# Modification of Biodegradable Polymers through Reactive Extrusion

Moura and A.V. Machado

## INTRODUCTION

Plastic materials produced from petrochemicals are used in a wide range of applications, such as packaging, automotive, health-care application, industry, and communication or electronic industries. Most of these polymers are extremely durable, requiring more than 100 years for their degradation. [1] Therefore, they may accumulate in the environment and become a significant source of environmental pollution. [1−3] After use, plastics can be disposed in different environments, such as composting facilities or soil burial, wastewater treatment facilities, and landfill. However, it has some adverse risks, like pollution of waterways due to high biochemical $O_2$ demand concentration, migration of plastic by-products to groundwater and surface water bodies, and soil and crop contamination. [4]

A possible solution to solve this problem could be to replace commodity synthetic polymers by biodegradable ones. However, it is necessary to take into account that any marketable plastic product must meet the performance requirements of its intended function, and most of the biodegradable polymers do not meet these functional requirements, that is, they do not have the performance specifications required for a given application. [4] Therefore, the development of biodegradable polymers with good performance, which after use would be susceptible to microbial and environmental degradation, using adequate solid waste management disposal practices, without any adverse environmental impact became a challenge. [5]

REX has been used as an attractive method to prepare new materials based on biodegradable polymers. It allows preparing new materials, in the melt, by blending, polymerization, grafting, branching, and functionalization. [6−8] Polymerization or chemical modification reactions in the melt were identified as an efficient and economic way for low-cost production, which enhances the commercial viability and cost-competitiveness of these materials. [9,10]

Thus, in this chapter, it will be discussed how REX has been used in continuous production and modification of biodegradable polymers.

## BIOBASED AND BIODEGRADABLE POLYMERS

The words biobased and biodegradable both incorporate the prefix "bio," but they cannot be used indistinctly. Both biobased and biodegradable polymers can form the basis of an environmentally preferable and sustainable alternative to conventional polymers, based exclusively on petroleum feedstocks. [11]

The American Society for Testing and Material (ASTM) defines a biobased material as "an organic material, in which carbon is derived from a renewable resource, via biological processes. These materials include all plant and animal mass derived from carbon dioxide ( $CO_2$ ) recently fixed via photosynthesis, per definition of a renewable resource.,"11,12

Therefore, a biobased material should be organic and contain carbon from biological sources, which is synthesized by many types of living mater (bacteria, animals, and plants), being portion of the ecosystem. [13] However, the use of a biobased material must take into account what happens to the product after the use and its impact in the environment since the most important factor of sustainability and environmental responsibility lies in the disposal of the products after use. [13] Thus, the U.S. Department of Agriculture (USDA), in the ASTM D6866, defined a percentage of carbon that is required to carry the term biobased. [14] This standard was developed to attest the biological content of bioplastics, that is, to determine exactly the amount of the material that comes from renewable resources.

For example, high-density polyethylene (HDPE) can be totally biobased, that is, containing only renewable carbon, but it is still nonbiodegradable. Thus, a polymer that contains only renewable raw materials could be or not biodegradable; it depends also on the molecular structure and on the chemical or biological methods used for polymerization. Accordingly, for single-use and short-life disposable material applications, biobased materials should be engineered to be biodegradable. [11] A product that is entitled biobased does not mean that it is based entirely on renewable resources. Rather, many of these products combine both petroleum- and natural-based materials in order to provide satisfactory properties and simultaneously reduce the overall amount of synthetic polymers contained in the products.

Biodegradable polymeric materials can be disposed in safe and ecological ways through waste management's composting, soil application, and biological wastewater treatment. According to ASTM 6400-99, [15] the common definition of biodegradable is a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae. Essentially, a polymer is called biodegradable when under the right conditions, the microbes in the environment can chemically break down the polymer chain and use it as a food source. The process of biodegradation essentially converts carbon into energy, taking place in many environments including soils, compost sites, waste management facilities, water treatment facilities, and marine environments. However, not all materials are biodegradable under the same conditions. While some are susceptible to microbes found in a wastewater treatment plant, others need microbes found in the soils. [16]

Biodegradable polymers can be divided into natural and nonrenewable synthetic polymers. The former are produced in nature during the growth cycles of all organisms, [17] and their synthesis generally involves enzyme-catalyzed, chain growth polymerization reactions of activated monomers, which are typically formed within cells by complex processes, and the latter are petroleum based.

The biodegradation process occurs in two different steps: First, the long polymer chains are shortened or cut at the carbon-carbon bonds. [16] This process can be started by different factors including heat, microbial enzymes, moisture, or other environmental conditions. This first step is not a synonym of biodegradation and is usually called degradation. [16] In the second step, called biodegradation, the short carbon chains are used as a food source and are converted into water $(H_2O)$, biomass, carbon dioxide $(CO_2)$, and methane $(CH_4)$ (depending upon process taking place under aerobic or anaerobic conditions). Figure 6.1 illustrates the biodegradation process under aerobic conditions.

Moreover, there is also a difference between biodegradable and compostable polymers. Even if both breakdown of the polymeric chain into smaller fragments, due to the action of microorganisms, and transformation of the latter into $CO_2, H_2O$, minerals, and biomass and/or $CH_4$ occur, a compostable polymer should disintegrate and biodegrade quickly and must not leave visible, distinguishable, or toxic residues. To be called compostable, a product should meet D6400 standard, [15] which is the regulatory framework for the United States and sets a less stringent threshold of $60\,\%$ biodegradation within 180 days, again within commercial composting conditions.

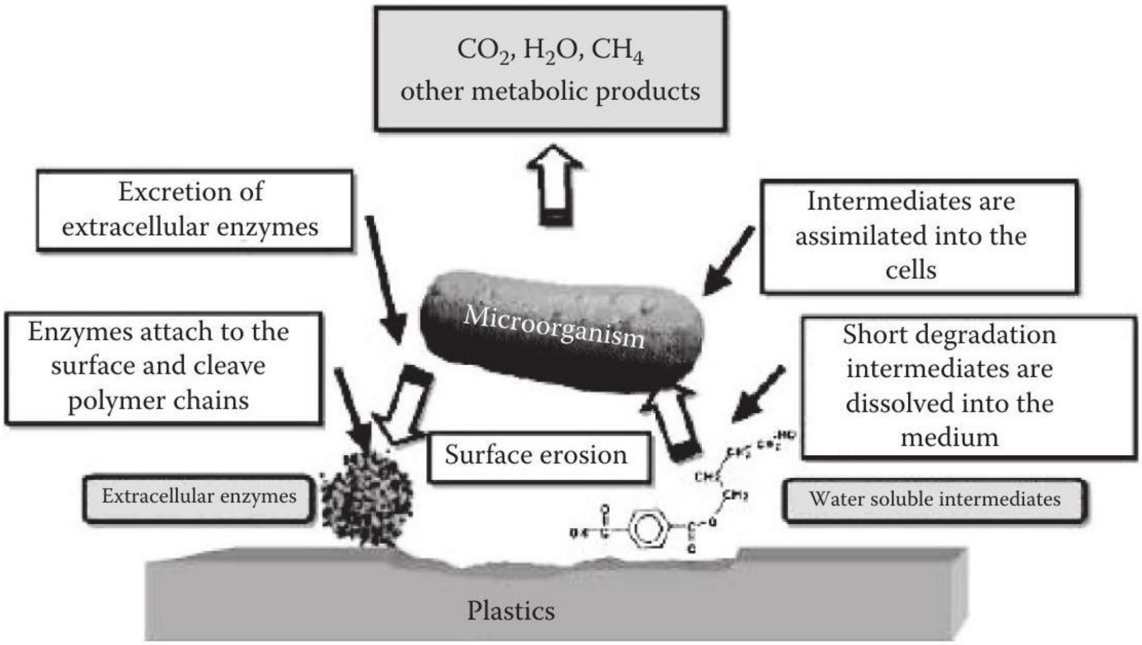


Figure 6.1 General mechanism of plastic biodegradation under aerobic conditions. (From Mueller, R.J., Biodegradability of polymers: Regulations and methods for testing, in Biopolymers, Steinbüchel, A., Ed., vol. 10., Wiley-VCH, Weinheim, Germany, 2003.)

Unfortunately, most products are designed with limited concern in relation to its ultimate disposability. They are designed to be biobased, that is, they fragment into smaller fragments and may even degrade to residues invisible to the naked eye; thus, no products are completely biodegradable within a short period of time. These plastic residues will migrate into the water and in the ecosystem, causing damage to the environment. [19]

Biodeterioration and biodegradation of polymer substrate can rarely reach 100 % because a small portion of the polymer will be incorporated into microbial biomass and other natural process. [20,21]

## SYNTHETIC PLASTICS

The demand of synthetic polymeric materials has been fairly increasing during the last decades, and presently, they are one of the most attractive categories of materials. [22] This success is mainly related to their properties, namely, low cost, aesthetic qualities, and resistance to physical aging and biological attack. [23] It is estimated that global synthetic plastic production is approximately 140 million tons per year. [24,25] The most widely used plastics are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyurethane (PU), poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and nylons (Figure 6.2 and Table 6.1).

Polymer Chemical structure

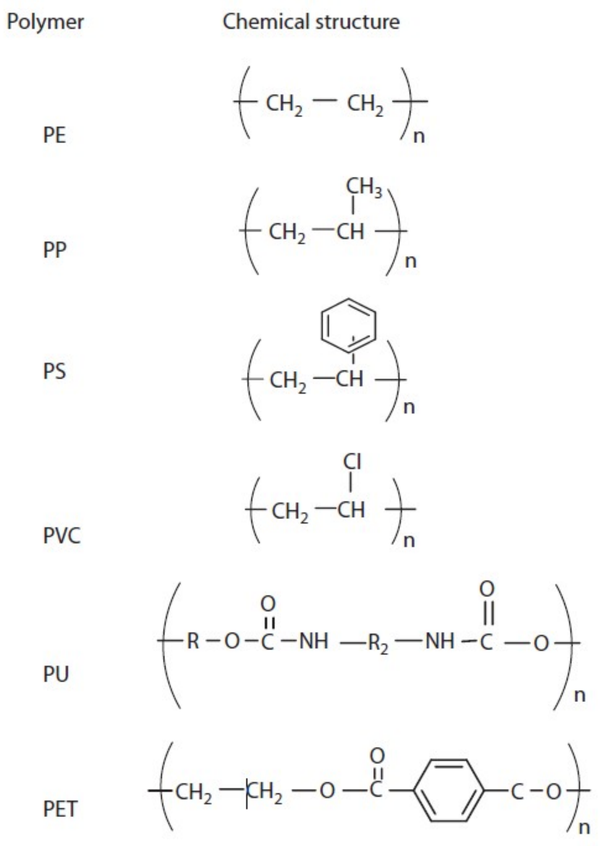


Figure 6.2 Structures of conventional plastics.

Table 6.1 Global Plastic Market

| Plastic Type | Market Share by Volume Produced (%) | Use |
|---|---|---|
| PE | 29 | Plastic bags, milk and water bottles, food packaging, motor oil bottles |
| PP | 12 | Bottle caps, drinking straws, medicine bottles, car seats, car batteries, bumpers, disposable syringes, carpet backings |
| PS | 9 | Disposable cups, packaging materials, laboratory ware, certain electronic uses |
| PVC | 17 | Automobile seat covers, shower curtains, raincoats, bottles, visors, shoe soles, garden hoses, and electricity pipes |

| | | |
|---|---|---|
| PU | 5 | Tires, gaskets, bumpers, in refrigerator insulation, sponges, furniture, cushioning, and life jackets |
| Others | 28 | |
| Total | 100 | |

Polyolefins are the synthetic polymers with the highest commercial success, accounting for more than 47 % of Western Europe's total consumption, 24.1 million ton per year. They present a combination of physical properties (flexibility, strength, lightness, stability, impermeability, and easiness of sterilization) that are ideally suited to a wide variety of applications such as food and drinks packaging. [26]

Synthetic polymers have an undesirable influence on the environment and a well-known resistance to degradation, [27] which became a problem with waste disposal. Once such material became part of the natural ecosystem, the negative effect is its long-lasting contribution to environmental contamination. [28] The growing environmental awareness and the new environmental regulations are forcing the industries to seek for more ecologically friendly materials for their products, namely, in applications where they are used for a short period of time before becoming waste. [22]

Under natural conditions, the degradation of synthetic plastics is a very slow process that involves environmental factors, followed by the action of wild microorganisms. [29−31] The degradation depends on physical and chemical properties, with hydrolysis or oxidation being the main mechanism. [32] Hydrolysis occurs by penetrating $H_2O$ into the polymer backbone, attacking the chemical bonds in the amorphous phase, and converting them into shorter $H_2O$-soluble fragments, promoting a reduction in molecular weight. Then, metabolization of the fragments and bulk erosion also occur, leading also to the loss in the physical properties, making it more accessible for further microbial assimilation. [33−35] Some synthetic polymers, generally vinyl polymers, are not susceptible to hydrolysis. Therefore, the prevailing degradation mechanism occurs by oxidation due to the presence of an oxidizable functional group. [36]

Due to the lower sensitivity to biodegradation, there is a tendency to replace such polymers by polymers that could undergo easily the biodegradable process. The use of these materials, namely, in applications with short life cycle, such as packaging, would be an ecological alternative for reducing the solid plastic waste. [37]

Some examples of synthetic polymers that are biodegradable are polylactic acid (PLA), poly( $\varepsilon$-caprolactone) (PCL), polyamides (PA), and poly(vinyl alcohol)

(PVA) and also some oligomeric structures, like ethylene, styrene, isoprene, butadiene, acrylonitrile, and acrylate. [38]

### Polyethylene

Synthetic materials like polyolefins are difficult to be biodegraded by microorganisms and have a long lifetime. [36,39,40] In its natural form, PE is not biodegradable due to the higher hydrophobic character and also high molecular weight, but a comprehensive study of polyolefins biodegradation has shown that some microorganisms could use polyolefins with low molecular weight. [41] Thus, to convert conventional PE into biodegradable PE, it is necessary to modify their characteristics, such as molecular weight and crystallinity degree, which contribute to the high resistance to degradation. [31]

Bonhomme et al. [42] and Wang et al. [43] performed biodegradation studies of PE. The results indicated that chemical degradation occurred by two different pathways: hydro- and oxobiodegradation. [42] Other researchers also observed that the oxidation products of polyolefins are biodegradable. [44–51] The explanation is that these products have low molecular weight values and incorporate $O_2$-containing groups, such as acid, alcohol, and ketone. This is the basis of the term oxobiodegradable polyolefins. Oxobiodegradation involves two stages. First, oxidative degradation occurs followed by the biodegradation of the oxidized products. When a molecule undergoes oxidative degradation, the size is reduced, and at a given size, the microbial degradation starts. It has been demonstrated that the biodegradation of polar molecular fragments from PE occurs quite quickly. [52] Another alternative to accelerate the attack of microorganisms to polyolefins is by blending biodegradable polymers, like starch, PCL, and PLA, to guarantee at least a partial biodegradation. This effect will be discussed later in this chapter.

### Ethylene Vinyl Acetate

Another synthetic polymer widely used in the packaging industry is ethylene vinyl acetate, which is a copolymer of ethylene and vinyl acetate. The weight percent of vinyl acetate usually varies between 10 % and 40 %, and the remainder is ethylene. It behaves like an elastomeric material in softness and flexibility and can be processed like other thermoplastics. The material has good transparency and gloss, barrier properties, low-temperature toughness, stress-crack resistance, hot-melt adhesive waterproof properties, and resistance to UV radiation. EVA copolymers have a broad range of industrial applications, such as packaging, adhesives, wire, cable, and health care. Also, due to the mechanical properties, these copolymers are used perhaps in a broadest spectrum of applications of any synthetic polymeric material. [53,54] Therefore, it would be interesting to have products made from this polymer with biodegradable potential.

## BIODEGRADABLE POLYMERS

Limited resources of petroleum-based polymers and increased environmental awareness have attracted a higher interest toward biodegradable and biobased polymers for industrial applications. [55] The use of these materials is an alternative to conventional nonbiodegradable plastics, which could contribute to the solution of the environmental problem. [56]

The consumption of biodegradable polymers has increased in the last decades. The target market is mainly packaging materials, hygiene products, agricultural tools, and consumer goods. Nevertheless, there is still a competition between commodity plastics and biodegradable ones due to the low cost of the former. [57]

Biodegradable polymers can be derived from renewable or petroleum resources (Figure 6.3). Thus, industry, beyond nonbiodegradable petroleum-based plastics and the renewable source-based biodegradable polymers, is also thinking in terms of aliphatic/aromatic ratio by using chemical processes to achieve petroleum-based biodegradable plastics. [58]

According to Narayan, [12] biodegradable polymers can be divided as follows:

1. Biopolymers or natural biodegradable polymers formed in nature during the growth cycles of all organisms. The synthesis implies enzyme-catalyzed, chain growth polymerization reactions of activated monomers, which are formed within cells by some metabolic processes (e.g., starch and cellulose).
2. Polymers with hydrolyzable backbones-these polymers are susceptible to biodegradation, which includes aliphatic polyesters, PA, and PU.
3. Polymers with carbon backbones-the biodegradation of this kind of materials involves first an oxidation process. An example is PVA, which is not susceptible to hydrolysis. Biodegradable vinyl polymers contain functional groups that are easily oxidizable, and a catalyst is added to promote their oxidation or photooxidation, or both. [60]

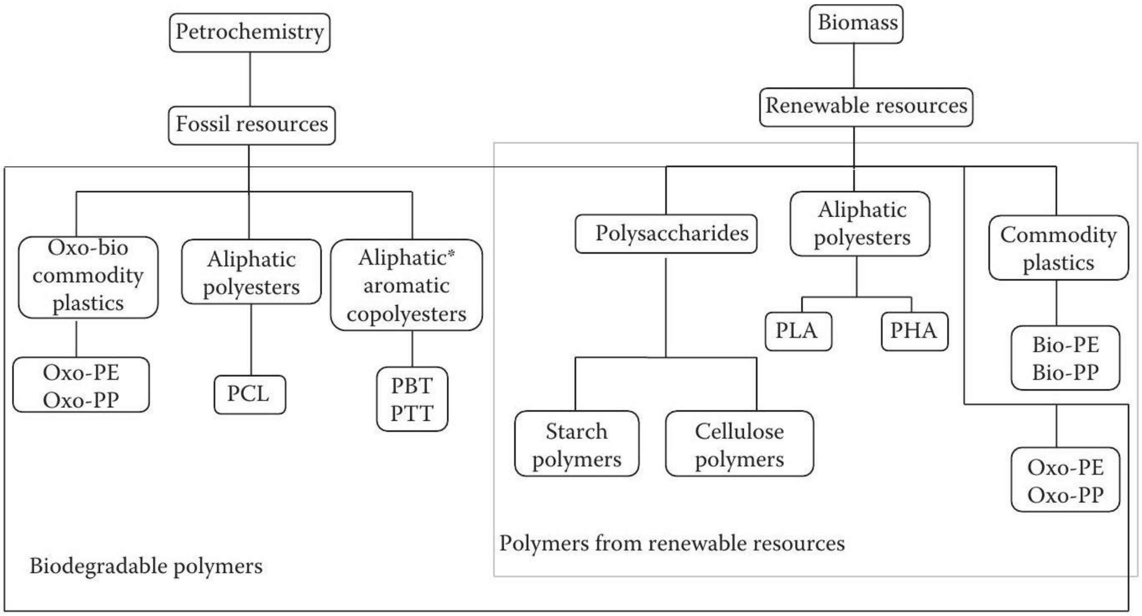


Figure 6.3 Resources of biodegradable polymers. *Partially from chemistry. (From Camino, G., Conference of Bioplastics and Related Materials, Gargnano, Italy, 2009.)

## Aliphatic Polyesters

Aliphatic polyesters or aliphatic-aromatic copolyesters are the most known petroleum sourcederived biodegradable polymers. [61] In recent years, there is a growing interest on the synthesis and development of fully biodegradable polymers, such as PCL, polyhydroxybutyrate (PHB) and its copolymer with hydroxyvaleric acid, PLA, and aliphatic polyesters from different lactic acid derivatives. [62–64]

Aliphatic polyesters made from dimethyl esters and diols are expected to be of the most economically competitive biodegradable polymers. [65,66] Moreover, it was found that polyesters derived from diacids of medium-sized monomers ( $C_6-C_{12}$ ) are more readily degraded by microorganisms than those derived from longer monomers. [67] A synthetic polymer can only be biodegradable by enzyme catalysts if the polymer chains are able to fit into the enzymes active site. This is the reason why flexible aliphatic polyesters are degradable and the rigid aromatic polyesters are not. [60,68,69] Another major feature of these polymers is their compatibility with the natural environment and their ability to undergo hydrolytic and biological degradation. [70] Their biodegradability depends mainly on their chemical structure and especially of the hydrolyzable ester bonds in the main chain, which are susceptible to microbial attack. Other factors such as molecular weight, crystallinity degree, stereoregularity, and morphology also affect the rate of biodegradation. [65,71,72]

The most important synthetic aliphatic polyesters are PLA and PCL, which are usually prepared by ring-opening polymerization (ROP) of the respective cyclic monomers (L,L-lactide [LA] and ε-caprolactone [CL]). This method provides sufficient polymerization control, resulting in polymers with required molecular weight and with the desired end groups.

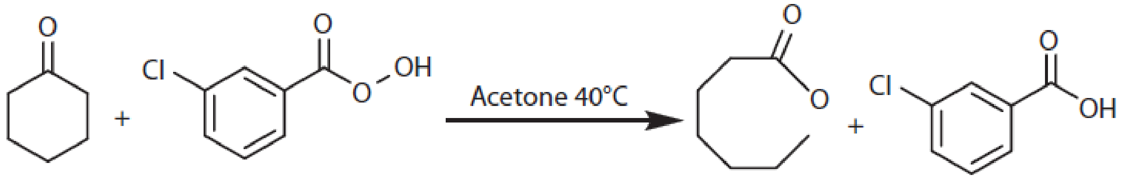


Figure 6.4 Synthesis of CL monomer.

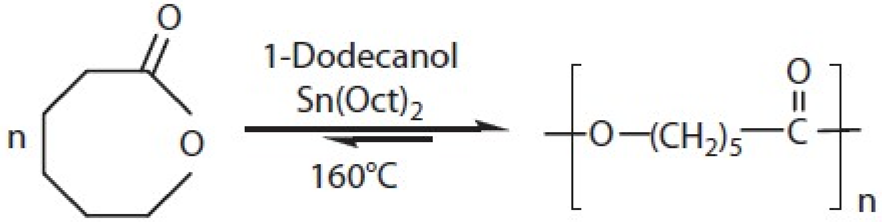


Figure 6.5 Synthesis of PCL.

## Poly(ε-Caprolactone)

PCL is prepared from ROP of CL, as illustrated in the Figures 6.4 and 6.5. PCL is appreciated by its biodegradable properties; it can be biodegraded aerobically by a large number of microorganisms in various microbiological environments. [73] Moreover, due to its flexibility, it has been found to be miscible with many other polymers. [60,73] However, the high cost and low performance of PCL for some applications have prevented its widespread industrial use. [74]

## Polylactic Acid

PLA can be derived from renewable and petroleum-based resources. [75] The production of PLA presents advantages over other synthetic materials: (1) PLA can be obtained from renewable agricultural sources (e.g., corn), (2) its production consumes $CO_2$, providing significant energy savings, and (3) PLA is recyclable and compostable. [76–78]

Early economic studies have shown that PLA is an economically feasible material that can be used as a packaging material. [79] PLA properties are determined both by the polymer architecture (stereochemical makeup of the backbone) and the molecular weight, the latter being controlled by the addition of hydroxylic compounds. The control of the polymer stereochemical architecture allows precise control over the crystallization rate and the crystallinity degree, mechanical properties, and processing temperature. [80] PLA is a polyester with one of the highest melting temperatures, around $160^\circ C - 180^\circ C$. PLA can exist as two stereoisomers, designated as D and L, or as a racemic mixture, designated as DL. While the D and L forms are optically active, the DL form is inactive. Poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) are semicrystalline while poly(DL-lactic acid) (PDLLA) is amorphous. [81]

Bacterial fermentation is used to produce LA from corn or cane sugar. However, LA cannot be polymerized as a useful product because during polymerization reaction, molecules of $H_2O$ are generated, and its presence degrades the forming polymer chain. Thus, PLA of high molecular weight is produced from ROP of LA using a catalyst (Figure 6.6), by solvent-free continuous process and distillation method. [38] This mechanism does not generate additional $H_2O$, and thus, a wide range of molecular weights are accessible.

PLA is currently used in industrial packaging and biomedical applications. [82] Nevertheless, it has been demonstrated that it is not suitable for hard tissue regeneration due to its weak mechanical properties. [83–87]

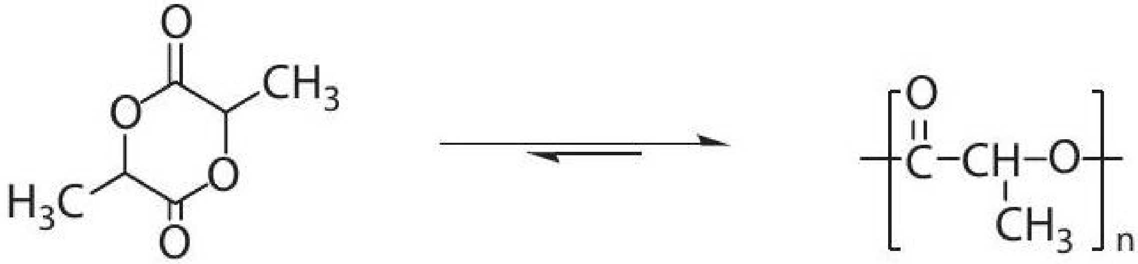


Figure 6.6 Synthesis of PLA.

## Starch

Starch is a carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds containing, generally, $20\% - 25\%$ amylase and $75\% - 80\%$ amylopectin. It occurs widely in plants, like rice, corn, cassava, and potatoes. In all of these plants, starch is produced in form of granules, varying in size, and in composition according to the plant used. Starch granules are hydrophilic, and the $H_2O$ content of starch varies with relative humidity changes. While the branched amylopectin component contains crystalline areas, the linear amylase is mostly amorphous. Starch granules can be gelatinized in $H_2O$ at lower temperatures in alkaline solution and can be used as a thickening, stiffening, and gluing agent, giving wheat paste. [88]

There are several degradable plastics made from starch. [12,60,89] For instance, a fully biodegradable starch-based polymer is prepared from corn or potato starch, along with smaller amounts of foodgrade additives. The resin is suitable for manufacturing injection-molded pieces, films, and starchbased loose-fill packaging material. [90] These pieces degrade in an active biological environment.

Starch has a wide variety of applications including adhesives and industrial emulsions, construction, glass fiber, medical gloves, personal care, packaging, and agricultural.

The interest in this biopolymer has been recently renewed due to its abundance, low cost, availability, biodegradability, and possibility of blending with conventional polymers, and it can be processed using conventional polymer processing equipment, such as extrusion and injection molding. [91]

## MODES OF BIODEGRADATION

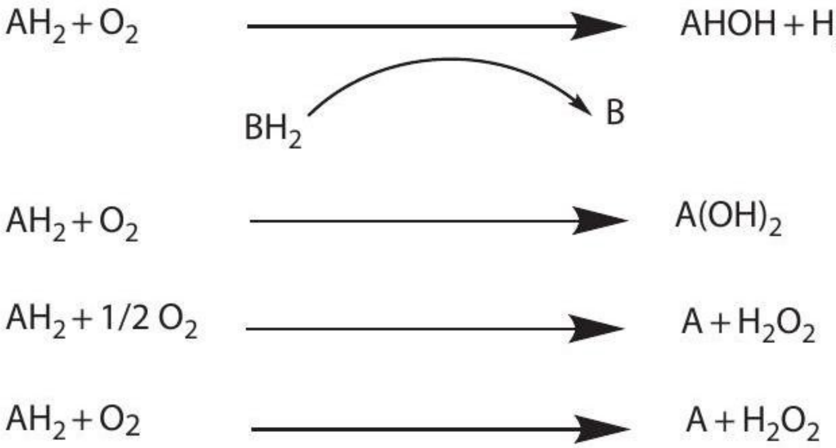
### Enzyme Mechanisms

Two categories of enzymes are involved in biological degradation of polymers: extracellular and intracellular depolymerases. [92,93] Such kind of enzyme has different action mechanism; some enzymes change the substrate through a free radical mechanism, while others follow alternative chemical routes (typical examples are biological oxidation and hydrolysis). During degradation, exoenzymes from microorganisms break down complex polymers, yielding smaller molecules of short chains, like oligomers, dimers, and monomers. These are small enough to pass the semipermeable outer bacterial membranes to be utilized as carbon and energy source. However, the biodegradative pathways associated with polymers are determined by environmental conditions. When oxygen ( $O_2$ ) is available, aerobic microorganisms are mostly responsible for destruction of complex materials, with the formation of biomass, $CO_2$, and $H_2O$. Contrarily, under anaerobic conditions, microorganisms are responsible for polymer deterioration, being the primary products microbial biomass, $CO_2, H_2O$, and $CH_4$ [94]

Polymer degradation involves changes in physical properties due to the chain scission along the polymer backbone. [95,96] Since the degradation mode depends on the initiation process, it can be classified as thermal, mechanical, photochemical, biological, or chemical. [96] Additionally, the environmental conditions such as moisture, temperature, and type of microorganisms influence polymer degradation. Moreover, it also depends on the structural properties of the polymer, as chain orientation, stereochemical configuration, crystallinity degree, molecular weight, molecular weight distribution, and degree of cross-linking are among the important ones. [97−99]

### Biological Oxidation

Many enzymes can react directly with $O_2$, which has a special role in the metabolism of aerobic organisms. The enzyme can be hydroxylases (Equation 6.1), which is responsible for the hydroxylation, that is, a chemical process that introduces hydroxyl groups ( -OH ) into the organic compound, or can be oxygenases (Equation 6.2), in this case transfers $O_2$ from molecular $O_2$ to the substrate. The substrate has another type of biological oxidation when the $O_2$ molecule is not incorporated into the substrate but rather functions as a hydrogen acceptor. Enzymes of this type are called oxidases, and one type produces $H_2O$ (Equation 6.3) and the other peroxides (Equation 6.4).



$$AH_2 + O_2 \xrightarrow[BH_2 \curvearrowright B]{} AHOH + H_2O$$

$$AH_2 + O_2 \longrightarrow A(OH)_2$$

$$AH_2 + 1/2\ O_2 \longrightarrow A + H_2O_2$$

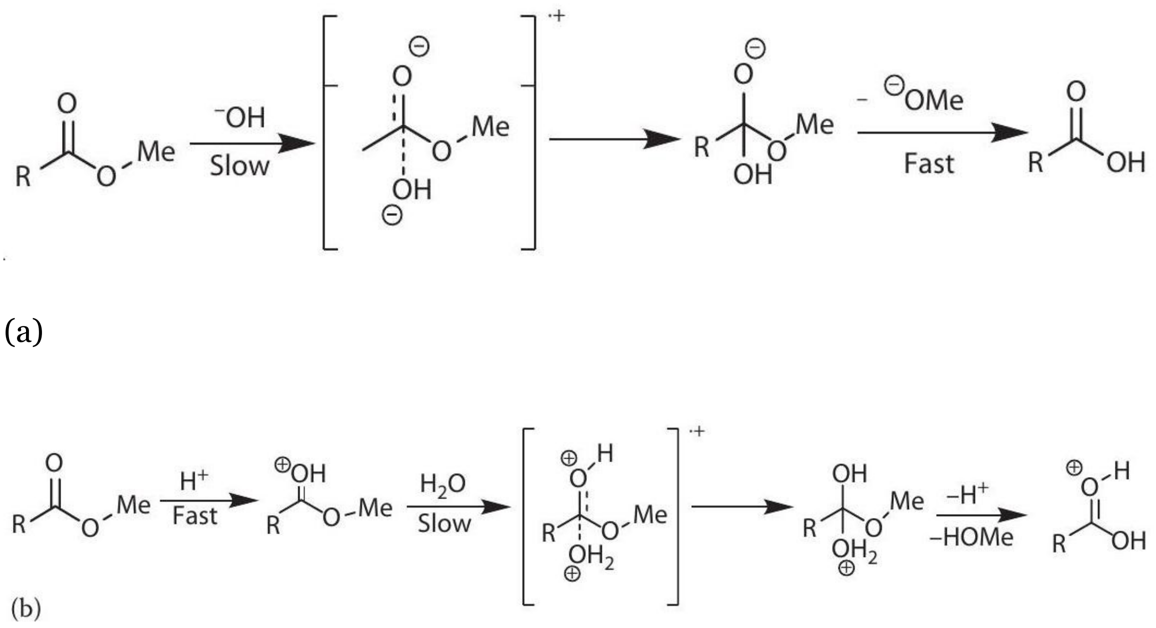
$$AH_2 + O_2 \longrightarrow A + H_2O_2$$

Biodegradable polymers disposed in bioactive environments degrade not only by the enzymatic action of microorganisms such as bacteria, fungi, and algae but also by nonenzymatic processes, such as chemical hydrolysis that breaks down the polymer chains.

## Biological Hydrolysis

Polymers with hydrolyzable backbones have been found to be susceptible to biodegradation. Among others are polyglycolide (PGA), PCL, poly(lactic-co-glycolic) (PLGA), polyether-polyurethane, and poly(amide-enamine)s.

Hydrolysis occurs by scission of chemical bond in the main chain by reaction with $H_2O$.[81] The hydrolysis of esters can occur through both acid- and base-catalyzed mechanisms. While in the base-catalyzed mechanism (Figure 6.7a), the reactant goes from a neutral species to a negatively charged intermediate; in the acid-catalyzed (Figure 6.7b), a positively charged reactant goes to a



(a)

(b)

Figure 6.7 Base-catalyzed (a) and acid-catalyzed (b) ester hydrolysis mechanisms.

$$R_1-COOR_2+H_2O\longrightarrow R_1-COOH+R_2OH$$

Figure 6.8 General equation of ester hydrolysis.

positively charged intermediate. Additionally, the mechanism associated with hydrolysis of ester linkage in neutral or acidic media is different from the one in alkaline media. [100] Both in neutral and acidic media, the hydrolysis is initiated by protonation and is followed by the addition of $H_2O$ and the cleavage of the ester linkage. [100] In alkaline media, hydroxyl ions ¿are attached to the carbonyl carbons and followed by the breaking of the ester linkages.

Several different hydrolysis reactions can occur in biological organisms, being the general equation represented in Figure 6.8. The degradation kinetics of different raw materials changes substantially, which might be attributed to the hydrophilic or hydrophobic nature of the different polymers.

## BIODEGRADATION PARAMETERS

Biodegradation is a very complex process, which is affected by different factors, including type of microorganism, polymer features, and nature of pretreatment. Furthermore, polymer molecular weight, mobility, crystallinity degree, type of functional groups, tacticity, and additives play an important role. [93,101]

### Effect of Polymer Structure

Biodegradability is mainly determined by the molecular structure and the length of the polymer chains. [102–104] Natural polymers, as starch, are generally degraded in biological systems by hydrolysis followed by oxidation. [105] Most of the synthetic biodegradable polymers contain hydrolyzable backbones. For instance, ester linkages are susceptible to biodegradation by microorganisms and hydrolytic enzymes. Since many proteolytic enzymes specifically catalyze the hydrolysis of peptide linkages adjacent to substituents in proteins, polymers containing substituents, such as benzyl, hydroxyl, carboxyl, methyl, and phenyl groups, have been prepared, aiming that the introduction of these substituents might increase biodegradability. [106] Huang et al. [107] investigated the effect of stereochemistry on the biodegradation using monomeric and polymeric ester-ureas that were synthesized from D-, L-, and D,L- phenylalanines. They found out that after enzymecatalyzed degradation, the pure l-isomer degraded faster. Shuichi Matsumura et al. [108] studied the effects of stereoregularity on biodegradation of PVA by Alcaligenes faecalis and observed that the biodegradability of PVA was influenced by its stereoregularity, being the isocratic moiety more biodegraded. Another parameter that influences the degree of biodegradation is the hydrophilic and hydrophobic character of polymers, since most enzyme-catalyzed processes occur in aqueous medium. Machado et al. [61] performed biodegradability studies in aqueous medium, and they found that a polymer containing both hydrophobic and hydrophilic segments (HDPE/PCL or HDPE/PLA) seems to have a higher biodegradability than HDPE, which contains only hydrophobic segments on its structure. Additionally, HDPE/PCL system showed higher biodegradability than HDPE/PLA. This result can be explained once more, based on the hydrophilic character of both polymers. It is well known, that PLA is more hydrophobic than PCL, which explains the smaller result obtained for the biodegradability results.

## Effect of Polymer Morphology and Crystallinity Degree

Synthetic polymers can have short repeating units, and due to this regularity, the crystallization is enhanced, making the hydrolyzable groups less accessible to enzymes. [109−111] On the contrary, if the repeating units are long, the polymer has less tendency to crystallize and consequently is more susceptible to biodegradation. It is well known that during degradation, semicrystalline polymers suffer some changes, namely, concerning the crystallinity degree. Firstly, the crystallinity of the polymers increases rapidly then levels off when the rate of crystallinity approaches 100 %. This occurrence is due to the disappearance of the amorphous phase because biodegradation occurs preferably in the amorphous regions of the polymer that have a higher mobility of the polymeric chains and, therefore, are more accessible to the microorganisms. [22] Moura et al. [112] investigated the miscibility and biodegradability of blends of EVA and PCL or PLA. They observed that the blend with coarser morphology (EVA/PLA) showed a smaller degree of biodegradability than the one of EVA/PCL, which exhibited finer morphology. Jenkins and Harrison [113] found that an increase in the crystallinity degree of PCL reduced the rate of biodegradation.

Chin-San Wu [114] dedicated his study to the physical properties of maleated-PCL/starch blend and its relationship with biodegradability. The results indicated that even though PCL-gMAH/starch shows higher compatibility, a slightly lower biodegradation rate was observed in a soil environment compared to the uncompatibilized one. J. K. Pandey et al. [115] found out that the biodegradability of polyester increases with compatibilization within PCL-starch compositions. Also, Chang-Sik Ha and Cho [116] observed that the rate of enzymatic degradation of poly(3hydroxybutyrate) ( $P(3\,HB)$ ) films decreases with an increase in crystallinity, and it was also influenced by the size of $P(3\,HB)$ spherulites. It was suggested that the PHB depolymerizes, firstly hydrolyzes the amorphous $P(3\,HB)$ chains on the surface of the film and subsequently erodes $P(3\,HB)$ chains in the crystalline state. [117] Other factors, such as shape, size, and number of the crystallites, have also a significant effect on the chain mobility of the amorphous regions and thus affect the rate of the degradation.

### Effect of Molecular Weight

A lot of studies have been performed on the effect of molecular weight on the biodegradation rate. [56,108,118] An increase of molecular weight results in a decline of degradability by microorganisms. Contrarily, monomers, dimers, and oligomers of a polymer's repeating units are much easier to degrade and mineralize. [38]

Some polymers remain relatively immune to microbial attack as long as their molecular weight remains high. While some plastics, such as polyolefins and PS, do not support microbial growth, low-molecular-weight hydrocarbons can be degraded by microorganisms. Some natural molecules, such as starch and cellulose, suffer conversions to low-molecular-weight components by enzyme reactions, which occur outside the cells. [60] Nevertheless, this process cannot be applied to some polymers, when their molecules are too big to enter into the cells.

Photodegradation and chemical degradation may decrease sufficiently the molecular weight to enable microbial attack. For instance, low-density polyethylene (LDPE) with an average molecular weight of $M_w = 150{,}000\ g/mol$ contains about 11,000 carbons. [60] Decreasing molecules of this size to biologically acceptable dimensions requires extensive destruction of PE chains. This destruction could be partly accomplished by blending PE with biodegradable or natural polymers.

## REACTIVE EXTRUSION

### Reactive Process

This method differs from conventional ones, where synthesis was made separately and extruders were used only for processing (melting, pumping, and shaping). [119] REX is receiving much attention as an industrial technique because it has several advantages, such as continuous process, versatility, low cost, good heat transfer, short residence time, wide range of temperatures, high viscosity, and it is a solvent-free process. [10,120] Moreover, it is an attractive route for melt blending, filler dispersion, and various reactions (e.g., (co)polymerization, grafting, branching, and functionalization), [6−8,121] combining polymer processing and chemical reaction.

Nevertheless, there are also some drawbacks in using an extruder as a chemical reactor, including limited residence time, efficient heat transfer, medium polarity, and high viscosity leading to possible strong viscous dissipation, which can promote side reactions, like thermal degradation. [121]

REX is a very complex process since it has to deal with several parameters, such as processing, chemical reaction, and heat transfer. Due to the mixing capability and higher heat and mass transfer, twin-screw extruders are generally used for REX. [122] Twin-screw extruders can operate in counterrotating and corotating way, being the latter preferred in the REX process. The main interest on using the corotating system is, namely, because of the high speed and throughputs, better temperature control, adjustable residence time distribution, and continuous stable flow through the die. [10,123]

According to Xanthos, [124] many types of reactions can be performed in an extruder, including bulk polymerization, grafting reactions, interchain copolymer formation, coupling/cross-linking reactions, controlled degradation, and functionalization.

## Reactive Blending of Immiscible Polymer Blends

Blending of polymers has become an attractive method to prepare new polymeric materials with enhanced properties and relative low cost. [125−130] However, there are two different types of polymer blends, miscible and immiscible blends. The former are characterized by the presence of only one phase and the existence of only one glass transition temperature ( $T_g$ ). Contrarily, immiscible blends are phase separated, exhibiting the $T_g$ and melting temperatures ( $T_m$ ) of each blend component. It is well known that the blend features strongly depend on the properties of the individual components, but morphology is a key factor for producing polymer blends with enhanced properties. [129]

Immiscible blends can have important industrial application if they are compatibilized. [131] The main challenge of compatibilization is to generate good adhesion between the phases and fine morphology. [130,131−135] Essentially, three methods have been used to compatibilize immiscible polymer blends, which are the following [121,136−141] :

1. Ex situ compatibilization-it consists of the addition of a presynthesized block or a graft copolymer, which has blocks or grafts identical to the ones existing in the polymers of the blend.
2. In situ compatibilization-block of grated copolymers and synthesized at the interface during blending, in this cases, both polymers should have reactive groups.

3. Cross-linking or "dynamic vulcanization"-one of the phases cross-links, which stabilizes the morphology and avoids coalescence.

Ex situ compatibilization allows controlling the molecular architecture of the copolymer added. [121] This copolymer, called compatibilizer, should locate at the interface, reduce the interfacial tension, improve dispersion, and stabilize the morphology. [121] A major drawback of this method is that each polymer blend requires a specific copolymer, whose preparation requires specific chemical routes and reaction conditions. [121,142] Besides, due to thermodynamic and dynamic reasons, there are always some copolymer chains which cannot get to the interface where they are most needed. Dispersion of the copolymer in matrix is not simple, and its diffusion to the interface is generally a slow process.

In situ compatibilization of immiscible polymers produces desired copolymers, through interfacial reactions between reactive polymers during blending. This method is more attractive and
cost effective because it allows producing the copolymer at the interface without separate preparation step. [142] When one of the polymers does not contain reactive groups, it needs to be to be functionalized previously. Generally, polymers grafted with maleic anhydride are extensively used as compatibilizers. [143−145]

Other parameters like thermodynamic and rheological properties and composition and processing conditions (screw configuration, time, screw rotation speed, temperature, throughput, etc.) have a strong influence on the morphology development during blending. [146]

### Preparation of Blends of Nonbiodegradable and Biodegradable Polymers

As stated before, polyolefins constitute the majority of thermoplastics currently used as packaging materials. Since the use of plastics continuously increases, the problem of postconsumer recycling has become an important issue for economic and environmental reasons. [147] Nevertheless, recycling would be neither practical nor economical for certain applications such as bags, agricultural mulch films, and food packaging, since these materials contain many organic residues and have a low lifetime. For these applications, it would be better to use plastics that could degrade into safe by-products under normal composting conditions. [147] Thus, blending biodegradable polymers, such as starch, PCL, and PLA, with nonbiodegradable polymers, such as PE, has received considerable attention. [27,61,148,149] The reasoning behind this approach is that if the biodegradable component is presented in sufficient amount and if it is removed by microorganisms in the waste disposal environment, the plastic containing the remaining inert components should disintegrate and disappear. [60]

Starch can be used like an additive in two different ways in biodegradable plastics: it can be compounded into plastics in the form of biodegradable filler, [90] which is added to various resin systems to make films that were impermeable to

$H_2O$ but permeable to water vapor, [150] and it can be plasticized with $H_2O(5\%-20\%)$ and compatibilized with other polymers to become part of the polymeric matrix. Since thermoplastic starch (TPS) is a very hydrophilic product, research has been performed to modify the starch structure by acetylation to reduce the hydrophilic character of the chains. [151–153] Avérous et al. [152] described changes in mechanical properties of TPS and its relationship with crystallinity, plasticizer content, and $H_2O$ during aging. They found that the moisture sensitivity and the critical aging have led to the necessity to associate TPS with another biopolymer. Association between polymers can be as a form of blends or multilayer products. Nevertheless, most of the times, compatibilization is required in order to promote adhesion between the polymers and to achieve the product specification. Many biodegradable TPS blends have been developed, such as starch/PCL, starch/cellulose acetate, and starch/PLA. [154,155] Also, this kind of materials can to be mixed with synthetic polymers (such as PE and PP) in order to create plastic products more degradable than conventional synthetic plastics.

Blends of PE and starch can be melt-processed to obtain products with PE-like properties. Starch, either in its virgin form or chemically modified, has been used to increase its compatibility with the polymer matrix in order to produce this type of blends. It was found that the effective accessibility of the starch, which is required for extensive enzymatic hydrolysis and removal, is achieved only if the starch content exceeds $30\%$.[60] However, increasing the amount of starch leads to a decrease in mechanical properties, and the resulting material has poor properties when compared to conventional polyolefins. These worsening properties arise from the different polar characteristics of starch and most of the synthetic polymers, which leads to poor interfacial adhesion. Nakamura et al. [27] investigated the incorporation of different starches (native, adipate, acetylated, and cassava starch) in an LDPE matrix to study the possibility to obtain partially biodegradable materials. The results indicated that the increase of the starch into the LDPE matrix was responsible for the reduction on mechanical properties of the products when compared with conventional LDPE (Table 6.2).

Table 6.2 Tensile Test for LDPE/Starch Compounds

| Sample | Tensile Strength (MPa) | Elongation (%) | Young Modulus (MPa) |
|---|---|---|---|
| Pure LDPE | $12.9 \pm 0.2$ | $131.9 \pm 4.8$ | $139.3 \pm 6.8$ |
| LDPE+5wt.% native starch | $12.7 \pm 0.2$ | $58.0 \pm 1.5$ | $113.1 \pm 7.0$ |
| LDPE+10wt.% native starch | $11.9 \pm 0.1$ | $50.1 \pm 1.5$ | $122.6 \pm 5.1$ |
| LDPE+20wt.% native starch | $11.3 \pm 0.1$ | $30.9 \pm 1.6$ | $151.7 \pm 11.2$ |

| | | | |
|---|---|---|---|
| LDPE+5wt.% RD125 | 12.5 ± 0.2 | 55.6 ± 3.7 | 118.9 ± 6.1 |
| LDPE+10wt.% RD125 | 12.1 ± 0.1 | 50.3 ± 1.5 | 131.9 ± 5.6 |
| LDPE+20wt.% RD125 | 11.1 ± 0.1 | 35.0 ± 1.8 | 151.2 ± 9.7 |
| LDPE+5wt.% adipate starch | 12.9 ± 0.1 | 52.6 ± 1.4 | 118.5 ± 6.5 |
| LDPE+10 wt.% adipate starch | 12.2 ± 0.1 | 43.5 ± 1.0 | 129.3 ± 9.7 |
| LDPE+20wt.% adipate starch | 11.3 ± 0.1 | 33.7 ± 1.1 | 150.8 ± 3.6 |
| LDPE+5wt.% cassava starch | 12.7 ± 0.1 | 55.6 ± 1.9 | 113.3 ± 5.3 |
| LDPE+10wt.% cassava starch | 12.0 ± 0.2 | 49.2 ± 1.4 | 119.0 ± 7.8 |
| LDPE+20wt.% cassava starch | 11.4 ± 0.2 | 36.9 ± 1.3 | 149.9 ± 6.2 |

Therefore, a lot of research work has been done in order to improve the compatibility/adhesion between starch and PE, including the modification of starch, [156−158] modification of PE, [60] and/or the introduction of a compatibilizer. [159−163] The compatibilizers include, among others, ethylene-acrylic acid (EAA) copolymer, PE grafted with maleic anhydride (PE-g-MA), and EVA. EAA is one of the most effective compatibilizer used, but it must be used in high amounts to achieve satisfactory mechanical properties. Unfortunately, EAA lowers the biodegradation rate of starch, while at the same time, it accelerates the thermo-oxidative degradation of LDPE/starch blends when used in low amounts together with a pro-oxidant. [159] The results showed that using PE-g-MA as compatibilizer, a much better dispersion of starch within the PE matrix together with a significant reduction in the phase size was achieved. [60,159,162] Moreover, concerning the biodegradability results, it was observed that the compatibilized blends showed a slightly lower biodegradation than the uncompatibilized ones. [159,160]

Blending PE with other biopolymers, such as PLA and PCL, has also been studied. [148,149] Matzinos et al. [149] observed that the effect of PCL on the mechanical properties of LDPE/TPS/PCL materials depends not only on its content but also on the final morphology. Machado et al. [61] investigated the mechanical and rheological properties and the potential for biodeterioration of HDPE blended with biodegradable polymers, such as PLA, PCL, and Mater-Bi (TPS with PLA or PCL), in a corotating twin-screw extruder. They observed that adhesion between PLA and HDPE, even with the addition of PE-g-MA, was not good enough to improve the mechanical properties, which were similar to the value observed to pure PLA.

Better adhesion was observed for PCL and HDPE blend. The differences observed in morphology when either PCL or PLA were used were attributed to their chemical structures. The ratio between ester links/aliphatic chains is higher for PLA than for PCL, affecting the polarity. [57] Thus, the polarity of PLA is higher than that of PCL, and consequently, the compatibility of PCL with HDPE is better. For this reason, also mechanical properties obtained for the HDPE/PCL system were enhanced compared to HDPE/PLA system. The morphology of all HDPE/Mater-Bi blends (Figure 6.9a through c) similar to the individual components of the blends can be detected, which can be associated with the interfacial tension among the components. The addition of Mater-Bi (including PLA/TPS or PCL/TPS) has a minor effect on mechanical properties.

The biodegradation potential, based on bacterial counts in the biofilm surface of the blends (ASTM G22-76), showed that HDPE/PCL has a lower resistance to bacterial attack than HDPE/ PLA. Moreover, the addition of $30\%$ starch to HDPE/PLA blend enhanced its biodeterioration

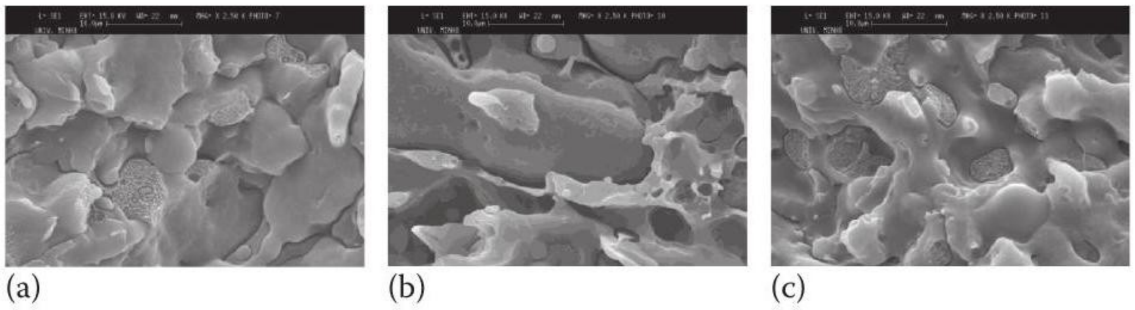


Figure 6.9 SEM micrographs of blends of HDPE with (a) SPLA 50 ( $50\,wt\%$ TPS + $50\,wt.\%$ PLA), (b) SPLA 70 ( $30\,wt.\%TPS+70\,wt.\%$ PLA), and (c) with SPCL ( $30\,wt.\%TPS+70\,wt.\%$ PCL).

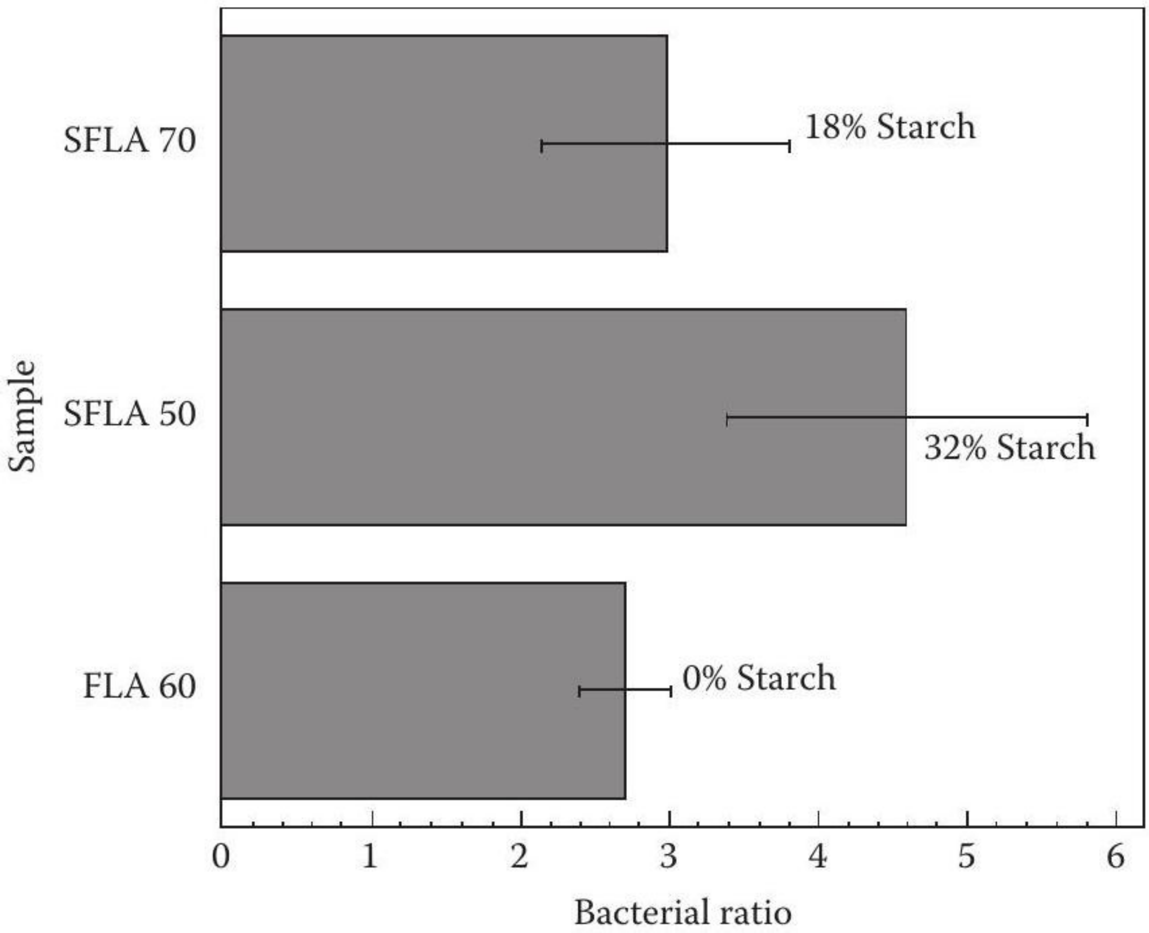


Figure 6.10 Bacterial ratio as a function of % starch (0%, 18%, and 32%).

potential, but the same was not observed in the case of the HDPE/PCL blend containing only 18 % starch.

Concerning the effect of the amount of TPS ( 0 % ,18 %, and 30 % ) on the biodeterioration potential of PLA blends, the study indicated that the ratio between bacterial counts obtained was not significantly different in the cases of the blends containing 0% and 18% of starch but increased significantly in the case of 30 % (Figure 6.10). The results suggested that the amount of starch might have been to low or simply not available at the polymer surface for bacterial growth in the blend containing 18 % starch. At 30 %, starch decreased the resistance of the blend to bacterial attack and promoted microbial growth. This result may be attributed to crystallinity and hydrophobicity of starch as biodegradation occurs preferably in the amorphous regions because of the higher mobility of the chains and their accessibility to the microorganisms. Also, starch, being less crystalline compared to PLA, is more prone to microbial attack. Additionally, its hydrophilic nature characterized by a higher number of -OH groups in structure compared to PLA promotes swelling in the culture medium, enhancing biodeterioration.
M. Mihai et al. [164] and N. Ljungberg et al. [165] studied the miscibility of polyolefin/PLA blends and found out that due to the differences in their chemical structures, a weak interfacial adhesion and poor dispersion were achieved.

A similar system was investigated by A. Kramschuster et al. [166] and M. Shibata et al. [167] using a different approach. They used PE-b-PLLA as a compatibilizer, and it was possible to improve the dispersion and achieve smaller PE particles in the PLLA phase (Figure 6.11b).

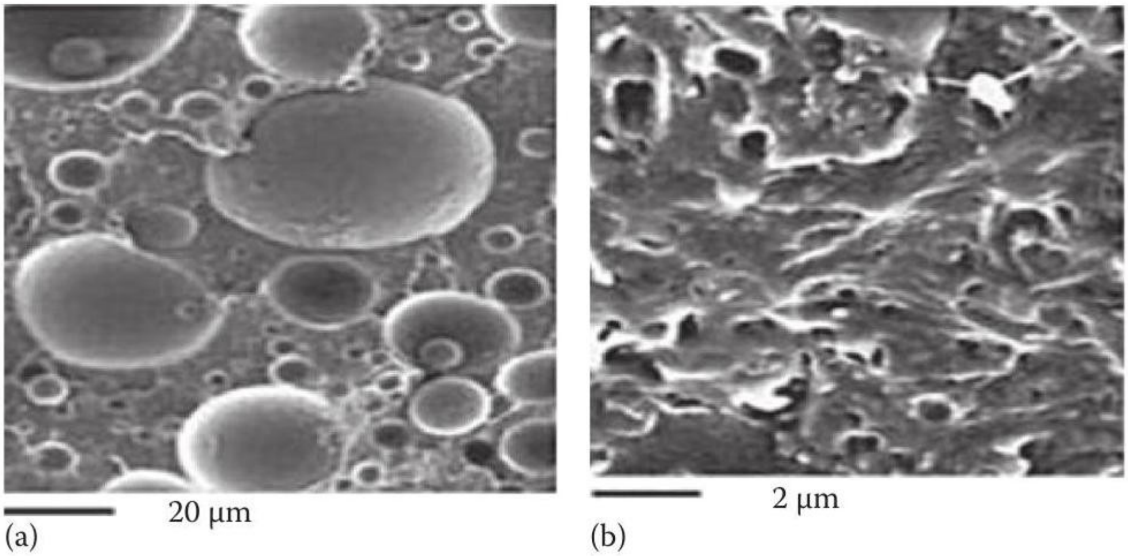


Figure 6.11 SEM micrographs of (a) 80:20 PLLA/LDPE and (b) 80:20:10 PLLA/LDPE/PE-b-PLLA blends.

## Polymer Modification

Instead of blending polymers A and B , the monomer of A can be polymerized in the presence of polymer B. The functional groups of polymer B, located along the chain or at the end, can be initiating sites, from which an A chain could grow (Figure 6.12). This way, grafted or block copolymers can be formed.

Generally, there are three main ways of synthesizing block or graft copolymers:

1. Living copolymerization
2. Chemical modification by postpolymerization
3. Coupling between two appropriately functionalized polymer chains

Figure 6.13 illustrates schematically approaches 1 and 2, which can be associated with the "grafting from" method and the approach 3 with "grafting onto" method.

Structures of copolymers obtained through methods 1 and 2 are specifically relevant to REX since they could not be obtained by classical copolymerization method. As referred before, the chemical reaction occurs at the interface, and thus, a large quantity of copolymer is difficult to obtain. This interfacial reaction leads to compatibilization of the blends during mixing. [168]

## Living Polymerization

Living polymerization is also called controlled polymerization. This method was developed by Michael Szwarc [169] in 1956 in the anionic polymerization of styrene with an alkali metal/naphthalene system in tetrahydrofuran (THF). This method is used for synthesizing block copolymers

ROP of various cyclic biodegradable monomers, such as lactams, lactones, 1,4-dioxane-2-one, lactides, and also carbonates, in a twin-screw extruder has been widely studied due to the reaction kinetics being compatible with the process conditions (high monomer conversion in a very short range of time at high temperature and good control of the structure through the judicious choice of the polymerization catalyst). The major interest in these copolymers is also based on their potential to participate in the development of biodegradable polymeric materials.

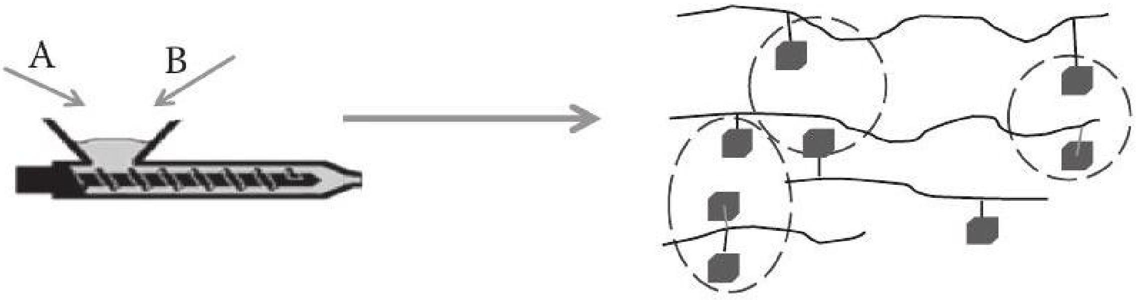


Figure 6.12 Schematic representation of in situ polymerization.

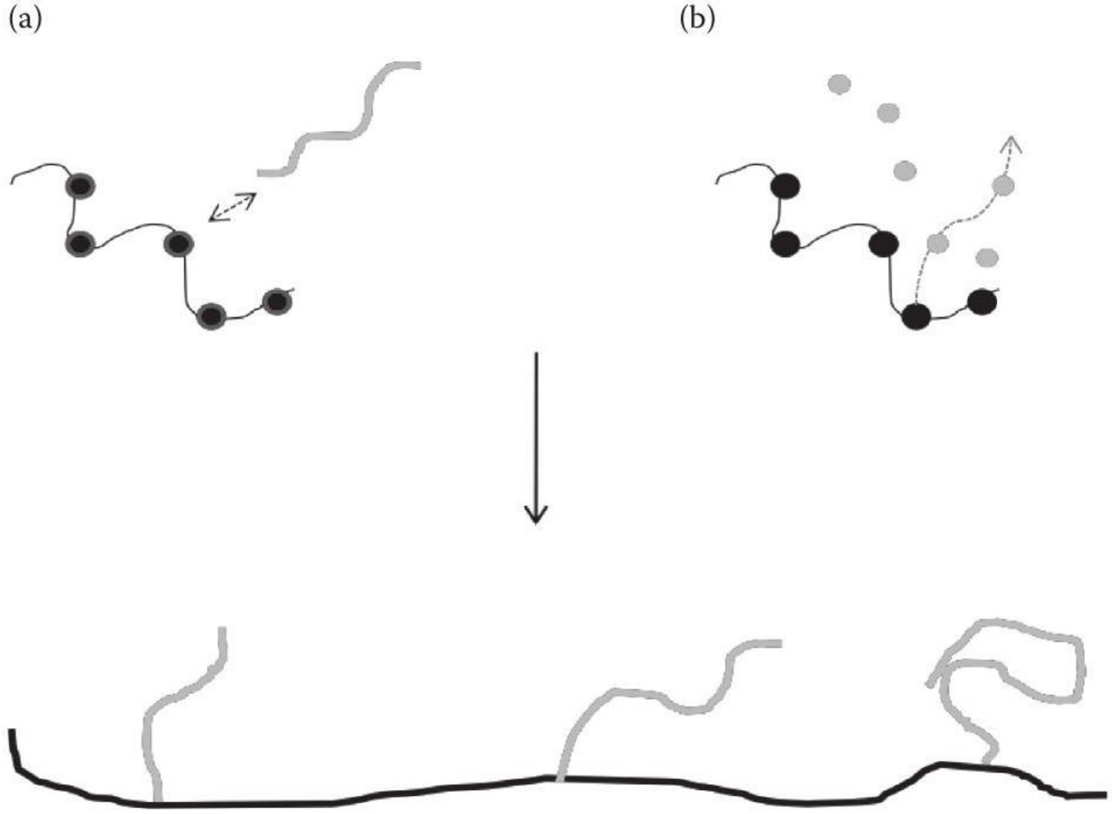


Figure 6.13 Schematic representation of (a) "grafting onto" and (b) "grafting from" methods. (From Machado, A.V. et al., Reactive polymer processing and design of stable micro- and nanostructures, in Advances in Polymer Processing from Macro to Nano Scales, Thomas, S. and Weimin, Y., Eds., Woodhead Publishing Limited, Cambridge, U.K., pp. 579-615, 2009.)

Raquez et al. [170] published a review on specific homo- and copolymerization carried out by REX, where it was showed, for the copolymerization of CL with 1,4-dioxan-2-one, that in approximately $2\ min$, $100\%$ of conversion was obtained at $130^{\circ}C$ using $Al(O_{\sec}\ Bu)_3$ as catalyst. It was observed that an increase in the copolymerization yields an increase in the molar fraction of CL. The ROP of CL by $Al(O_{\sec}\ Bu)_3$ active species is well controlled and proceeds via so-called coordination-insertion mechanism, which yields polyester chains endcapped by an active aluminum alkoxide bond. [171] As a result of the trifunctionality of $Al(O_{\sec}\ Bu)_3$, it allows the initiation and propagation of three growing polyester chains per one aluminum atom. A three-arm star-shaped PCL with an average molecular weight of each arm around $200{,}000\ g/mol$ has been successfully produced in the extruder within a mean residence time of less than 5 min (monomer conversions in excess of 95%). [172] Similarly, a new process has been developed for the continuous production of PLA using REX, using tin octoate ( $Sn(Oct_2)$ ) added with one equivalent of triphenylphosphine (as cocatalyst), which not only enhances the kinetics of LA by ROP but also eliminates any side degradation reactions, such as transesterification reactions. [173] Actually, it has been shown that the addition of one equimolar amount of a Lewis base like triphenylphosphine on 2-ethylhexanoic $tin(II)$ salt ¿ significantly enhances the LA polymerization rate in bulk. This kinetic effect has been accounted for the coordination of the Lewis base onto the tin atom, making easier the insertion of the monomer into the metal alkoxide bond of the initiator/propagation active species. [174] This tin alkoxide bond is formed in situ by reaction of alcohol and the tin(II) dicarboxylate. As reported in polymerization of CL catalyzed by aluminum trialkoxides, the LA ROP proceeds via the same "coordination-insertion" mechanism involving the selective $O_2-$¿ acyl cleavage of the cyclic ester monomer. The addition of one equivalent of $P(C_6H_5)_3$ onto $Sn$¿ allows reaching an acceptable balance between propagation and polymerization rates, so that the polymerization is fast enough to be performed through a continuous one-stage process in an extruder. [175] Using this process is also possible to produce PLA with controlled molecular weight by the addition of alcohol.

Raquez et al. [9] investigated the PLA production, based on molecular parameters, using batch bulk polymerization and a single-stage continuous REX. Even though the conversion was similar ( 98.5 % and 99 %, respectively), the time necessary to reach this conversion was very different ( 40 vs . 7 min ). Moreover, the molecular weight obtained was different, which was related with the diffusion and the reactivity of the monomer. Byong Jun Kim and James L. White [176] described how feed rate and feed order of comonomers influenced the formation of lactam-lactone copolymers, their structure, and molecular weight.

The polymerization of CL and LLA, using calcium ammoniate catalyst treated with ethylene oxide (EO) and propylene oxide (PO), was studied by Longhai Piao et al. [177] Both exhibited high activity, and they found that the living ROP behaved a quasi-living characteristic.

## Chemical Modification by Postpolymerization

Another way to prepare block or graft copolymers through the "grafting from" method consists of polymerizing a monomer in an extruder in the presence of functionalized prepolymer or polymer (end or pendant functional groups initiating the monomer polymerization). Postpolymerization modification to incorporate monomer units focuses on two types of reactions. One is the removal of the protecting groups, where monomers with the desired functionality are incompatible with one or more components of the selected polymerization process. The functional monomers are polymerized with a protected functional group, which is deprotected to provide the desired functionality after the reaction is complete. The other approach is to copolymerize monomers with one functional group then convert that functional group into the desired functional group after the first polymerization is complete. [178]

The postpolymerization modification of monomer units method has some advantages, namely, it allows incorporation of functionality that is incompatible with the polymerization process, allows also the characterization of the initial copolymer prior to further functionalization, and facilitates "grafting from" reactions. [178]

The preparation of prepolymers or macromonomers with functional end groups, so-called telechelic polymers, is another approach to structurally unconventional architecture. [179] The functional end groups are introduced either by functional initiation or endcapping of living polymers, or by a combination of the two. Therefore, monomers that were not able to copolymerize can be incorporated in a copolymer. Telechelic prepolymers can be linked together using chain extenders such as diisocyanates. [180] In this process, it is essential that the structure and end groups of the prepolymers can be quantitatively and qualitatively controlled. [181] REX has been used as a simple way of producing segmented copolymers. [182] Lee Bet and White [183] investigated the in situ polymerization of caprolactam using isocyanate-terminated telechelic poly(tetramethyl ether glycol) (PTMEG). The analysis of polyetheramide triblock copolymer indicated that the conversion of caprolactam was around 95%.

A method to produce biodegradable aliphatic polyesters by REX was developed by Jacobsen et al. [175] They dedicated their studies to the effect of triphenylphosphine on the efficiency of $Sn$¿ as a catalyst for the ROP of LA to produce PLA. A corotating closely intermeshing twin-screw extruders has often been used for polymerization reactions, but in any case, the reaction time was sufficiently smaller than the residence time in the extruder. In this case, a sophisticated screw design has been used to ensure further enhancement of the polymerization reaction by using mixing elements. Under these conditions, it was possible to realize a single-stage process to polymerize LA and to produce a PLA that can be used right away from the process for any known polymer processing technology.

Stevels et al. [182] reported the polymerization of l-lactide initiated by both a hydroxyl-terminated PCL and a polyethylene glycol (PEG). More recently, a new process has been developed for the production of PLA using REX, based on a new catalytic system that not only enhances the ROP kinetics of l-lactide but also suppresses side and degradation reactions. This process can be used to produce PLA continuously in larger quantities and at lower costs than before. [175]

The ROP of lactones in the extruder under anhydrous conditions has also been reported and can be catalyzed by Lewis acids (CL), [172,176,184,185] LA, [175,186] or base (CL with sodium hydride). [187] Lewis acid-catalyzed (aluminum tri-sec-butoxide) grafting of CL on starch has been carried out under anhydrous conditions in the extruder to form high-molecular-weight grafts. [185,188,189] A similar process has been used to graft CL on poly(ethylene-co-vinyl alcohol) by REX under anhydrous conditions. [190,191]

Becquart et al. [192] studied the functionalized poly(vinyl alcohol-co-vinyl acetate)-g-CL copolymers resulting from the in situ polymerization of the lactone ring. They found that the -OH groups were essential to initiate the polymerization.

Jae et al. [193] dedicated their work to the synthesis of triblock copolymers composed of PPG and PCL. The degree of CL conversion and the molecular weight of PCL increased linearly with the polymerization time or with the feed ratio of CL. The study of the ROP of the CL initiated by titanium phenoxide ¿ evidenced that, on average, one phenoxide ligand initiates the ROP. [194] Second, an increase of the polymer molecular weight was observed after complete monomer conversion, with a decrease of phenoxyl ester end groups concentration. Actually, this phenomenon is due to transesterification reactions favored with end groups in case of polymerization with $Ti$¿. In fact, the $C-O$ bonds of phenoxyl ester terminal is more prone to nucleophilic substitution than the $C-O$ bond in repetitive unit due to the influence of phenyl group on electronic delocalization. This leads to more selective transfer reactions and consequently to more efficiency for grafting reactions (Figure 6.14).

Recently, Moura et al. [112] prepared grafted copolymers of EVA/PLA and EVA/PCL using in situ polymerization of LA and CL in the presence of molten EVA. The process takes the advantage of the living character of PLA and PCL chains growing from LA and CL monomers by ROP to increase, through the specific exchange reaction between the living PLA or PCL end chain and the acetate groups of EVA, the probability of grafting and consequently the concentration of the formed copolymer. When polymerization of the cyclic monomer initiated by the $Ti$¿ takes place in the presence of molten EVA, two reactions occur, leading to the grafting process shown in Figure 6.15 for CL (the mechanism being the same for LA).

First, a transfer reaction between the acetate group of the EVA and the living Ti-O-polyester end bond results in EVA chain functionalized by $Ti$¿ and polyester functionalized by an acetate group (Figure 6.15a). Then, this new titanate species would react either on an ester function of polyester chain (Figure 6.15b [1]) or on the phenoxyl ester end group (Figure 6.15b [2]), the latter reaction being favored according to the previous explanations.

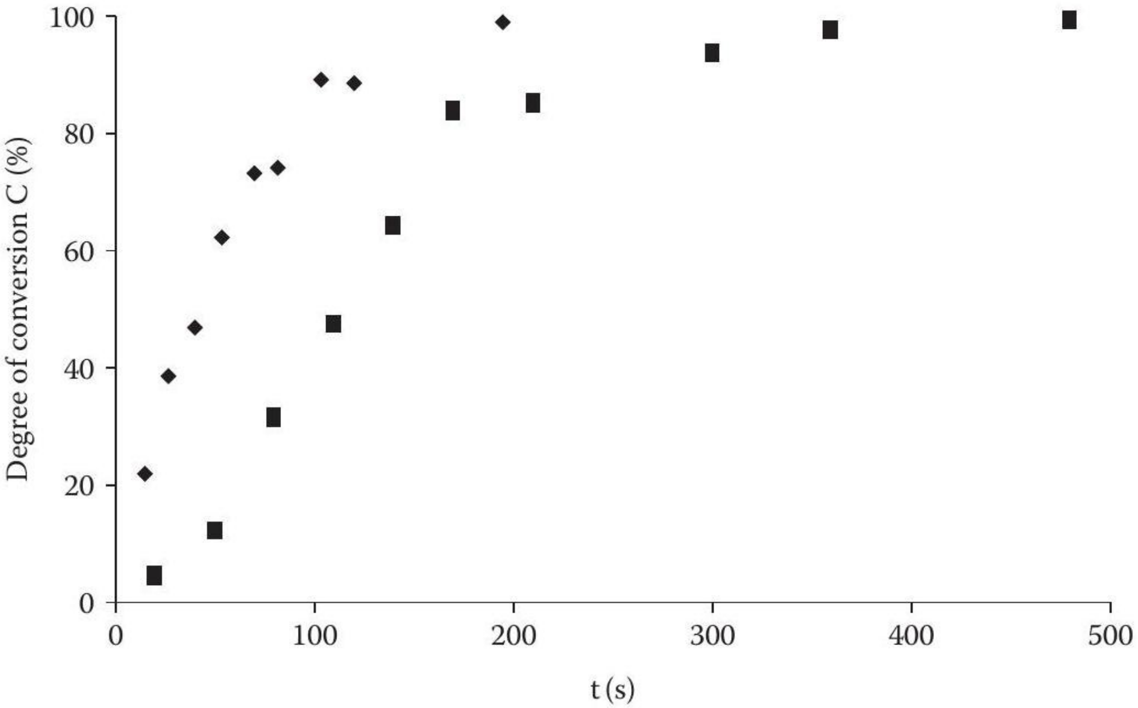


Figure 6.14 Time conversion curves for the bulk polymerization of CL between the rheometer plates at $T = 100^{\circ}C \left(M_0/I_0 = 300\right)$ initiated with titanium *n*-propoxide ( ↓ ) or titanium phenoxide (■). (From Cayuela, J. et al., Macromolecules, 39, 1338, 2006.)

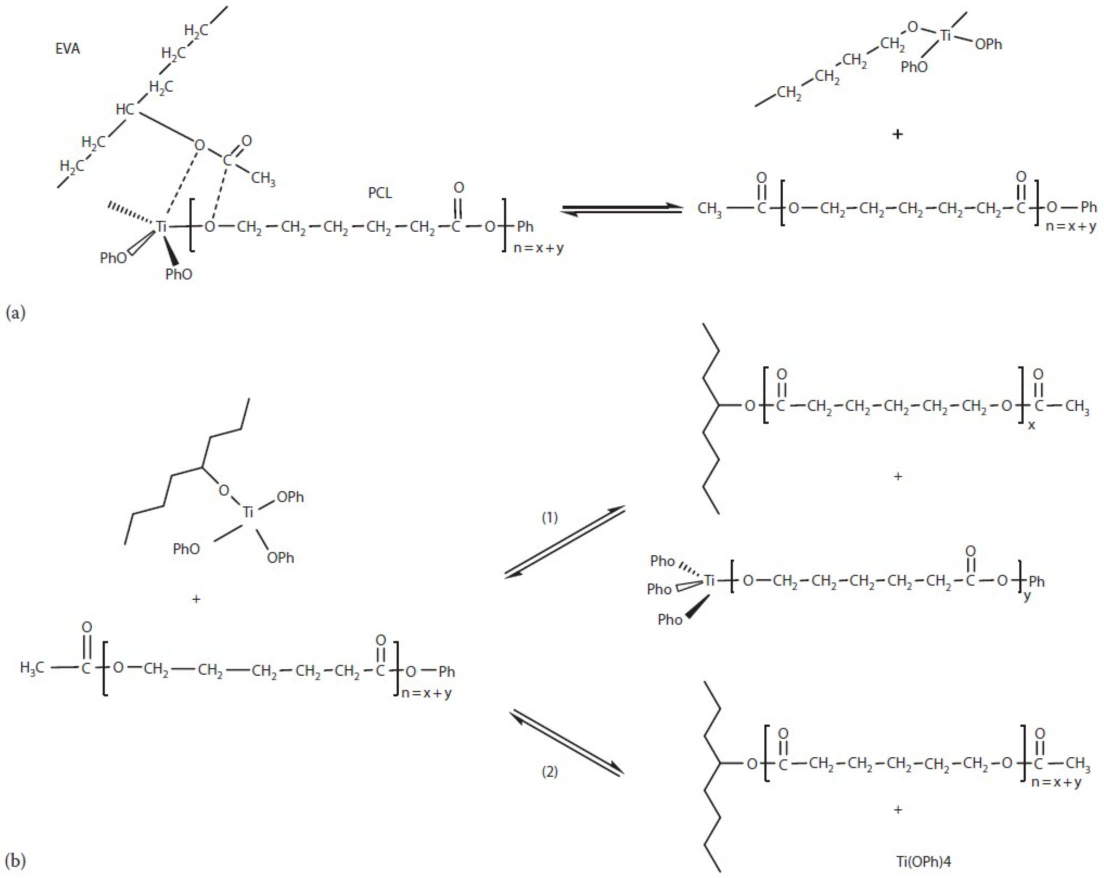


Figure 6.15 Reaction mechanism of EVA-g-PCL copolymer formation. (a) Transfer reaction between the acetate group of the EVA and the Ti-O-Polyester bond; (b)-(1) Transfer reaction between the new species and either an ester function of polyester chain; (b)-(2) Transfer reaction between the new titanate species on the phenoxyl ester end-group.

The morphology of the polymer blends (Figure 6.16a and b) and the samples obtained by in situ polymerization (Figure 6.16c and d) consists of dispersed particles in the EVA matrix, but significant differences can be noticed among them. Figure 6.16a, EVA/PLA blend exhibits a coarse morphology. Even though PCL is also dispersed in the EVA matrix, the size of the dispersed phase is much smaller. However, the dispersed phase of the samples obtained by in situ polymerization is very small when compared to the physical blends morphology, being almost undetectable for EVA-g-PCL sample. This decrease can be explained by the copolymer formed during reaction, which acts as compatibilizer, decreasing the interfacial tension between blends components and, consequently, the size of the dispersed phase.

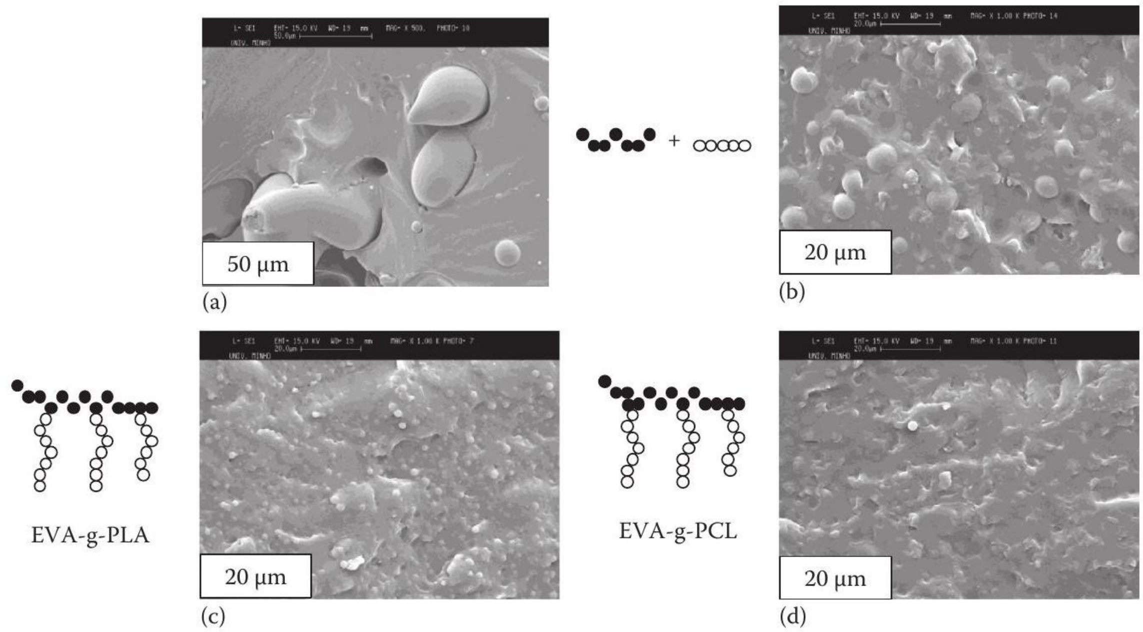


Figure 6.16 SEM micrographs of (a) EVA/PLA, (b) EVA/PCL, (c) EVA-g-PLA, and (d) EVA-g-PCL.

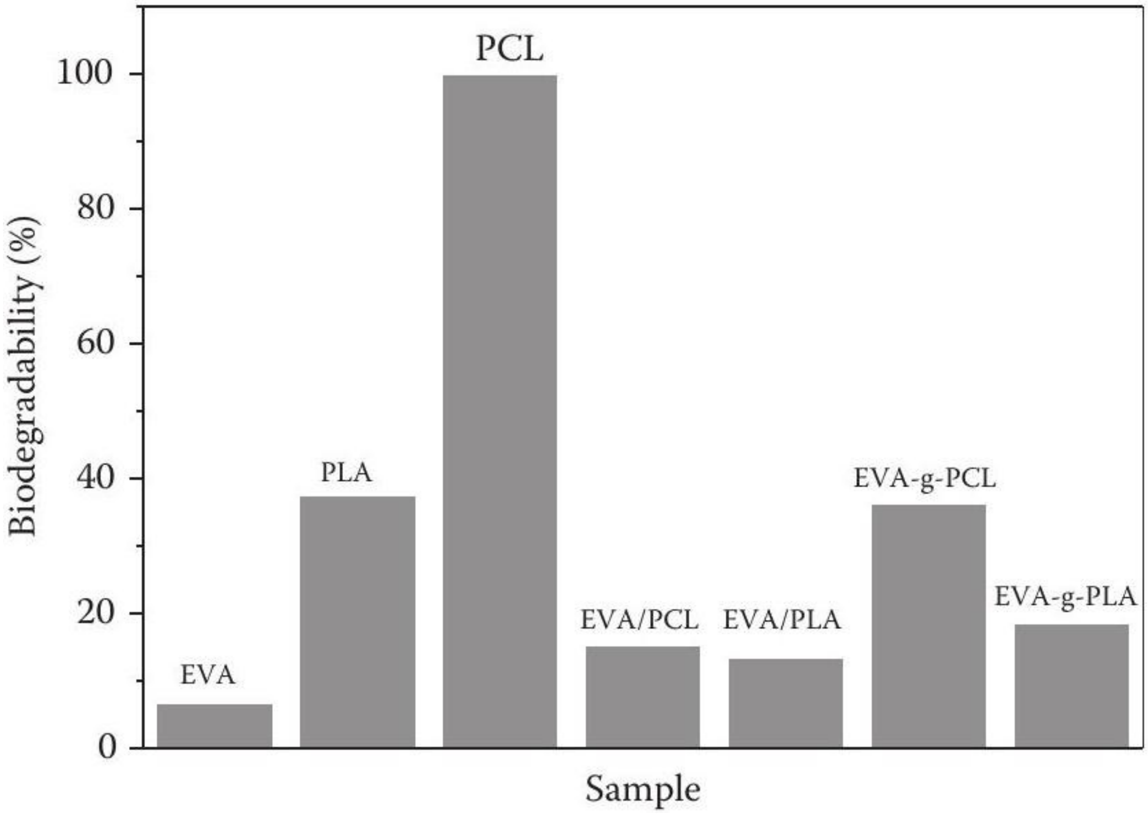


Figure 6.17 Biodegradability of polymers and all samples according to ISO 14851(1999).

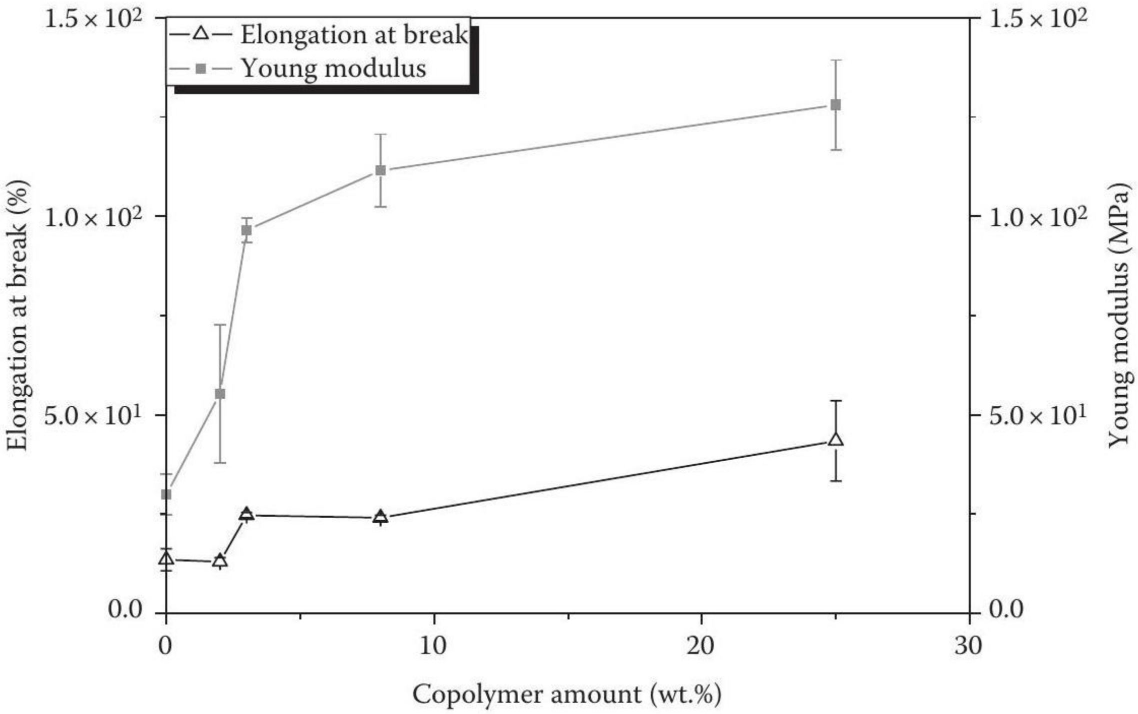


Figure 6.18 Young modulus and elongation at break as a function of copolymer amount.

The samples prepared by in situ polymerization, mainly for EVA-g-PCL sample, exhibit the better mechanical performance. [112] Moreover, differences in biodegradability behavior were observed, being EVA-g-PCL the more biodegradable sample (Figure 6.17).

## Coupling between Two Appropriately Functionalized Polymer Chains

Moura et al. [195] also dedicated their studies to the synthesis of EVA-g-PLA copolymers by transesterification reactions between EVA and PLA catalyzed by titanium propoxide ¿. They found out that the amount of grafted copolymer (EVA-g-PLA) had a significant effect on biodegradation, mechanical properties, and other physical properties as well (Figure 6.18).

Elongation at break and Young modulus as a function of copolymer amount indicated that an increase of copolymer amount increases these properties. This enhancement can be attributed to the formation of EVA-g-PLA copolymer and its compatibility effect, which are related to the chemical structure of the copolymer formed, its amount, and its effect as compatibilizer.

## CONCLUSIONS

This chapter focused of the preparation of biodegradable polymers using different approaches by reactive extrusion. It is possible to adapt the chemistry, by the right selection of the catalytic system, and the processing parameters to use REX for (1) production of compatibilized blends of biodegradable polyesters and synthetic polymers, (2) synthesis of aliphatic polyesters by catalyzed ROP, and (3) chemical modification of polymers. There is no doubt that the earlier examples are only some illustrations of the huge potential of REX, a solvent-free melt process, in the field of the biodegradables polymers.

## ACKNOWLEDGMENTS

The authors would like to thank the Portuguese Foundation of Science and Technology (FCT) for financial support (PTDC/AMB/73854/2006).

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