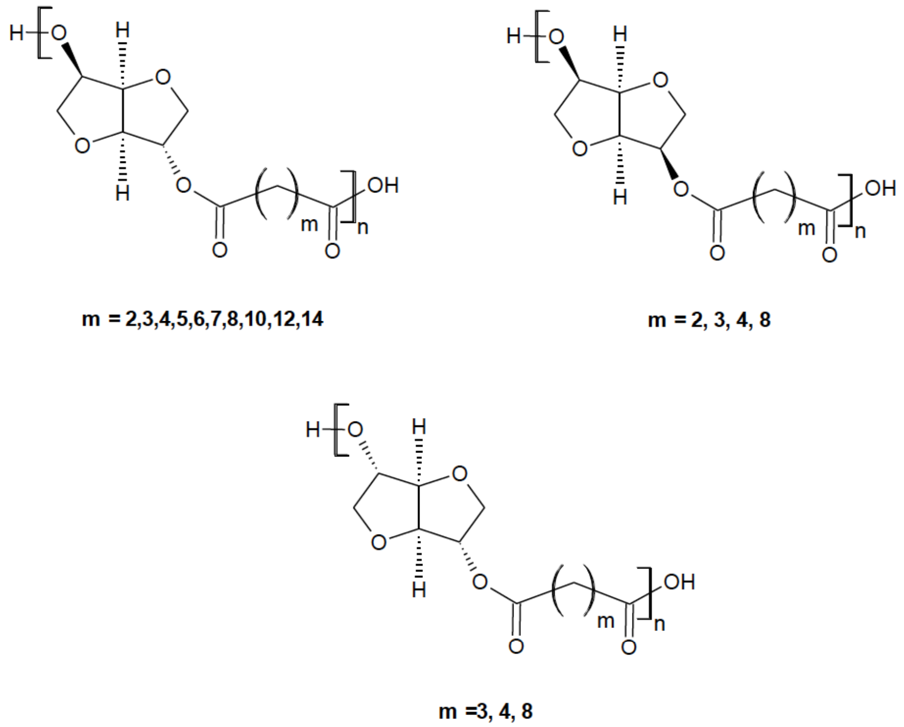
Okada *et al*. have reported a series of biodegradable polyesters based on 1,4:3,6-dianhydrohexitols and various diacid chlorides with methylene units ranging from 2 to 10 (Figure **2**). The polymers were synthesized by bulk polycondensation at 140-180 °C without catalyst. The polymers were collected after precipitation in methanol and high molecular weight lie in the range of 7000-30000 g/mol were obtained. Various degradation studies such as soil burial, enzymatic degradation and hydrolytic degradation in presence of phosphate buffers were conducted to evaluate the degradability of the polymers [60-63].

Moreover, Kricheldorf *et al*. have reported the synthesis of biodegradable copolyesters based on silylated isosorbide and sebacoyl chloride [64-65]. Biodegradable polyesters and copolyesters having furan moieties were reported by Okada *et al*. where transesterification approach was employed and titanium isopropoxide was used as a catalyst. These polymers were synthesized in high molecular weight and their biodegradability was demonstrated by enzymatic degradation method [66-67]. Isosorbide base polymers were not only demonstrated biodegradability but also employed in bone tissue engineering as porous scaffolds [68]. Noordover *et al*. have reported on the another interesting property of 1,4:3,6-dianhydrohexitols based polyesters as a powder-coating resins [69-71].

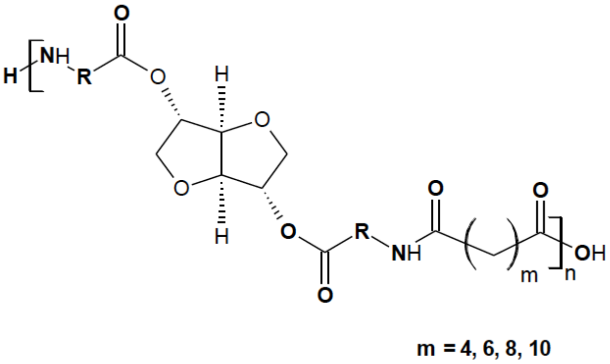
1,4:3,6-dianhydrohexitols based biodegradable poly(ester amide)s (Figure **2**) were reported by Okada and Kricheldorf [72-73]. The method consist two steps, in the first step 1,4:3,6-dianhydrohexitols reacts with α-amino acids in the presence of *p*-toluenesulfonic acid monohydrates. The second step is the polycondensation of *p*-toluenesulfonic acid salts of *O,O'*-bis(α-aminoacyl)-isosorbide with bis(*p*-nitrophenyl)esters of aliphatic dicarboxylic acid. The polycondensation was carried in the presence of trimethylamine in NMP at 40 °C [73]. Okada *et al*. investigated the thermal properties and biodegradability of the synthesized poly(ester amide)s. These polymers were found amorphous in nature and different degradation method such as soil burial and enzymatic degradation method has confirmed the biodegradability and revealed its dependence over the molecular structure [72].

The biodegradability of the isosorbide based poly(esters carbonate)s were studied by Okada *et al*. [53] The copolymers were synthesized by polycondensation of isosorbide, diphenyl sebacate and diphenyl carbonate in the presence of Zn acetate catalyst. The biodegradability were determined by soil burial test and it was found that the polymers containing high amount of carbonate (26%) degraded rapidly as compared to polymers containing less amount of carbonate (4%) [74].

Yokoe *et al*. have published a series of paper describing synthesis and degradation of copolycarbonate based on 1,4:3,6-dianhydrohexitols [75-77]. In their work, at first sugar carbonates, namely 1,4:3,6-dianhydrohexitols diphenyl carbonates were synthesized followed by the bulk polycondensation with various alkanediols in the presence of Zn acetate and titanium tetraisopropoxide as catalyst. The copolycarbonates were synthesized in high molecular weight lie in the range of 10000-20000 g/mol and their biodegradability were evaluated by the environmental and enzymatic degradation studies [77]. Moreover, Yokoe *et al*. have prepared polycondensates of 1,4:3,6-



1,4:3,6-Dianhydrohexitols based biodegradable polyesters



1,4:3,6-Dianhydrohexitols based biodegradable poly(ester amide)s

Figure 2: 1,4:3,6-dianhydrohexitols based polyesters and poly(ester amide)s [72,73].

dianhydrohexitols and oligo(ethylene glycol)s. It was found that the polycondensates were amorphous in nature and T_g decreases with increasing chain length. The trend of biodegradation correlated with the T_g values and found that the polymers which are having high T_g as compared to the test temperature shown less degradability, because at the glassy state polymer chains remain less mobile [78]. Yokoe *et al*. have also synthesized a biodegradable functionalized polycarbonate based on L-tartaric acid and 1,4:3,6-dianhydrohexitols. L-tartaric acid has introduced hydroxyl functionality as well as enhanced the biodegradability of the polycarbonates [79]. The functionalized polycarbonates were synthesized by a protection-deprotection method, in the first step hydroxyl groups of tartaric acid were protected with acetal groups and after polymerization acetal deprotection was employed using trifluoroacetic acid to generate a series of polycarbonate with pendent hydroxyl groups [80].

2.2.2. Ring Opening Polymerization

The ring opening polymerization of lactones is a striking method to synthesize aliphatic polyesters. This method has potential advantages relative to the condensation polymerization process. The former does not require equimolar balance of functional groups that is essential for the synthesis of high molecular weight polymer by the latter. Moreover, it shows the characteristics of a living polymerization, by this means a polymer with controlled molecular weight can be prepared. Ring opening polymerization has been widely used for the polymerization of cyclic esters and diesters, such as butyrolactone, valerolactone, ε-caprolactone, lactide and glycolide.

2.2.2.1. Ring Opening Polymerization: Method and Catalyst Systems

Most commonly used mechanism is coordination-insertion mechanism as ring opening polymerization proceeds in a 'living' manner. Although different kind of mechanisms for ring opening polymerization have been accepted this involves initiation by either an anionic, cationic, coordination-insertion or an activated monomer mechanism. Various metal alkoxides such as Mg, Sn, Ti, Zr, Zn alkoxides are used as catalysts where metal atoms contain free p or d orbitals of favorable energy involve in mechanistic pathway [81-86].

The mechanism involves the coordination of the carbonyl oxygen of lactone to the Lewis acidic metal alkoxide complex as shown in Figure **3** [81]. Thereby the nucleophilicity of the alkoxide part as well as the electrophilicity of the carbonyl group increases. Subsequently, the alkoxide moiety attacks at the carbonyl carbon and the cleavage of the acyl-oxygen bond initiate the ring opening of lactone. It generates a new metal alkoxide species that can re-initiate the cycle [81, 83-84].

Different kind of metal complexes such as Sn (IV), Al (III), Zn (II), Fe (II), Ti (IV), and Y (III) have been found to be suitable for ring opening polymerization. In general, the catalyst employed for the ring opening polymerization mainly consists of organometallic compounds, lewis acids and different salts of metals [82, 84-94].

The tin complexes such as tin(II) 2-ethylhexanoate or stannous octoate [$Sn(Oct)_2$] is found to be efficient catalysts for ring opening polymerization of lactone since it gives high conversion of monomer with high yield and have low cost and low toxicity [95-97]. The other examples of catalysts explored for ring opening polymerization are titanium biphenoxy-alkoxide, tin alkoxides and phenoxides, aluminum alkoxides, zinc alkoxides, zinc lactate, yttrium and lanthanum alkoxides [77-79, 82-84].

2.2.2.2. Functionalized Polymers from ROP

Functional biodegradable polymers have attracted a great deal of attention, since it is the class of materials that combines the features of enhanced hydrophilicity, high degree of chemical functionality, tunable biodegradability and bioadhesion. These striking properties make these materials more suitable for applications such as controlled drug delivery and pharmaceuticals. Various functional aliphatic polymers by ring opening polymerization are shown in Chart **1**.

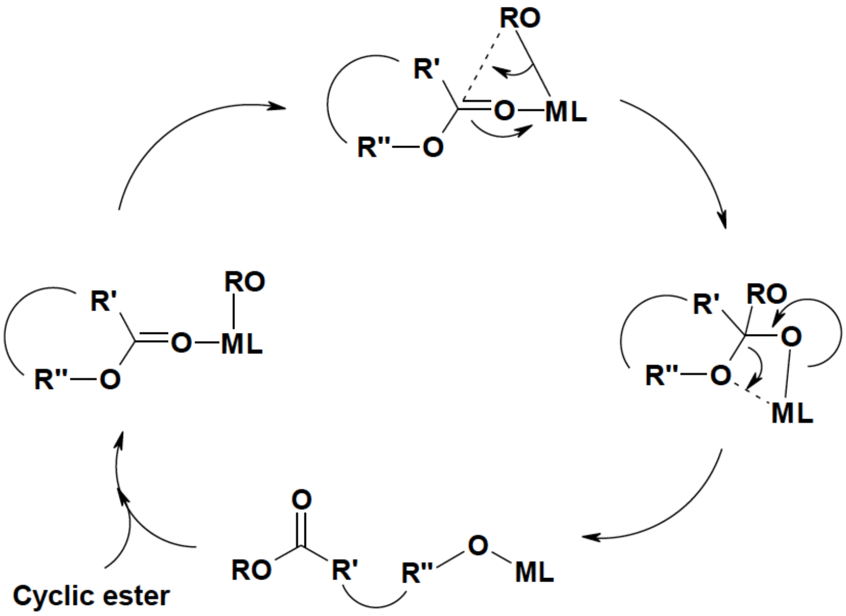


Figure 3: Generalized mechanism for ring opening polymerization [81].

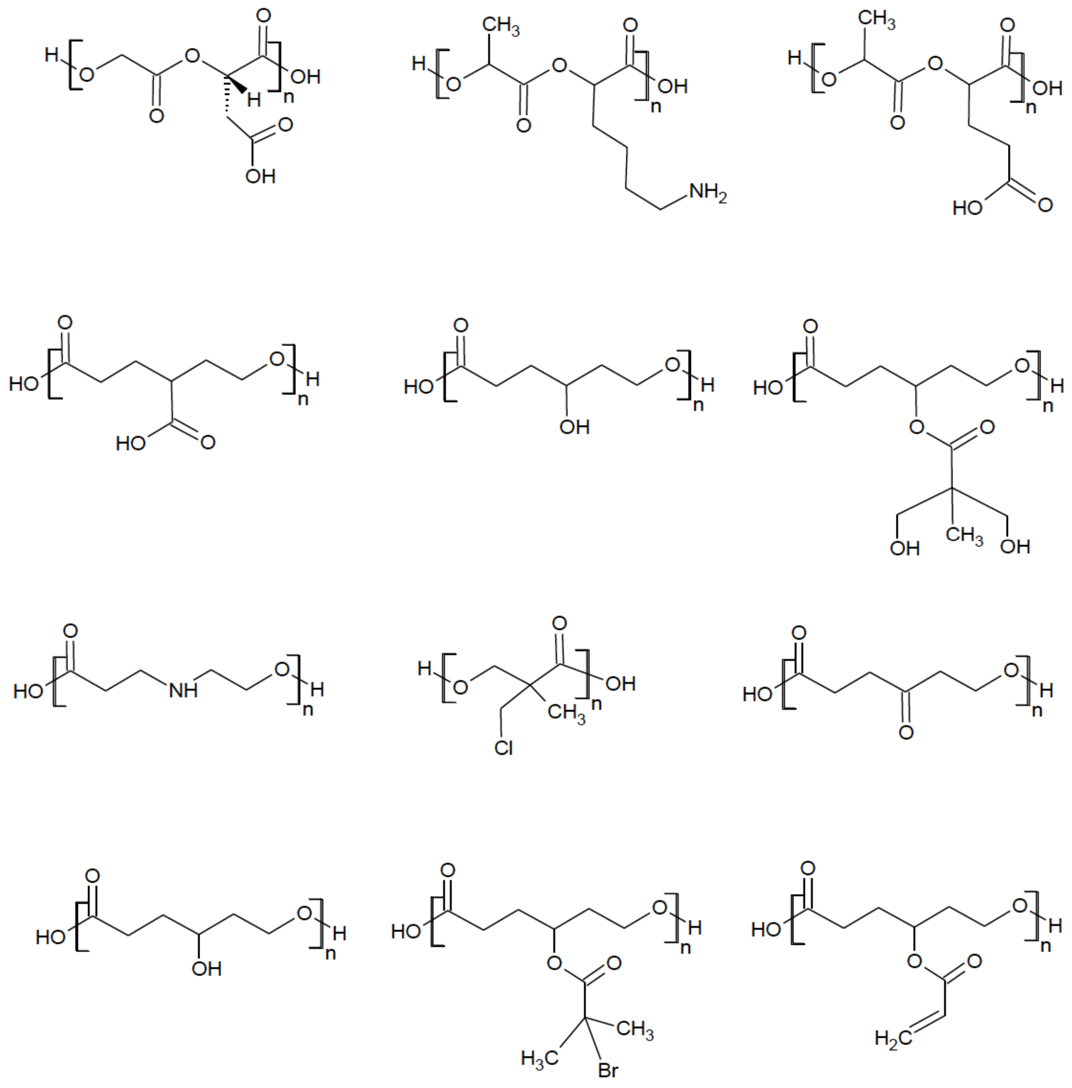


Chart 1: Various functional aliphatic polymers by ring opening polymerization [77-87].

The synthesis of glycolide based poly(ester) with pendant carboxylic acid by the ring opening polymerization of 3(S)-[(benzyloxycarbonyl)-methyl]-1,4-dioxane-2,5-dione have been reported. A benzyl deprotection method was employed to generate carboxylic groups alone the polymer chain that enhanced the rate of polyester hydrolysis as compared to PLA [98-99]. Trollsas *et al*. were prepared PCLs with pendent carboxylic acids by the ring opening polymerization of benzyl γ-(ε-caprolactone)carboxylate followed by acid deprotection [100].

The side-chain-functionalized lactide analogues from commercially available amino acids have been synthesized and the resulting functionalized cyclic monomers can be homopolymerized and copolymerized with lactides using stannous octoate as a catalyst. A quantitative deprotection approach gave new functional poly(lactide)-based materials with amino, hydroxyl or carboxyl side chains along a poly(lactide) [98, 101].

Tian *et al*. have reported a series of papers on the synthesis of aliphatic polyesters having keto group by the ring opening polymerization of 5-ethylene ketal ε-caprolactone followed by deprotection [102-105]. Moreover, Tian *et al*. have also demonstrated that the keto groups were reduced into hydroxyl groups by using $NaBH_4$ resulting in the aliphatic polyester with hydroxyl pendent groups [103].

Liu *et al*. synthesized a chloro-substituted lactone (α-chloromethyl-α-methyl-β-propionolactone) and polymerized with ε-caprolactone. Subsequently, these chloro functionalized polymers were reacted with pyridine to convert chloromethyl groups into quaternary ammonium salts [106]. Hedrick *et al*. were reported on the synthesis of aliphatic polyesters with pendent bromide groups by the ring opening polymerization of bromo substituted cyclic ester γ-(2-bromo-2-methyl [propionyl)-ε-caprolactone [107].

Aliphatic polycarbonates show biodegradability, biocompatibility and low toxicity, which are essential requirement for biomaterials. Furthermore, presence of functional groups along the polycarbonate chain can make these materials a potential candidate for biomedical filed. Al-Azemi *et al*. have reported on the synthesis of water soluble polycarbonates having pendent carboxylic groups by enzyme-catalyzed ring-opening polymerization of 5-methyl-5-benzyloxycarbonyl-1,3-dioxan-2-one. Catalytic hydrogenation to remove benzyl groups yields polycarbonate having pendent carboxyl substituents on the main chain [108]. Liu *et al*. have also reported on carboxyl functionalized polycarbonates by ring opening polymerization of cyclic carbonate monomers, 5-methyl-5-methoxycarbonyl-1,3-dioxan-2-one and 5-methyl-5-ethoxy carbonyl-1,3-dioxan-2-one [109]. Aliphatic polycarbonates, poly(ester-carbonate)s with pendent amino groups and water soluble polycarbonates with pendent amino and carboxylic groups were reported by using ROP [110-112].

Moreover, Wang *et al*. have reported on the hydroxyl functionalized polycarbonate by the ring opening polymerization of 5-benzyloxy-trimethylene carbonate followed by the benzyl deprotection [113]. Yang *et al*. synthesized a biodegradable aliphatic poly(ester-carbonate) bearing functionalizable carbonate building blocks [114]. Guan *et al*. have reported on the biodegradable block copolymer with pendent carboxyl groups based on L-lactide, 2-methyl-2-benzoxycarbonyl-propylene carbonate, poly(ethylene glycol) using diethyl zinc as a catalyst [115]. Also, many researchers for example, Xie *et al*., Hu *et al*., and Xie *et al*. have synthesized different functionalities with carboxyl, cinnamate and hydroxyl functionalities, respectively [116-118]. The poly(ester-carbonates) synthesized by Xie *et al*. have photolablie 2-nitrobenzyl protecting groups which deprotect on the application of UV irradiation [116].

Various groups have reported on the synthesis of aliphatic polycarbonate with pendent groups having double or triple bond. For example the synthesis of a biodegradable aliphatic poly(L-lactide-*co*-carbonate) bearing pendant acetylene groups prepared by ring-opening copolymerization of L-lactide with 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one in the presence of benzyl alcohol as initiator with $ZnEt_2$ as catalyst [119-121].

Chen *et al*. reported a functional polycarbonate with cyclohexene side chains by the ring opening polymerization of 2,2-(2-pentene-1,5-diyl)trimethylene carbonate using various organometallic catalysts [119]. He *et al*. reported on the synthesis of a functional polycarbonate with pendent allyl ether groups by the ring opening polymerization of a six-membered cyclic carbonate, namely 5-allyloxy-1,3-dioxan-2-one. Moreover, a post-polymerization approach was employed for the epoxidation of allyl groups by *m*-chloroperoxybenzoic acid [121].

2.2.3. Other Developments in Functionalized Polymers & Combination of Different Methodologies

Cunningham *et al*. reported on a novel stimuli responsive tri-block copolymer PEG-b-(PLA-ss-PLA)-b-PEG (ssBCP) consisting of polyethylene glycol (PEG) and polylactic acid (PLA) by combining facile carbodiimide coupling reaction and ring opening polymerization. Glutathione reducing agent causes an increase in the micelle size and enhanced reductive bond cleavage in the co-polymer thus, aiding in drug release. The micelles have PEG corona thereby, improving the interaction tendency and colloid stability [122].

Xu *et al*. used novel mPEG based macroinitiatiors to synthesize PLA via ring opening polymerization to give pH stimuli sensitive and amphiphilic co-polymer (mPEG-Hyd-PLA). The polymer was loaded with 2.4-3.5% of two drugs namely Doxorubicin (DOX) and paclitaxel (PTX). These polymers exhibited pH sensitivity by the cleave-dissociate-release process and have applications in drug delivery [123]. Petrova *et al*. prepared a novel triblock co-polymer. The first step was the modification of α-methoxy- ω hydroxy-poly(ethylene oxide) (MPEO) with p-toluenesulfonyl chloride. Second step was to form a hydrophilic diblock polymer MPEO-b-PEtOx via ring opening polymerization of 2-ethyl-2-oxazoline (EtOx) using tosyl-MPEO as the macroinitiator. In the final step, the double hydrophilic triblock co-polymer was formed by carry out polymerization of ε-caprolactone via ring opening polymerization using the diblock co-polymer as the macroinitiator. Further, self-assembling, thermo-sensitive nanoparticles were synthesized using the synthesized polymer which find application in biomedical field [124].

Recently, studies have been reported on biodegradable polymers prepared through combination of two different methodologies namely, ROP and

ATRP. Xiong *et al*. combined two polymerization techniques, continuous activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) and ring opening polymerization to synthesize a novel pH/redox stimuli-responsive and amphiphilic cross-linked polymer [poly(ε-caprolactone)-b-poly(poly(ethylene glycol) methyl ether methacrylate-co-p-(2 methacryloxyethoxy) benzaldehyde)]$_4$ [4-AS-PCL-P(PEGMA-co-MAEBA)]. The polymer have application in insoluble chemotherapeutic delivery for cancer treatment [125].

Wang *et al*. combined ring opening polymerization to give PLA and atom transfer radical polymerization to give further hydrogentation with Pd/C under normal pressure to synthesize block co-polymer poly(lactic acid)-block-poly(ascorbyl acrylate) (PLA-block-PAAA) consisting of hydrophobic poly(lactic acid) and hydrophilic poly(ascorbyl acrylate) (PAAA). The polymer exhibited self-assembling and amphiphilic properties [126]. Guo *et al*. used N-isopropylacrylamide (NIPAAm), tert-butyl methacrylate (tBMA) and caprolactone (CL) via ring opening polymerization (ROP) and atom transfer radical polymerization (ATRP) to synthesize self-assembling stimuli responsive support materials for pectinase enzyme immobilization by electrostatic interaction [127].

Many researcher have recently worked on in-situ ROP methodology for novel biodegradable polymers. Kim *et al*. synthesized novel honeycomb patterned thin films using a composite of poly(3-caprolactone) matrix and reinforced with oleic acid-capped magnetic nanoparticles via in-situ ring opening polymerization followed by solution casting. The synthesized films find application in molecular electronics in the film form [128]. Mao *et al*. prepared layered double hydroxides (LDHs) /PCL nanocomposites by carrying out in situ ring opening polymerization to form LDHs-g-PCL followed by solution casting of the blend film containing LDHs-g-PCL and pure PCL films under humid conditions. These synthesized films can be effectively used as packaging material due to the enhanced physical and biodegradation properties [129]. Park *et al*. used in situ ring opening polymerization using tin(II) octoate as an initiator followed by solution casting method under humid conditions to synthesize novel photosensitive honeycomb pattern composite films containing PCL and 4-dimethylamino-40-(6-hydroxy hexyloxy) azobenzene (Azo) [130].

Recently researcher have also reported novel catalysts for ROP to produce biodegradable polymers. Yuan *et al*. synthesized a novel catalyst, complex of cerium (IV) diolate, to polymerize ε-caprolactone with narrow molecular weight distribution. The catalyst was formed using a core of 13-nuclear cerium (IV)-oxo and a shell of 18 N-phenylaminedienthanolate [131]. Njogu *et al*. carried out ROP of ε-caprolactone using a novel catalyst of the composition $[(AgO_2C_2F_3)_2.L_2]$ formed by reaction of 2-pyridinyl Schiff base ligands with $AgO_2C_2F_3$ to form silver based complexes. The ligands used for this purpose were prepared by a mechanochemical technique which formed co-ordination bonds with silver (I) using nitrogen atoms in imine and pyridinyl [132]. Roymuhury *et al*. used novel complexes of dimethyl aluminium containing bidentate aminophenolate ligands as a catalyst to polymerize L-lactide and rac-lactide via ring opening polymerization [133]. Rosen synthesized hexablocks of poly(lactic acid) of defined lengths through ROP using a novel magnesium based catalyst. The catalyst used had a bipyrrolidine backbone which was in a complex with benzyl magnesium chloride. Thus, a tailor made polymer with modifiable properties was synthesized [134].

Phillips *et al*. have reported a high molecular weight biodegradable polymers derived from RAFT (Reversible Addition Fragmentation Chain Transfer) polymerization. The biodegradable polymers with pyridyl disulfide end-group were prepared and the described method have the applicability to polycondense a variety of monomer having functionalities such as (meth)acrylates and acrylamides [135]. Gatti *et al*. have reported the controlled radical polymerization of 2-hydroxyethyl methacrylate functionalized with a controlled no. of ε-caprolactone units through RAFT polymerization. The method allows a good control over the molar mass of the final polymer with a low PDI and polymer solution produces nanoparticles suitable for drug delivery applications [136]. Hu *et al*. have reported a light responsive copolymer poly(spiropyrane)-block-poly(ethylene glycol) based on RAFT polymerization. The copolymer has the ability to self-assemble into spherical micelles and the light controlled released was studied as well. The spherical micelles of copolymers have a potential application in drug delivery [137]. Sponchioni *et al*. have reported a thermo responsive amphiphilic block copolymers via RAFT and ROP polymerization. The copolymers possess a temperature dependant self-assembly behaviour that forms nanoparticles at temperature below lower critical solution temperature and have potential application in drug release [138].

Cui *et al*. have prepared biodegradable and pH responsive polymer capsules through silica particles as templates for surface grafting of poly (acrylic acid) (PAA) and PAA-co-poly(polyethylene glycol) acrylate) (PAA-PPEGA) block polymers via RAFT polymerization. The reported capsules were non-toxic, water soluble and biocompatible and have application in controlled drug release [139]. Guégain *et al*. have reported two class of degradable polymers, first based on methyl methacrylate (MMA) and 2-methylene-4-phenyl-1,3-dioxolane (MPDL) and second based on oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and MPDL through NMP and ROP polymerization. The tenable degradation studies of copolymers P(MMA-co-MPDL) and P(OEGMA-co-MPDL) have been carried out and have application in controlled drug delivery [140]. Kukut *et al*. have reported a biodegradable microspheres based on graft copolymers for long-term sustained release of a drug. The graft copolymers prepared by combination of NMP and ROP polymerization and have polystyrene backbone and pendant chain of l-lactic acid and glycolic acid [141].

2.2.4. Enzyme Catalyzed Polymerization

Enzyme is a sophisticated biocatalyst with three-dimensional structure that catalyzes a bio-chemical reaction with high efficiency and selectivity. Enzyme catalyzed polymerization can be either step polymerization or ring opening polymerization. However, here it has been discussed separately, since enzyme catalyzed polymerization has its distinct characteristics. Enzyme catalyzed polymerization offers several advantages over chemical catalysis since in latter process various organometallic catalysts are used which are hazardous in biomedical applications. Various advantages of an enzyme catalyzed polymerization are listed below [142-143].

1. The resultant polymers are obtained with high enantio and regio selectivity with a good substrate conversion efficiency
2. Enzyme catalyzed polymerizations end up with polymers having well-defined structures
3. The polymerization is carried out under mild reaction conditions i.e. temperature, pressure and pH
4. The removal of enzymes from resultant polymers is not very necessary since enzymes are recyclable and non-toxic materials
5. The polymerization can also be carried out in bulk media, organic media and various interfaces

The enzyme catalyzed reaction takes a long reaction time to achieve a complete conversion of monomer. Generally, low molecular weight polymers are obtained in this method with a low polydispersity index. An enzyme catalyzed polycondensation reactions involves three step: first step is a initial rapid transesterification, followed by the second step that involves a significant increase in molecular weight and finally third step that is a very slow polymerization reaching the limiting molecular weight of the polymer [142-144].

The enzyme catalyzed ring opening polymerization initiate with a complex formation between carbonyl oxygen and enzyme followed by the ring opening that leads to the formation of the acyl-enzyme intermediate or enzyme-activated monomer. This is a rate determining step of enzyme catalyzed ring opening polymerization. This step is followed by the propagation step where, hydroxyl group of monomer undergo in a nucleophilic attack on the enzyme-activated monomer and thus the incorporation of monomer is started and regenerate the active centre for next monomer unit [142-143, 145-146].

2.2.4.1. Enzyme Catalyzed Polycondensation Reactions

A variety of polyesters have been synthesized using different diacids and diols by enzyme catalyzed polycondensation reactions. Kobayashi at. el. have synthesized a lipase catalyzed low molecular weight polymer using sebacic acid and 1,8-octanediol [147]. Aliphatic polyesters under mild conditions have been synthesized by Tsujimoto *et al*. using divinyl sebacate or adipate with glycerol. This study revealed that such polymerizations provide high yield and molecular weight when carried out under reduced pressure [148]. Mahapatro at. el. have prepared polyesters using linear hydroxyacids of variable chain length catalyzed by Novozyme-435, where it was found that present of water in the polycondensation system facilitated to increase the molecular weight [149]. Moreover, Iwata *et al*. have demonstrated that polymerization of caprolactone with 11-mercapto undecanoic acid and 3-mercapto propionic acid yield polyesters containing thioester groups using Novozyme-435 [150].

2.2.4.2. Enzyme Catalyzed Ring-Opening Polymerization

Enzyme catalyzed ring-opening polymerization is one more attractive way to prepare various kinds of new biodegradable polymers by ring opening of lactones, lactides and macrolides. Panova *et al*. have synthesized novel polymers based on propyl malolactonate, a four membered lactone in the presence of *candida rugosa* lipase, using toluene as a solvent. The study revealed that rate of polymerization enhanced when reaction carried out at 45 or 60 ºC as compared to room temperature [151].

Uyama *et al*. have demonstrated that the initial rate of polymerization depends on the ring size of the monomer and found it increased with increase in ring size. The polymerization of 13-membered lactone carried out much faster as compared to caprolactone. Also, a high temperature (75 ºC) facilitated to achieve polymer with high molecular weight [152]. Kumar *et al*. have synthesized diblock copolymers using lipase catalyzed polymerization. In this study ring opening polymerization of lactone were carried out in the presence of novozyme-435, using toluene as a solvent. Where mono-terminate hydroxyl groups of polybutadiene of varying chain length were employed as an initiator for ring opening that resulted in a series of diblock copolymers [153].

2.2.4.3. Factors Influence the Enzyme Catalyzed Polymerization

Various reaction parameters like water content of reaction, solvent, enzyme concentration, temperature, and source of enzyme have crucial effect over the molecular weight of the synthesized polymers [142-143]. The conformational flexibility of an enzyme regulates by the water bound to the enzyme surface or the reaction water content of the enzyme catalyzed polymerization. The researchers have demonstrated that the rate of monomer conversion increased with increases in water content. However, after a certain range of water content the number average molecular weight of the product decreased with increases in water content [142-143, 154].

Solvent has a vital role in an enzyme catalyzed polymerization since it determines the enzyme stability and regulates the screening of substrates and products. Moreover, the rate of polymerization depends on the solubility and viscosity of the monomers and resultant polymer in a particular solvent. Since it determine the conformation and diffusivity of the polymer in the solution, which alter the reactivity towards an activated monomer or chain end. The nature of solvent is also a decisive factor for the enzyme catalytic activity. For example, hydrophilic solvents deprive the hydration water from the enzyme, thereby disfigure the catalytic conformation and reduce the enzyme catalytic activity. On the other, hydrophobic solvents allows the water to remain over the enzyme surface, thus retain enzyme catalytic activity [142-143].

Different researchers have studied the effect of enzyme concentration on the rate of polymerization [147]. It has been found that the increasing the enzyme concentration increases the rate of monomer conversion but at the same time decreases the number average molecular weight of the polymer. The effect of temperature on the rate of enzyme catalyzed polymerization depends on the thermal stability of the enzyme at that temperature. Various methods such as immobilization of enzyme and selection of solvent provide possibility to drive an enzyme polymerization at elevated temperatures. The effect of temperatures ranging from 60 to 105 ºC on caprolactone polymerization has been studied by the Gross at al. and demonstrated that the rate of monomer conversion increased with an increase in temperature [155-156].

3. PHYSICAL PROPERTIES OF BIODEGRADABLE POLYMERS

This section describes the physical properties of most widely used biodegradable polymers derived from nature for example cellulose and starch and synthesized in laboratory such as poly(glycolide), poly(L-lactide), poly(ε-caprolactone), poly(butylene succinate), etc. There are various factors which govern the physical properties of biodegradable polymer for example, composition of the repeat units, flexibility of the polymer chains, presence of polar groups, degree of branching, molar mass, crystallinity, orientation, etc.

Cellulose $(C_6H_{10}O_5)_n$ is a polysaccharide containing a linear chain of ringed glucose molecules with 1-4 glycoside linkages and exists in interchangeable crystalline structures. It has a unique ribbon-like conformation. Starch is semi-crystalline polysaccharide containing glycoside linkages consisting of branched amylopectin as well as helical and linear amylose [157].

Poly(glycolide) is a simplest linear aliphatic polyester in terms of chemical structure. It is thermoplastic crystalline material with a degree of crystallinity lie from 45-55 %. PGA is insoluble in the most of the organic solvents, however it can be dissolved in fluorinated solvents such as hexafluoroisopropanol and hexafluoroacetone. It has a T_g of 36-40 ˚C above room temperature and a very high T_m of 220-225 ˚C. The low solubility and high T_m of

PGA limits its application in drug delivery devices [85-86, 158].

Poly(L-lactide) (PGA) is semicrystalline thermoplastic polymer. Since lactic acid has a chiral nature, therefore the properties poly(lactide)s depend on the stereoisomer used for their preparation. For example, poly(L-lactide) and poly(D-lactide) are semicrystalline material whereas poly(DL-lactide) is an amorphous polymer. It has a degree of crystallinity of 37% and soluble in halogenated hydrocarbons, tetrahydrofuran, dioxane, hot benzene etc. Poly(L-lactide) is a white fibrous material with a T_g of 55-65 ˚C and T_m of 160-180 ˚C [81, 84-86, 158-162].

Poly(ε-caprolactone) is a tough, semicrystalline polymer with a degree of crystallinity of 50%. PCL drew much attention as a biomaterial due to its flexibility that combines with biodegradability. It has a T_m of 60 ˚C and T_g of -60 ˚C and can be employed in injection molding, extrusion, and film blowing. It is a potential candidate for controlled drug release applications, since it has low T_m and show permeability to low molecular species [85-86, 158].

Poly(butylene succinate) (PBS) is a white crystalline thermoplastic with a crystallinity of 57 %. It is soluble in halogenated hydrocarbons, DMSO, DMF, THF, dioxane, etc. It has good processability with a T_g of -37 ˚C and T_m of 116 ˚C. It can be processed in various molded product, for example, injected, extruded and blown materials [163]. Figure **4** schematically represents the salient physical properties of widely used biodegradable polymers.

Poly(butyrate adipate -*co*-butylene terephthalate) (PBAT) is a random copolymer which has low crystallinity, thus, exhibiting high flexibility and toughness properties. The T_g value for PBAT are reported to be -30 to -35 °C and has a wide melting point range from 110-120 °C [164].

Some other examples of aliphatic biodegradable polyesters are poly(1,4-dioxan-2-one) and poly(1,5-dioxapan-2-one) which include both ester and ether linkages. The former is a crystalline material whereas latter is amorphous. Poly(1,4-dioxan-2-one) has good tenacity, flexibility and elasticity similar to those of human tissues that make it a potential material for biomedical applications. In contrast, poly(1,5-dioxapan-2-one) is a sticky and gel like material at body temperature [85-86].

4. WATER SOLUBLE BIODEGRADABLE POLYMER

Water soluble polymers are a distinct class of biodegradable polymers having biomedical applications due to their enhanced biodegradability. The most versatile example of such kind of polymers is Poly (vinyl alcohol) (PVA). Many other polycarbonates, polyester-carbonates and polyesters are also reported as water soluble polymers. PVA is a biodegradable, semi-crystalline thermoplastic polymer with a high hydrophilic character due to the ability of forming hydrogen bonding with water molecules. PVA has good thermal stability and chemical resistance but highly hydrophilic characteristics results in poor mechanical and barrier properties. To make such polymers appropriate for packaging applications their blends

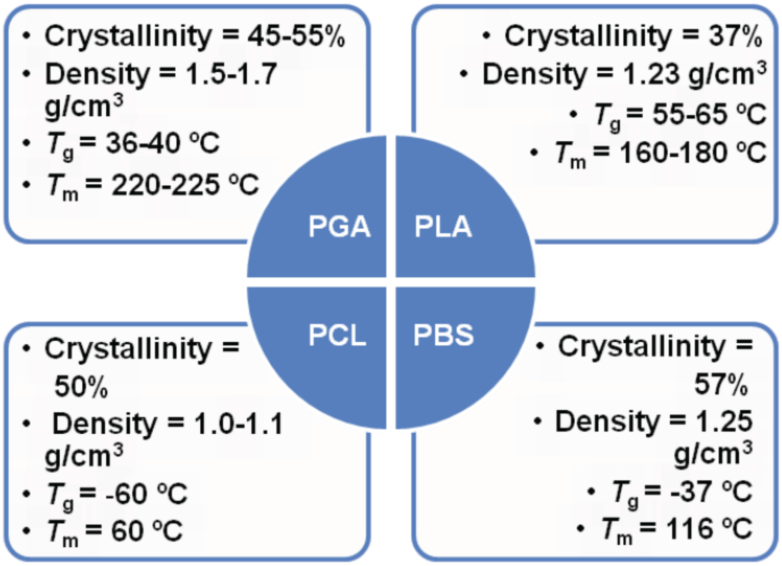


Figure 4: Physical properties of widely used biodegradable polymers [85-86, 158-162].

have been made incorporating fillers such as cellulose etc. that improves its physical and barrier properties. This section emphasized on the polymers, blends and composites of water soluble polymers that make them different from other non-water soluble biodegradable polymers in-terms of properties and degradation pattern.

Rashid *et al*. synthesized environment friendly packaging material from blends of carboxymethyl cellulose (CMC) and poly (vinyl alcohol) (PVA) using casting method. CMC is a cellulose ether and a copolymer of b-D-glucose and b-D-glucopyranose 2-O-(carboxymethyl) monosodium salts. In this work CMC/PVA blend films with and without HCl with different compositions were prepared and films have shown good biodegradability [165]. Moreover, PVA and CMC bioactive films prepared by Fasihi *et al*. and stabilized them via a Pickering emulsion to improve its antioxidant and antimicrobial properties. The polymer blend was emulsified with oleic acid (OE) and incorporated with rosemary essential oil (REO). Essential oils contain phenolic and terpenoid compounds, which show high antimicrobial properties. Therefore, the application of essential oils in active packaging is important in-view of preservative free foods and its packagings to control the microbial growth of food products [166].

An electrospinning technique was adopted by Chahal *et al*. for nanofibers from modified cellulose (MC) and polyvinyl alcohol (PVA) for a scaffolding material in bone tissue engineering. PVA present in the blend increased the spinnability as well as improved the mechanical and thermal properties of the nanofibers. As the percentage of PVA in the nanofibers decreased, the crystallinity of the nanofibers decreased, thus, making them suitable for scaffolding applications. The nanofibers are non-woven in nature, thus, the pores are interconnected making the nanofibers suitable for cell attachment and nutrient transfer [167].

A biodegradable polymer blends containing cellulose and PVA has been synthesized by Hameed *et al*. using solvent as an ionic liquid, 1-butyl-3-methylimidazolium Chloride (BMIM)Cl which can be used for food packaging applications. In this work cellulose and PVA were dissolved in the ionic liquid separately and then mixed followed by the precipitation in excess of ethanol. Ionic liquid is soluble in ethanol and recover afterwards. The blends were made in the form of films, rectangular blocks and fibres and out of the three forms, the film showed optical transparency over the entire film composition. (BMIM)Cl was recycled in this process thus making it eco-friendly and cost-effective [168].

Qiu *et al*. synthesized biodegradable composites containing microfibrillated cellulose (MFC) suspension and PVA which can be used as a substitute for non-biodegradable plastics. Glyoxal is considered to be a suitable crosslinking agent for the blend due to its low toxicity and good biodegradability. Glyoxal was added to the blend to make PVA partially insoluble and to give chemical crosslinking between pure PVA, pure MFC and MFC-PVA to improve the mechanical and thermal properties of the blend. MFC were obtained by shearing and homogenization processes carried over cellulose fibres thus giving short length MFCs. It was demonstrated that nanofibrillated and microfibrillated cellulose caused inhibition to crystallization of PVA [169].

Susane *et al*. synthesized composites containing polyvinyl alcohol (PVA) and reinforcement material such as cellulose in trifluoroacetic acid (TFA) which acts a plasticizer. The blend formed has hydrogen bonds between hydroxyl groups present in the polymers which gives well blended composites. TFA tends to react with the hydroxyl groups present in the cellulose to give trichloroacetate derivatives and solubilizes cellulose. Hence, the intermolecular and intramolecular hydrogen bonds between the cellulose molecules break and hydrophobicity of the composite increases. Thus, produced composites can be used as hydrophobic plastics or films [170].

The composite films for food packaging application using PVA, chitosan and cellulose nanocrystals (CNC) prepared by E. Fortunati *et al* using solvent casting method. The nanocrystals used were derived from barley straw and husk using two different techniques, enzymatic and chemical alkaline pretreatment followed by acid hydrolysis. The composite have applications as food packaging material [171].

Robert *et al*. prepared two biodegradable polymer blends containing cellulose acetate (CA) and two water soluble polymers, namely, bio-sourced hydroxyethyl cellulose (HEC) and PVA. Plasticization of CA was carried out by triacetin, PVA by glycerol and that of HEC using a two-step method with an appropriate plasticizer to achieve better properties and processability [172].

The degradation pattern of PVA has enzymatic degradation methodology where due to the presence of dehydrogenase and oxidase enzymes, PVA initially undergoes specific oxidation of 1,3-hydroxyl groupsto give (beta)-hydroxilketones and 1,3- diketone moieties. Then the moieties undergo carbon-carbon bond cleavage due to the presence of specific (beta)-diketone hydrolase to give methyl and carboxyl ketone end group compounds [173].

Many researchers have reported on water soluble polycarbonates having applications in biomedical field. Wang *et al*. reported on a functionalized water soluble polycarbonate useful for biomedical applications. The reported polymers are amorphous in nature and soluble in water and most of the organic solvent and have relatively faster hydrolytic degradation rate [174]. Lee at el. reported on water-soluble poly(ester-carbonate) having pendent amino and carboxylic groups on the main-chain carbon through melt ring-opening/condensation reaction of trans-4-hydroxy-N-benzyloxycarbonyl-L-proline (N-CBz-Hpr) with 5-methyl-5-benzyloxycarbonyl-1,3-dioxan-2-one (MBC). The author studied the effects of monomer compositions on the glass-transition temperature. The values of T_g of the copolymers depended on the molar fractions of cyclic carbonate and it is reported that decrease in cyclic carbonate fraction increases the T_g. [112]. Zhang *et al*. reported on a water-soluble polycarbonate poly(2-dimethylaminotrimethylene carbonate) with dimethyl amino pendant groups using Novozym-435 as a catalyst through ROP of six membered monomer dimethylaminotrimethylene carbonate. The authors studied the *in vitro* cytotoxicity assay that showed polycarbonate with low cytotoxicity [175].

A novel class of water soluble polyesters are reported by Dhamaniya *et al*. based on tartaric acid derivatives. The hydroxyl functionalized polymers are soluble in water and solubility vary with the diol chain length in polymer structure. These polymers could have applications in controlled drug delivery [58].

5. BIODEGRADABLE POLYMERS BASED ON CO_2

CO_2, a greenhouse gas significant contribution to air pollution and also has a sizable contribution to global warming and greenhouse effect. Therefore, utilizing and thus, consuming CO_2 through various process has been one of the primary research topics recently. Carrying out copolymerization CO_2 as a monomer along with epoxides to give biodegradable polycarbonates has been considered to be one of the solutions to this problem. The use of epoxide has proven to make the polymer multi-functional. Double metal cyanide complexes have been commonly used as a catalyst for polymerization, however, novel catalysts have also been put in use for this purpose. The use of epoxides for various catalysts, reaction conditions or additional monomers have been used for polymerization in order to improve the polymerization efficiency, to improve the biocompatibility and biodegradability or to make the polymer suitable for diversified applications in electronics, biomedical or other allied fields. This section have the methods, catalysts used for polycarbonate synthesis as well as various blends formed by the CO_2 based polymer with other biodegradable polymers and their applications [24, 176-177].

Kim *et al*. prepared polycarbonates by copolymerizing CO_2 and several epoxides, in the presence of double metal cyanide (DMC) as the catalyst. However, it was demonstrated DMC is a more suitable catalyst for copolymerization for epoxides of alicylic oxide type rather than the alkylene oxide type [21]. On the contrary, a series of novel catalysts based on Chromium Schiff complexes were used by Niu *et al*. to carry out alternate co-polymerization of racemic propylene oxide along with carbon dioxide in the presence of (4-dimethylamino) pyridine to produce polycarbonates. The catalyst when subjected to 40 °C and under 1.5 MPa with the binary catalyst system molar ratio of 1:1 during the reaction gave maximum efficiency. When N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-phenylenediamino chromium III (NO_3) was used as a catalyst, product with highest selectivity was obtained, whereas, N,N'-bis(3,5-dichlorosalicylidene)-1,2-phenylenediimino chromium III (NO_3) catalyst gave highest activity during polymerization [178].

Moreover, polymerization of carbon dioxide and cyclohexane oxide was carried out by Cuesta-Aluja *et al*. using two catalysts, namely, 5,10,15,20-tetra(2,6-difluorophenyl)porphyrinatomanganese(III) acetate complexes and 5,10,15,20-tetra(2,6 dichlorophenyl) porphyrinatomanganese(III) acetate to give poly(cyclohexane carbonate). Co-catalyst was not used for the polymerization. The catalysts were highly effective for both, cyclo-addition of terminal epoxides with high selectivity with CO_2 using substrates such as epichlorohydrin, propylene oxide, styrene oxide and 1,2-epoxytetradecane as well as for selective copolymerization of cyclic epoxides with CO_2. The author also suggested that the presence of halogen atom in the catalyst can be one of the reasons for the good performance of the catalyst [22]. Another novel catalyst was used by Lu *et al*. to carry out polymerization of CO_2 and a mixture of racemic epoxides to produce propylene carbonates. A catalyst based on chiral salenCo-(III)/quaternary ammonium halide was used and it was proven that the catalyst action was effective giving a good yield. Since, mild conditions were prevalent in the system and no organic solvent was used for the reaction, the polymerization reaction was considered to be environment friendly [23].

Liu *et al*. also used a new catalyst to polymerize a copolymer containing CO_2 and four epoxides to give poly (vinyl cyclohexene carbonate) (PVCHC). The four epoxides used were cyclohexene, allyl glycidyl, propylene oxide and 4-vinyl-cylcohexene-1,2-epoxide. The catalyst was basically based on (3,3′-dithiodipropionic acid) DTDPA starter along with (salen) CoTFA/[bis(triphenylphosphine)iminium ([PPN]TFA) binary system. The synthesized polymer can be further sulphonated to make the polymer suitable to be used as a polymer surfactant. The disulphite bond in the sulphonated PCCMA polymer can be broken under mild reductive conditions, thereby, making the polymer redox responsive in nature [179].

Synthesis of novel biodegradable polycarbonates using CO_2 along with soyabean oil-based terminal epoxides (SOTE) was reported by Chang *et al*. Several additives such as epichlorohydrin and soap in the ratio of 17.3:1 along with 2.4% cetyltrimethylaluminium bromide (CTAB) (taken with respect to 1mol soap) were added during the reaction. The reaction was carried out for 28.4 min under reflux conditions using a Box-Behnken experimental design. All of these parameters together gave optimum properties to the polycarbonates. The synthesized polycarbonates found applications in packaging materials [180]. Biodegradable polycarbonates (PC-g-EGm) were prepared using CO_2 along with methoxyethoxy (MEMO) or (methoxyethoxy)ethoxy (ME2MO) and binary (salen)Co(III)-Cl/PPNCl as the catalyst by Zhou *et al*. The polycarbonate derived from two units of oligoethylene glycol also denoted as PC-g-EG2 was soluble in water at room temperature to give a clear solution. The synthesized polycarbonates were thermo-sensitive. Thus, they could degrade at temperatures equivalent to body temperatures, thereby, making them suitable for biomedical applications [176].

Polycarbonates used in biomedical applications could also be synthesized from CO_2 and propylene oxide with an alternate arrangement of CO_2 and the epoxide was reported by Geschwind *et al*. The polymer was also incorporated with (1,2-epoxy-5-hexene) EH to enhance the properties. Thus, this process can be a facile alternative to the ring opening polymerization using six-membered cyclic groups to synthesize a similar polymer. Double bonds can be introduced to the polymer chain using this technique. PLA can be incorporated in the chain to make the polymer biodegradable, thus, making the polymer suitable for biomedical application [24].

Moreover, a novel multi-arm polymer derived from hyperbranched poly (propylene oxide) (hbPPO) along with poly(propylene carbonate) (PPC) was prepared by Hilf *et al*. The hbPPO was the core and PPC formed the flexible arms. The flexible arms were formed by copolymerization using glycidol, macroinitiator hbPPO along with CO_2 and propylene oxide (PO) as the monomers. (R, R)-(salcy)CoOBzF5 was used as a catalyst for efficient polymerization. The synthesized polycarbonate contained polyols, thus, making it suitable for polyurethane synthesis along with a compound containing isocyanate group [25]. Whereas, Liu synthesized polycarbonates (PPCMA) using CO_2, propylene oxide and maleic anhydride as the co-monomers and zinc adipate (ZnAA) as the catalyst to give upto 30% ester content [26]. Moreover, aliphatic polycarbonates (PPCIAn) were synthesized by Song *et al*. by copolymerizing CO_2, propylene oxide (PO) and itaconic anhydride (IAn). IAn was incorporated in PPC to increase the molecular weight and the polymer yield. The polycarbonates consisting of upto 5% (mol%) IAn in comparison with the PO content exhibited optimum mechanical and thermal properties. These polymers are crosslinkable and degradable in nature, thus, they are suitable for biomedical applications or can be used as plastics [181].

The polycarbonates (PC) can be combined to form blends or composites with biodegradable polymers, thus, making the synthesized polymer degradable. Since, the PC derived from CO_2 consume one of the major air pollutants and PC/biodegradable polymer blend is degradable, these polymer blends can be used a substitute for various non-biodegradable polymers and plastics used in biomedical, packaging and other allied applications.

Liu *et al*. used a bimetallic catalyst supported over a polymer to polymerize CO_2, PLA and propylene oxide to give biodegradable polycarbonates (PPCLA). Thus, the synthesized polymer finds applications in controlled drug delivery [182]. Whereas, Lee *et al*. synthesized PLA and PC blends (70/30 wt %) using various compatibilizers. It was demonstrated that on incorporation of 5 phr SAN-g-MAH compatibilizer, the blend exhibited optimum mechanical, rheological and morphological properties. As the blend containing SAN-g-MAH has enhanced tensile and impact strength, the hydrolytic degradation of the blend took longer time as compared to other blends containing other compatibilizers [177]. A study on degradation characteristics was carried out by Yuryev *et al*. and polycarbonate/PLA polymer blends where exposed to deionized water. It was demonstrated that the hydrolytic degradation of the blend took place in two stages: 1) water diffusion and pit formation. 2) water transportation through pits causing PLA degradation accompanied with water absorption. As the PLA undergoes degradation, the pH of the solution reduces thereby, causing degradation of the polycarbonate component [30].

On the other hand, another biodegradable polymer, namely PHBV was blended with PPC using the solution casting method as reported by Tao and was subjected to various conditions conducive to degradation of the blend to observe its degradation properties. It was observed that the blend components were immiscible and the PPC component was amorphous, whereas, PHBV exhibited higher degree of crystallinity. It was further demonstrated that the thermal stability of the blend enhanced on incorporation of PHBV. It was proven that PHBV was more susceptible to natural environment, thus, causing it to degrade under the action of enzymes in the soil suspension. However, the PPC component was prone to simulated conditions, since, on hydrolysis PPC underwent random chain scission causing degradation. The author further stated that PLA can be incorporated in the blend to improve the blend characteristics [27].

Hwang *et al*. synthesized polycarbonates using propylene oxide and CO_2 using zinc glutarate as the catalyst. The process was made environment friendly by using PO as the reaction medium, thereby, not generating any organic solvent waste. PCL was incorporated in the blend because of its compatibility with the comonomers and biodegradation properties to form poly(propylene carbonate-*co*-caprolactone). It was demonstrated that the polymer degrades under enzymatic degradation conditions using lipase enzyme. It was further demonstrated that PCL degrades to more extent than the other polymers present in the blend, thus, making the polymer suitable for biomedical applications [28].

6. BIODEGRADABLE POLYMERS AS 3D MATERIALS

3D printing, alternatively called as additive manufacturing is basically a printing operation carried out using computer controlled devices to produce 3D objects by laying layers of material over one another. The data of the required product is stored in an additive manufacturing file in the computer. The most commonly used technique for biopolymers for 3D printing is the fused deposition modelling (FDM). A filament derived from a thermoplastic material is fed into an extruder which has a heating unit attached to it. The heated filament extruded from the printer is laid in the form of the required object and which hardens immediately to give rigid layers.

Biodegradable polymers, particularly, PLA has been extensively used as a filament for 3D printing. PLA and other biodegradable polymer filaments can be incorporated with nanoparticles or nanofillers to form a blend or a composite, in order to enhance the properties of the filament and thus, of the final printed object. 3D printing has a major application in the formation of scaffolds and in other tissue engineering applications. Since, the scaffolds are derived from biodegradable polymer filaments, they are biocompatible and biodegradable under enzymatic action. Thus, these scaffolds undergo degradation after a specific time period and thereby, saves the cost and risk of carrying out a second surgery for the implant or scaffold removal. The pore size, size distribution and geometry of the scaffold can be varied using 3D printing technique which is not possible using the other conventional techniques. The 3D structure can appropriately mimic the extracellular matrix and can be synthesized as per the requirement of the patient, thus, making it best suited for the patient's body aiding in acceptance by the body and faster recovery [31, 183-185].

6.1. PLA as a 3D Printing Material

Sabatina *et al*. used PLA filaments as the input to inexpensive fused deposition method (FDM) 3D printing technique to print different woven and knitted textile substrates. The prints had good quality and adhesion properties and thus, the printed samples could be used to manufacture garments [29]. Similarly, wearable electronics, medical braces, foot insoles were printed by using FDM 3D printing technique various knitted and woven cotton, wool and other substrates using PLA filament as reported by Pei *et al*. [186]. A novel electro-hydrodynamic jet printing with FDM technique (E-FDM) was employed by Zhang *et al*. to prepare 3D printed tissue regeneration scaffolds with using poly(lactic acid) PLA filaments with different structure sizes. The 3D printing technique gave high speed and high resolution prints i.e. upto submicron level and directly used PLA filament [187].

3D scaffolds used in bone tissue engineering applications could also be prepared using FDM 3D printing of PLA as reported by Wang *et al*. These scaffolds were further given inexpensive cold atmospheric plasma (CAP) surface treatment to incorporate nano-scale extracellular matrix properties and biocompatibility in them. CAP consists of several ionized gases such as reactive oxygen and nitrogen species, electrons, ions, free radicals, etc. The treatment initially consists of application of high voltage to the surface in presence of helium gas followed by treatment at room temperature. The CAP surface modification improves wound healing and sterilization properties of the printed specimen aiding in bone regeneration and cell attachment [188].

Zhuang *et al*. synthesized conductive graphene doped polylactic acid (G-PLA) composites using programmed mixing printing method. These G-PLA were used in 3D printing to yield products with good anisotropic heat and resistance distribution. These properties exhibited by the printed objects were dependent on the extrusion ratio as well as the mix ratio used during the printing operation. It was observed that, with increase in the G-PLA content in the printed sample, the resistance of the sample reduced, thus, reducing the heating of the material on exposure to electric field. These composites can be used to 3D print different plastics with custom modified properties or polymer materials which have applications in different fields such as architecture, engineering, etc. [183].

Moreover, FDM 3D printing carried out using grapheme incorporated PLA filament also produced patient specific implants and orthopedic scaffolds with graded porosity and optimum density as reported by Bustillos *et al*. The polymeric chains were restricted by graphene giving reduction in crystallinity, enhancement in the creep resistance and other mechanical properties. The 3D sample prepared from these composites exhibited superior wear and creep resistance as compared to that prepared using pure PLA filaments [189]. Sanatgar *et al*. used FDM 3D printing technique to print polymers or nanocomposites to print on textile substrates such as PLA on PLA fabric, multi-wall carbon nanotubes/PLA (CNT/PLA) nanocomposites on PLA fabrics nanoparticles of carbon black/PLA (CB/PLA) on PLA fabric substrates. CB and CNT used as conductive polymer nanocomposites (CPCs), thus, the printed samples containing them can be used in static dissipative and radiation shielding applications [190].

Application of continuous fiber reinforced thermoplastic composites (CFRTPCs) in printing 3D samples which could be used in aviation and aerospace applications was carried out by Tian *et al*. The developed 3D printed samples were light-weight and an efficiently performing alternative to conventional materials. These CFRTPCs were formulated using polymer matrix of poly (lactic acid) (PLA) filament and reinforcement of continuous carbon fibers which were fed to fused deposition modelling (FDM) 3D printers simultaneously. Fiber content of 27% gave optimum mechanical properties to the composite. Layer thickness of 0.4 mm to 0.6 mm exhibited optimum bonding between the layers [184]. Moreover, novel PLA grafted cellulose nanofibers (PLA-g-CNFs) by grafting L-lactide monomers on cellulose nanofibers (CNFs) using ring-opening polymerization were synthesized by Dong *et al*. Grafting is carried out to avoid the aggregation of hydrophilic nanocellulose in hydrophobic PLA [191].

Other additives such as iron oxide (Fe_2O_3, Fe_3O_4) nanoparticles were incorporated in PLA filaments to synthesize multi-well plates by Su *et al*. These plates were used for FDM 3D printing. The iron oxide nanoparticles used for the fabrication have intrinsic peroxidase properties, thus, the prepared printed samples can be used as reusable reactionware. It was also suggested that the consumption of iron oxide can be reduced if only the inner wall was printed using the functionalized multi-well plates instead of the complete reactionware using the same technique as mentioned above [192]. Guo *et al*. synthesized a flame retardant bionanocomposite by melting 82% PLA, 1% Cloisite 30B (C-30B) and 17% melamine polyphosphate (MPP) to obtain optimum mechanical properties as well as to give an easy compounding and high performance formulation [193].

6.2. PCL as a 3D Printing Material

Hollander *et al*. employed PCL filaments using a model drug indomethacin in 3 concentrations using hot-melt extrusion technique. These modified filaments were used to print T-shaped prototypes of intrauterine system using FDM 3D printing technique. The morphology and other properties of the filament and printed samples were dependent on amount of drug loaded in the sample [31]. On the other hand, Mendoza-Buenrostro *et al*. embedded PCL nanofibers using electrospinning technique in FDM fabricated layers of PLA filament to produce a biodegradable 3D hybrid scaffold. Three techniques namely, FDM, micromilling and electrospinning have been combined to achieve multi-scale and multi-material manufacturing [194].

Antimicrobial wound dressing from 3D scanned templates were prepared by Hassan *et al*. using novel PCL based filaments reinforced with metal ions which can be used in inexpensive FDM 3D printing machine. The printed specimens contain silver and copper particles which show good bactericidal properties against common bacterium causing skin infections and aid in wound healing process, thus, the specimens can be used in producing patient specific wound dressings. The metal ions were incorporated in the filament using hot melt extrusion technique. These printed dressings were anatomically adaptable. Hence, they were more efficient than the conventional flat dressings and could be modified according to the shape, size and antimicrobial activity requirements [195]. Roncaa *et al*. reported 3D nanocomposites with poly(ε-caprolactone) matrix and hydroxyapatite nanoparticles as a reinforcement using 3D fiber deposition technique. It can be demonstrated that the biological performance such as cell adhesion and spreading as well as mechanical properties of the nanocomposite improved with the incorporation of the hydroxyapatite nanoparticles. The prepared nanocomposite can be used in scaffolding applications [185].

6.3. Other Biodegradable Polymers as a 3D Printing Material

Use of a novel filament derived from composites from polyhydroxyalkanoate and modified palm fiber which can be used as 3D printing filament to give low cost, eco-friendly imitation wood was reported by Wu *et al*. PHA was modified with maleic anhydride using the grafting technique to give PHA-g-MA, whereas PF was treated with silane coupling agent to improve the mechanical properties and to increase the interfacial adhesion of the blend [196].

7. BLENDS OF BIODEGRADABLE POLYMERS

Polymer blending is known to be the most effective method for modification of polymer characteristic such as thermal resistance, mechanical strength, barrier properties, degradation rate etc. The obtained blends generally have properties that are not shown by their separate components. The properties of blends depend on many factors such as methodology of preparation, fractions of the components, and types and properties of added additives.

A proper homogenization of two components imparts the strong adhesion at the phase boundary. This is difficult to achieve as blending components have thermodynamic immiscibility in case of majority of polymers. Due to this immiscibility, polymer blends tend to separate into two or more distinct phases. Phase morphology have high influence on the properties of polymer blends. The end morphology of multiphase polymer blends depends on both intrinsic factors such as structure of blend composition and interfacial tension as well as extrinsic factors such as shear conditions, viscosity ratio, and processing parameters. In general, the processing of polymer blends is an easy, low-cost, scalable way to enhance the properties of the pristine polymers, therefore it is an interesting way to develop biodegradable polymer blends for applications like biomedical and packaging.

7.1. Blends of PLA and PCL

PLA is a most promising biodegradable polymers and its high stiffness makes the polymer very promising for medical applications but high brittleness is a serious drawback and required toughening. The increase in PLA toughness can be achieved by their blending with soft, ductile polymers with a low glass transition temperature. Thus PCL could be a good option for blending due to its biocompatibility combined with ductility and low Tg.

Kelnar *et al*. used graphite nanoplatelet (GNP) for preparation of blends with PLA and PCL. The incorporated GNP works as reinforcements and electron microscopy was employed to know its presence in polymer blends [197]. Malinowski prepared PLA/PCL blends using co-rotating twin screw extruder and incorporated with triallyl isocyanurate (TAIC). These blends were exposed to electron beam irradiation which led to crosslinking of macromolecules thereby hindering the phase separation of the blend components [198]. Ostanfinska *et al*. reported on PLA/PCL blends of 80/20 composition by varying the viscosity of the PLA component using the melt mixing followed by compression moulding methods. It was studied that a decrease in the PLA viscosity led to an increase in the average particle size of PCL thereby reducing the toughness properties of the matrix. The PLA component in the blend influenced the stiffness properties whereas, the PCL component in the blend influenced the toughness properties of the blend and these properties were dependent also on the particle size distribution of the components in the matrix. Thus, these blends can be converted into tailor made products which are suitable for tissue engineering applications [199].

Wachirahuttapong *et al*. synthesized PCL/PLA blends using Pluronic as the plasticizing agent using the melt blending technique. While Pluronic was added to the PLA/PCL blend of 90/10 and 85/15 composition, smaller sized PCL particles were obtained in the blend. It was demonstrated that the PLA was present in the blend in the form of spherulites [200]. Navarro-Baena *et al*. synthesized blends of PLA/PCL in various compositions to study their shape memory properties using the extrusion techniques. These blends can be low cost and easily processable alternatives for various agricultural, food packaging and biomedical applications. It was reported that the blend components formed different phases, since, they were immiscible [201]. Mofokeng *et al*. incorporated TiO_2 nanoparticles in PLA/PCL blends and reported that Tg (lass transition temperature) of the blend was not affected by the incorporation of the nanoparticles [202].

7.2. Blends of PLA and PHBV

Li *et al*. reported blend fibers of PLA and PHBV using melt spinning and hot drawing method. The blend gave overall good heat resistance and mechanical properties such as softness and tensile strength due to the absence of spherulites and increase in PHBV content. It was studied that the incorporation of PHBV in the PLA matrix gave better orientation and crystallization of the matrix [203]. PHBV/PLA blends with different compositions reported by Xu *et al*. which can be used for denitrification process. It was demonstrated that the denitrification efficiency improved on increasing the weight ratio value of the blend components [204]. Yang *et al*. reported PLLA/PHBV blend films using the transesterification process with zinc acetate catalyst. Melt blending technique along with the efficient catalyst used for the blend formation, produced a highly miscible blend with enhanced mechanical properties. It was demonstrated that the PLLA/PHBV co-polymer, itself acted as a compatibilizer for the blend formation, thereby, further enhancing the miscibility and ductility of the blend [205].

Zembouai *et al*. prepared PLA/PHBV blends in 50/50 composition and 5 wt% of PHBV-g-MA compatibilizer and 2 wt% of Cloisite 30B were incorporated in the blend to improve the blend properties. The blends were subjected to gamma irradiation which led to degradation of the blend. The blends can be used in applications related to packaging sterilization and food irradiation [206].

7.3. Blends of PLA and PHB

Arrieta *et al*. reported on optically transparent blend films containing PLA and PHB (Poly(hydroxybutyrate)) using the melt blending technique followed by film formation process. The PHB acted as an efficient nucleating agent which aided in PLA crystallization. 15% Acetyl (tributyl citrate) (ATBC) was added as a plasticizing agent which enhanced the processability of the films [207]. In further extension of this work Arrieta *et al*. reported on PLA/PHB (75:25) incorporated with CNC along with ATBC as the plasticizer by electrospinning technique. Optimum blend properties were obtained on incorporation of 15% ATBC and 1% CNC in the blend [208].

A PLA/PHB blend in 75/25 wt proportion suitable for food packaging and other one-time use applications where prepared by Abdelwahab *et al*. using Lapol 108 as the plasticizer. The plasticizer did not affect the properties of the pure PLA/PHB blend to a great extent. However, the addition of PLA in PHB reduced its biodegradability [209]. On the other hand, Nicosia *et al*. adopted the electrospinning technique to prepare novel PLA/PHB nanofibrous membranes which are suitable for biodegradable aerosol particle filtration applications. These nanofibers were further functionalized using 0.5% quaternary [DDA][NO_3] ammonium based ionic liquids, thereby, increasing their antifungal activity [210]. Armentano *et al*. adopted extrusion technique to prepare PLA/PHB blends using lactic acid oligomer as a plasticizer for better miscibility and properties. The author reported the use of the blends incorporated with 30% lactic acid oligomer for one-time food packaging with superior barrier properties and poor migration properties [211].

7.4. Blends of PLA and PBAT

Wang *et al*. reported on solution casting technique to prepare polymer blends of PLA and PBAT

(Polybutylene adipate-co-butylene terephthalate). The incorporated PBAT in small amounts in the film gives flexibility, mechanical, thermal, UV screening and anti-fogging properties to the blend, thereby making the films suitable for fresh fruits, vegetables and other food packagings [212]. Lu *et al*. reported on different PLA/PBAT blends using counter-rotating twin-screw extruder by varying viscosity ratios. It was observed that the compatibility of the blend components improved on increasing the viscosity ratio thereby improving the tensile strength and other mechanical properties. Thus, the blends with viscosity ratio 1.95 exhibited enhanced impact properties whereas the blends with ratio 0.4 and 0.77 exhibited enhanced tensile properties [213].

Internal batch mixing was employed by Nofar *et al*. to synthesized PLA/PBAT (25 wt%) blends incorporated with 1 and 5 wt% Cloisite 30B. In case of blends containing 1 wt%, the nanoclay particles were localized in the interface and acted as a droplet coalesce barrier at the interface. On the contrary, the blending technique and parameters affected the occurrence of dispersion of 5 wt% nanoclay particles in the blend. Thus, the nanoclay quantity can be modified according to the requirement to modify the blend morphology [164].

Arruda *et al*. synthesized films from PLA/PBAT blends in two compositions, 40/60 and 60/40 along with Joncryl ADR 4368 epoxy resin compatibilizer. Two types of morphology of PLA was particularly seen in the blend. Blends with 60% PLA showed skin-core morphology and the blend along with compatibilizer showed a coarse sheet or ribbon like morphology whereas, blends with 40% PLA without compatibilizer showed elongated and fibrillar morphology [214]. Thermal stability of PLA/PBAT blends was studied by Al-Itry *et al*. It was reported that the individual polymer components of the blend degrade, thereby causing an overall decrease in the weight and intrinsic viscosity of the blend. It was also demonstrated that the addition of a compatibilizer Joncryl which contains glycidyl methacrylate functional groups enhanced the thermal stability of the blend [215].

7.5. Blends of PLA and Natural Polymers

Muller *et al*. reported on PLA and TPS blends using glycerol as the plasticizing agent. It was studied that maximum amount of the plasticizer was present in the starch phase and do not penetrate in PLA phase. Blending of the two components resulted in heterogeneous, two phase structure at all compositions. The two components do not exhibit strong interfacial adhesion, thus, stress cannot be transferred through the surface, thereby, giving a blend of poor strength and mechanical properties [216]. Shirai *et al*. reported on blends based on PLA and TPS, such that both the blend components were plasticized using different plasticizers. PLA was plasticized using two plasticizers, namely, adipate esters and citrate esters to give different blends which aided in the pellet formation which were essential to form blend films. Whereas, starch was plasticized with glycerol and PLA was plasticized with low concentration adipate esters, particularly using DEA, the blend prepared had optimum mechanical and structural properties [217].

Quintan *et al*. reported on blends containing PLA, cellulose acetate (CA) and PLA grafted cellulose acetate polymers (CA-g-PLA). Cellulose acetate was plasticized using triacetin as the plasticizer in a twin-screw extruder to produce thermoplastic cellulose acetate. The CA/PPLA blend was obtained by ring opening polymerization of both D and L-Lactide. The plasticized PLA, CA as well as the PLA/CA co-polymers gave modifiable mechanical properties to the blend. The blends containing grafted polymer exhibited higher interfacial interaction between the CA and PLA phases [218]. Wang *et al*. reported on carbon fibers by stabilizing and carbonizing precursors derived from Lignin/PLA blends. The presence of PLA in the fiber formed hydrogen bonds with lignin and also improved the spinnability of the blend thereby producing cylindrical shaped fibers. Thus, the presence of hydrogen bonds in the blend cancelled out the negative effect of the presence of voids in the blend formed during the volatilization of PLA, thereby, giving good tensile strength to the carbon fiber. The fiber prepared from 80/20 lignin/PLA composition gave optimum tensile strength to the fiber [219].

7.6. Blends of PCL and Natural Polymers

Novel blends of cornstarch and PCL were reported by Shen *et al*. These blends aid in denitrification process carried out in constructed wetlands by acting as an external carbon source. The blends particularly capture bacteria Bacillus (24.25%) and Thauera (9.36%) during the denitrification process. The blends also efficiently captured the polysaccharides which predominantly consisted of sugars [220]. Figueiredo *et al*. reported on a novel technique to synthesize blend films from bacteria cellulose (BC) and PCL using the in situ polymerization method. The first step for blend formation was to form a dispersion of PCL powder was obtained in a BC culture medium consisting of *gluconacetobacter sacchari* bacteria. The dispersion was then subjected to agitated incubation to form the blend. The polymer blend can be used in food packaging and biomedical applications since, no organic solvent was used for the polymer synthesis and the polymer components are biodegradable as well as biocompatible [221].

7.7. Other Blends

Goonoo *et al*. reported on novel blend films from semi-crystalline polymer matrix along with anionic sulfated polysaccharides derived from seaweeds. Two types of blend films were obtained from two pairs of combinations. The combinations were polyhydroxybutyrate (PHB) and polyhydroxybutyrate-*co*-valerate (PHBV) with kappa-carrageenan (KCG) as well as polyhydroxybutyrate-*co*-valerate (PHBV) with fucoidan (FUC) giving PHB/KCG, PHBV/KCG and PHBV/FUC blends respectively. PHBV/KCG exhibited higher water uptake, demineralization potential and cellular activity amongst all the blends. The study suggests, this may be immiscibility of the polymers giving higher amount of hydrophilic biopolymer on the surface. Thus, the synthesized blend finds application in cell culture and tissue engineering field [222].

Torres-Huerta *et al*. reported on blends of commercial and recycled PET/PLA and PET/chitosan using the extrusion technique. The blend gave optimum mechanical properties on incorporating 5wt% and 10wt% of chitosan and PLA respectively. It was observed that the PET/chitosan blend had better miscibility as compared to the PET/PLA blend thereby, demonstrating that the components exhibited little interaction between them. The 95/5 PET/chitosan blend exhibited the best degradation and miscibility characteristics which were similar to those exhibited by the commercial BioPET samples [223].

8. BIONANOCOMPOSITES

Composites are materials which are synthesized by combining two or more materials such that the constituents remain separate and the final material exhibits enhanced properties different from the constituent materials. Nanocomposites are nothing but composites containing atleast one of the components in nanometer size. Biodegradable polymers in itself have several desirable properties however, in general, most of them exhibit poor barrier properties, brittleness and thermal stability. Such drawbacks can be overcome by combining them with other biodegradable polymers or nanoparticles which have very little or no negative effect on their biodegradability. These nanoparticles act as a reinforcement and thus, improve the strength properties as well. Nanocomposites can further be tailor-made by incorporating nanoparticles with application-specific properties such as anti-bacterial or anti-static properties. This review reports on nanocomposites prepared using a biodegradable polymer matrix and various nanofillers as reinforcements have been considered. Since, these nanocomposites have matrix based on biodegradable polymers, they are rendered biodegradable and biocompatible making them environment friendly and suitable for various packaging, biomedical and drug delivery applications [33, 224-227].

8.1. PLA Based Bionanocomposites

Pure PLA polymer exhibits poor thermal stability and mechanical properties such as brittleness and toughness. PLA matrix can be reinforced with other polymers or additives in nanometric sizes to overcome the drawbacks of pure PLA and further enhance the composite properties. PLA and graphene oxide based nanocomposites were reported by Kuang *et al*. by solution blending using supercritical CO_2 as a physical blow agent [32].

The solution casting technique was employed by Madkour *et al*. to prepare bionanocomposites containing MWCNT and graphene nanoplatelet as the reinforcements incorporated in PLA matrices using the solution casting method. The graphene nanofillers exhibited enhanced mechanical as well as thermal properties [224]. Use of pristine functionalized multiwalled carbon nanotubes (pMWCNTs) as a substitute for MWCNTs to prepare bionanocomposites using PLLA as the polymer matrix was reported by Amiriana *et al*. The pMWCNTs were synthesized by carrying out Friedel Crafts acylation on the MWCNTs to give their aromatic amine (MWCNT-NH2) products [225].

It is known that silver nanoparticles (AgNPs) are selected as the nanofillers because of their antibacterial, anticancer and wound healing properties. Sarkar *et al*. exploited this property to synthesize novel antimicrobial bionanocomposites using Poly-D, L-lactide-co glycolide (PLGA) as the polymer matrix and AgNPs as the fillers by the solvent casting technique [226].

Two techniques, namely, melt compounding and film blowing techniques were adopted by Herrera *et al*. to synthesize novel bionanocomposites. The first step of synthesis included melt compounding of 5 wt% chitin nanocrystals (ChNCs), 75 wt% PLA and 20 wt% glycerol triacetate plasticizer (GTA). The product from the first step was further diluted to 1 wt% ChNCs with PBAT and PLA and subsequently film blowing to give the bionanocomposite. The incorporation of chitin nanocrystals in the bionanocomposite, led to an enhancement in the mechanical, barrier properties, however, it led to a reduction in the fungal activity of the bionanocomposite [227].

A novel bionanocomposite was synthesized using electrospun 50:50 poly(L-lactide-*co*-caprolactone) as the matrix and was incorporated silver nanoparticles as the nanofillers by Samberg *et al*. The bionanocomposite exhibits antimicrobial properties due to the presence of silver nanoparticle fillers in it. The technique of the electrospinning the nanofibrous polymer gives a three-dimensional structure to the bionanocomposite which is similar to the natural environment present in the body and it can be easily modified according to the requirements. The separately synthesized silver nanoparticles are incorporated in the polymer solution which is followed by electrospinning. The prepared bionanocomposites can be used as scaffolds in skin tissue engineering operations [228].

Moreover, another PLA/PCL bionanocomposite was prepared by Esmaeilzadeh *et al*. using the solvent-evaporation method with a polymer matrix containing 80% of PDLLA and 20% of PCL (w/w) and bioactive glass nanoparticles (0, 1, 3 and 6wt%) as the reinforcements. PLA matrix is blended with the PCL matrix to overcome the poor mechanical properties of the PLA. Furthermore, inorganic nanoparticles such as bioactive nanoglass fillers are added to overcome the limitations of the polymer matrix blend [34].

8.2. PCL Based Bionanocomposites

3D scaffolds derived from a bionanocomposite using PCL matrix reinforced with hydroxyapatite (HA) nanorods can be prepared using an in situ solvothermal process as reported by Moeini *et al*. It was demonstrated that the strength of the bionanocomposites prepared using this in-situ method were stronger than those prepared by the conventional method. HA nanorods are well dispersed in the biodegradable polymer matrixes to overcome the limitations of PCL matrix. The HA reinforcments in the bionanocomposite exhibit chemical properties similar to the inorganic components present in the bone structure. HA also shows osteoconductive properties. Thus, the synthesized bionanocomposites find applications in preparing 3D scaffolds aiding in tissue and bone regeneration [229].

Guaras *et al*. have synthesized biodegradable polymer/clay bionanocomposites with anhydride-functional polycaprolactone (PCL-gMA) polymer matrix incorporated with thermoplastic starch (TPS). Three types of nanoclays were used as fillers in the composite: two organo-modified montmorillonites with a quaternary ammonium salt (C20A and C30B) and a natural montmorillonite. The bionanocomposite films were synthesized by melt intercalation and successive compression molding. The TPS was synthesized by adding a plasticizer to starch followed by application of heat and shear forces to it. In order improve the mechanical properties of the composite, a compatibilizer like maleic anhydride is added to the composite [230].

8.3. Other Polymer Substrates for Bionanocomposites

Bionanocomposites which find applications as packaging materials for several industrial products, especially in the food packaging applications have been synthesized by Reis *et al*. These bionanocomposites contain PHBV matrix and modified vermiculite (VMTO) and natural vermiculite (VMT) as the reinforcement using the melt intercalation method. The pure polymer as well as the natural vermiculite bionanocomposite exhibited higher biodegradability and better thermal stability as compared to the modified vermiculite bionanocomposite. By using nanoclay fillers the several limitations of PHBV pure polymer can be overcome. Vermiculite is the most suitable choice of nanofiller since, it shows a higher tendency to expand at high temperatures to become a lightweight material as compared to other lamellar nanoclay fillers [231].

Gumel *et al*. prepared a bionanocomposite with medium-chain-length poly-3-hydroxyalkanoate matrix and reinforced it with carbon nanofibers (CNFs) having high surface-to-volume ratio. CNFs present in the bionanocomposite help to overcome the drawbacks of the matrix. In order to enhance the construction of the bionanocomposite, acoustic sonication was used which led to a uniform distribution of CNFs in the matrix giving an improved physical morphology and thermo-chemical properties of the bionanocomposite. These properties render the synthesized bionanocomposites suitable for applications in drug delivery devices, biosensors and organic electroconductive materials [232].

Moreover, novel bionanocomposites were developed by Ahmadizadegan *et al.* consisting of polyimide/cellulose/TiO_2 (PI/BNCs) using inexpensive ultrasonic irradiation process [233].

9. BIODEGRADABILITY OF POLYMERS

There are a number of factors that contribute to the degradation rate of aliphatic polymers. The physical properties of polymer as well as its chemical structure have a crucial effect on the biodegradation of polymers. Various physical parameters such as molecular weight, crystallinity, molecular orientation, surface area, and glass transition temperature etc. determine the rate of degradation in a given set of degradation conditions. For example, PLGA, which is amorphous and hydrophilic in nature, degrades faster as compared to PCL which is crystalline and hydrophobic polymer [86, 234-235]. The chemical structure is also a governing factor for the rate of degradation, for example, polymers with side functional groups, such as, amino, hydroxyl, carboxyl, etc. are more degradable since the presence of functional groups increase the hydrophilicity of polymer backbone that facilitate the attack of water molecules at the labile bonds.

The homogeneous hydrolytic degradation of aliphatic polymers comprises the bulk and surface erosion of polymeric material. The former involves the erosion of material from the entire polymer volume, whereas in latter the material mainly erode from the polymer surface. The term degradation stands for the bond cleavage while erosion corresponds to the depletion of material, hence the erosion of the material is subsequent to degradation. The rate of degradation can be monitored by measuring molecular weight changes or by measuring weight loss. Moreover, there are various tools such as GC-MS, SEM, TEM etc. which can be employed to examine the characteristics of degraded products [86, 235-239].

The biodegradation is a process that degrades the polymer eventually in the water and carbon dioxide with help of microorganisms. Since the microorganisms are not able to transport long-chained, water insoluble polymeric material into the cell, therefore biodegradation initiates with excretion of the extracellular enzymes by the microorganisms. In this process microorganisms depolymerize the polymer outside the cells and produce water soluble lower molecular weight moieties. Once the microorganism intake the water soluble intermediates inside the cells various metabolic pathways are followed and as a result water, carbon dioxide and methane are produced as end product. Different test methods are used to examine the biodegradation of polymers. Here, three categories of test methods (1) field test, (2) simulation test and (3) laboratory test have been described which are broadly used [240-241].

The field test involves a degradation procedure where practical environmental conditions are employed and polymeric samples are subjected to degrade by burying in soil or placing in it a lake/river. This method has variable test conditions since environmental condition such as temperature, pH, and humidity cannot be controlled. It is a disadvantage of field test that is coupled with the poor quantitative recovery of disintegrated polymeric sample from the test site. To overcome the limitations of field tests, simulation tests are employed, where the environment is close to the field test and experiments are carried out in laboratory reactors so that the external parameters such as temperature, pH and humidity can be controlled. The examples of simulation tests are soil burial tests, aqueous aquarium tests, control composting tests etc. The mostly used biodegradable tests are laboratory tests, since environmental conditions are well defined. These tests are carried out in synthetic media and examples are enzymatic degradation tests, clear-zone tests, sturm-tests etc. [213, 240-245].

Luzi *et al*. reported on bionanocomposites using poly (lactic acid) (PLA) as the matrix reinforced with modified and un-modified nanocellulose crystals (CNC) derived from marine waste. The cellulose nanocrystals were modified using a surfactant to improve their dispersion the PLA matrix. The prepared bionanocomposites were then subjected to enzymatic degradation in aerobic condition, 50% relative humidity at 58 °C in the presence of the enzyme proteinase K. It was reported that enzyme could only degrade the L-lactic acid molecules from the matrix and not the D-lactic acid molecules and complete degradation was observed within 14 days [246]. Pelegrini *et al*. synthesized novel composites having poly (lactic acid) (PLA) as the matrix reinforced with buriti fiber and triacetin was used as a coupling agent using the compression moulding technique. The composite was subjected to simulated marine environment such as fish, algae and coral for 600 days to study the degradation trend. It was reported that the degradation of PLA improved on addition of the natural fiber in the matrix, due to the greater accessibility to the PLA matrix to water exhibited by the natural fiber reinforcement. It was further observed that the plasticizer inhibits degradation only upto 45 days. The algae *Bacillariophyceae Fragilariophyceae* class and diatoms present led to the degradation of the composite. The degradation was initiated by the absorption of water by the matrix which was followed by the hydrolysis process leading to complete degradation [247].

Zhao synthesized composites from PLA matrix reinforced with magnesium particles of varied concentrations using solvent casting technique. The composite was then subjected to *in vitro* degradation process using mouse osteoblastic cells. It was demonstrated that the magnesium particles enhanced the biodegradability of the composite as well as the magnesium ions could neutralise the acid products formed due to the degradation of PLA thereby, further supporting the degradation process [248]. Breche *et al*. synthesized a triblock polymer using PLA and poly(ethylene glycol) (PEG) to give PLA-*b*-PEG-*b*-PLA triblock copolymer. The block copolymer was then subjected to *in vitro* degradation at 37 °C in aqueous medium. It was demonstrated that the hydrolytic degradation lead to formation of water soluble oligomers [249]. Huang *et al*. synthesized a composite containing PLA as the matrix and natural rubber as the reinforcement using the compression molding and melt blending techniques. The composite was subjected to hydrolytic biodegradation at 58 °C using deionized water and the incorporated natural rubber did not show any effect on the biodegradation process [250].

9.1. Hydrolytic Degradation

Rocca-Smith *et al*. subjected food packaging grade PLA to different wet conditions such as 50% and 100% relative humidity at 50 ^{o}C and when the sample was immersed in water and saturated vapor for two months. It was observed that the polymer nature changed from glassy to rubbery in the temperature range of 55-60 ^{o}C. It was demonstrated that the sample treated at 50 °C in conditions 100% relative humidity underwent hydrolysis whereas the sample in the conditions of 50% relative humidity underwent physical ageing only. It was observed that the sample immersed in water released lactic acid an oligomers whereas the sample kept in saturated vapor retained these degraded products thereby catalyzing the degradation process. It was demonstrated that water also acts as a plasticizer thereby aiding the degradation process [251]. Franco *et al*. treated PLA to hydrolytic degradation by immersing the polymer in pure water and ethanol of two concentrations 50% and 95% for 180 days. The polymer immersed in 50% ethanol solution exhibited higher crystallinity and higher water absorption, thus, giving faster and efficient hydrolysis and degradation. It was demonstrated that the PLA matrix undergoes degradation with concurrent solvent induced crystallization i.e. the PLA molecules when immersed in organic solvent will crystallize and plasticize and increase their chain mobility [252].

9.2. Enzymatic Degradation

Karamanlioglu *et al*. studied the degradation of PLA using sterile compost for 54 days, microorganism rich compost for 57 days and soil extract for 54 days at 50 ^{o}C. It was demonstrated that degradation rates were faster in microorganism rich compost i.e. using biotic soluble factors than in soil extract or sterile compost. The degradation trend was also observed in soil, microorganism rich compost and sterile water at different temperatures such as varying to 25 to 55 °C. It was observed that efficient degradation took place at a temperature at or above 45 °C at specific humidity and environmental conditions. It was also reported that the degradation process enhanced by using microbial conditions than by using chemical hydrolytic degradation process [253]. Karamanlioglu *et al*. treated PLA samples to various fungi using incubation treatment at 25 °C and 50 °C for 8 weeks in soil or compost to study the degradation of PLA. It was observed that incubation at 50 °C gave efficient disintegration of PLA due to the involvement of extracellular esterases and presence of fungi such as *Aspergillus fumigatus* and *Thermomyces lanuginosus* [254]. Meischel *et al*. synthesized novel biocomposites containing poly(hydroxyl butyrate) as the matrix reinforced with zirconium dioxide. The composite was subjected to in-vivo degradation using femora of growing rats for 36 weeks. However, it was reported that the composite did not degrade completely in 36 weeks [255].

10. APPLICATIONS OF BIODEGRADABLE POLYMERS

Biodegradable polymers have various applications ranging from biomedical applications to agriculture implements. These applications are discussed in following sub-sections-

1. Biomaterials
2. Pharmaceuticals
3. Tissue engineering and surgical uses
4. Packaging and agriculture uses
5. Applications in fibers & textiles

10.1. Biomaterials

Non-toxicity, sterilizability, effectiveness and biocompatibility are the minimum requirements of biomaterials for their end applications in human body. Various biomedical applications of synthetic aliphatic polyesters are listed in Figure **5** [256-264].

10.2. Pharmaceuticals

Controlled drug delivery has versatile application in medicine, veterinary and agrochemical fields. Drug delivery system is an efficient way to release drugs for a desired duration with an optimum dose at the diseased sites in the body. The aim of drug delivery system involves a sustained release of drugs. Since the polymer is no longer required when the drug delivery has been accomplished therefore employed polymers should be absorbable. Different shapes of drug carriers such as nanospheres, microspheres, beads, cylinders and discs are used nowadays, out of them microsphere is widely used shape [158]. Solvent evaporation method is generally used for preparation of microspheres using polymers and copolymers such as, poly(ε-caprolactone), poly(L-lactide) and poly(glycolide-co-lactide) [85-86, 265-268].

10.3. Tissue Engineering and Surgical Uses

Tissue engineering is a technology to generate biological tissues for replacements of defective tissues when the lost part of the tissue is so large that it cannot be cured by conventional therapeutic methods. Biodegradable polymers are required to fabricate scaffolds for tissue regeneration for that it is necessary that employed polymers should have a sustained release of growth factors. Generally, scaffolds used in tissue engineering are porous and three-dimensional to support infiltration of a large number of cells into the scaffolds [256, 259, 264]. Various biodegradable polymers such as poly(L-lactide), poly(glycolide), and their copolymers poly(L-lactide-*co*-glycolide) have been used to fabricate cell scaffolds for engineering musculoskeletal tissue such as cartilage and bone [85, 260, 269-272].

Sutures are the most prominent use of biodegradable polymers and Dexon is the most widely used absorbable suture. Vicryl is the other example that is a copolymer compose of PLLA (8%)-co-PGA (92%) and PDS, poly(p-dioxanone) [265]. The other surgical use of biodegradable polymers is in fixation of fractured bones. Different other applications of biodegradable polymers in surgery are for hemostasis, sealing and adhesion to tissues [85-86, 158, 265].

10.5. Packaging and Agriculture Uses

The needs such as consumer products, packaging materials food processing and agriculture films can be accomplished through non-degradable polymers which are obtained from petroleum and oil based monomers. Since non-degradable polymers are biostable plastics

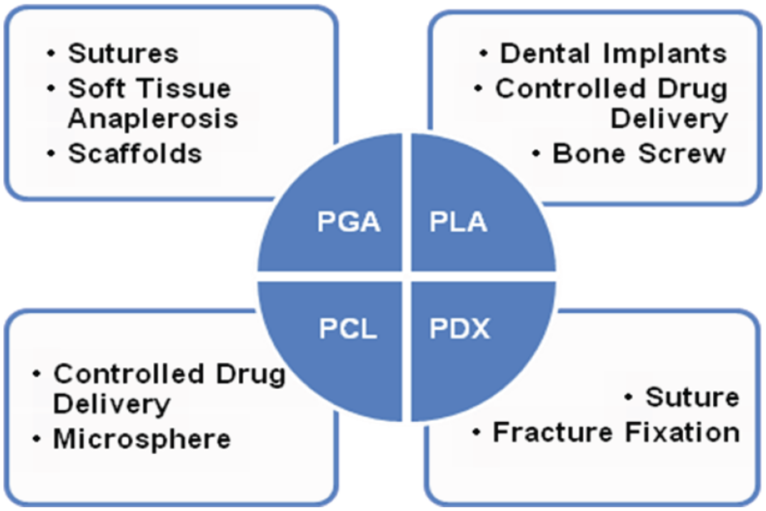


Figure 5: Biomedical applications of synthetic aliphatic polyesters [256-264].

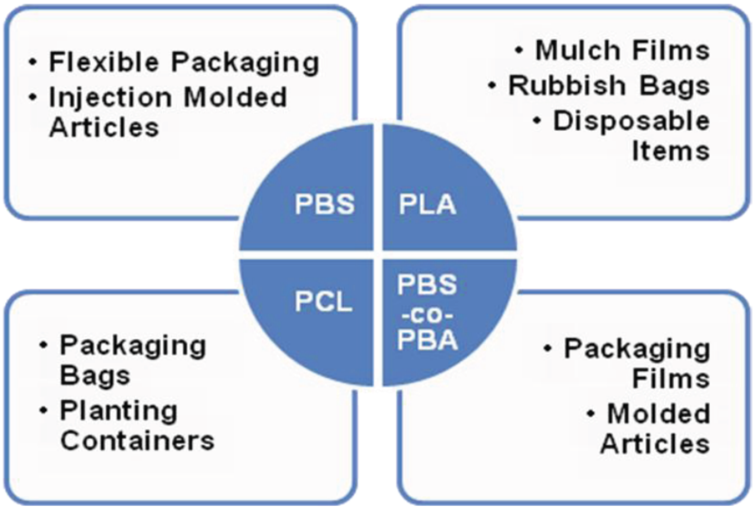


Figure 6: Packaging and agriculture applications of synthetic aliphatic polyesters [84, 86, 158, 163, 265].

and cause serious environmental pollution, therefore plastic recycling is an effective method to resolve the problem. However this method consumes a considerable amount of thermal energy and deplete the oil resources hence it would be indispensable to use biodegradable polymers. Generally, used synthetic aliphatic polyesters for packaging and agriculture are shown in Figure **6** [84, 86, 158, 163, 265].

10.5. Applications in Fibers & Textiles

Textile industry is one of the most prominent and never dying industry. Any product which is either derived from a fibre, yarn or fabric or has the final outcome in these forms is covered under textile applications. Polymer science and textile technology have various overlapping applications and use of both synthetic and natural biodegradable polymers to produce smart textiles is one of them. Due to the biocompatibility of the biodegradable polymers, they can be used as medical suture material or wound dressings in medical textiles, whereas, the rapid biodegradability of these polymers make them suitable for agrotextile applications. Similarly, the ease of production, availability and low cost of these polymers have made them suitable for various other textile applications such as packaging, e-textiles, etc. thereby, reducing the negative impact of the conventional textile polymers on the environment [273-276].

11. CONCLUSION

Biodegradable polymers have their great importance in biomedical and pharmaceutical field. The recent advances show that various new synthetic pathways have potential to make novel polymers for new biomedical applications, since their chemical modification and functionalization can be easily done. Moreover, synthetic functional polymers are a new class of biomaterials that open a scope for totally new biomedical applications. In this way synthetic biodegradable polymers are future material that can immensely contribute to the development of biomedical field. Similarly, biodegradable polymers derived from natural sources provide new alternatives for synthesizing bio-based polymers. Using reaction by-products such as CO_2 as monomers for subsequent polymerization is one of the highlights of the recent discoveries. Moreover, water soluble polymers are being considered as suitable alternatives to polyethylene and other plastics for one-time use bottles packaging materials. Another substitute for petroleum-based non-biodegradable polymers is by preparation of blends or composite polymers of biodegradable polymers with properties equivalent to the commercially non-biodegradable ones. The use of 3D printing technology, have further bolstered the use of biodegradable polymers in biomedical applications in the form of tailor-made scaffolds and grafts. These polymers are also found to be suitable for several other applications such as in the fields of green packaging and textile industry in the form of both fibres and fabrics. Thus, there is an extensive scope for further academic and industrial research of studying and commercially developing various products from these polymers suitable for different applications.

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