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# **Processing of Biodegradable Polymers**

Samuel Kenig and Amos Ophir

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# Preface

With the emergence of commercial biobased and biodegradable polymers (BDPs) and their blends, new potential routes have been opened to replace conventional fossil-based polymers, with the aim of reducing the carbon footprint of polymeric materials and the overall ecological burden of plastics.

This book covers the basic properties of BDPs according to their classifications: polyester-based, polysaccharides and proteins, the rheology of BDPs and their blends, and their numerous applications, with an emphasis on processing and reactive processing. However, BDPs are sensitive to the processing conditions due to their composition, which is tuned to bio-degradation. Hence, special attention has been directed to minimize the in-process degradation and enhance their final processed properties. To remedy some of the BDP processing shortcomings, special additives, fillers, and blends have been incorporated and developed with minimal effect on the BDPs' bio-degradation rate. All of these aspects of BDP processing are considered in this book, including their characteristics in extrusion, reactive extrusion, injection molding, compression molding, casting, electrospinning, and 3D printing, as well as the processing of recycled BDPs.

The processing of biodegradable polymers is an important stage bridging the technology of the BDP's composition, its final properties, and derived applications due to the structuring during processing of the polymer.

The book is directed toward scientists, engineers, and practitioners that deal with BDPs. It offers a comprehensive approach that includes not only a review of the science and technology of existing BDP compositions but also the appropriate processing methods and the derived applications.

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# Biodegradable Polymers' Composition, Properties, Processing, and Applications

Anna Dotan, Amos Ophir, and Samuel Kenig

This chapter aims to elucidate the relationship between composition, properties, processing, and applications of biodegradable polymers, which have attracted a growing interest in the commercial as well as the academic sector, with the goal of reducing and even eliminating the dependence on fossil fuels. Renewable, sustainable-type polymers trigger polymer biodegradability and all of these attributes can make a difference in the environment. Biodegradable polymers degrade by biological activity, particularly by enzymatic action leading to significant changes in the material's composition. In essence, biodegradable plastics should degrade, in a defined period, to simple molecules such as carbon dioxide and water. Polyesters are generally prone to biodegradation due to their potentially hydrolyzable ester bonds. Among the biodegradable polymers, the polyesters PLA (poly(lactic acid)), PHA (polyhydroxyalkanoate), and starch copolymers appear promising due to their natural and renewable sources. PLA is a linear aliphatic polyester produced by synthetic polycondensation of naturally produced lactic acid (corn). PHAs are aliphatic polyesters produced by a microbial process in a sugar-based medium, where the PHAs act as carbon and energy storage material in the bacteria. Such polymers are synthesized by microbes, with the polymer accumulating in the microbes' cells during growth.

This chapter reviews the chemical types of biodegradable polymers, their properties, blends, additives, and processability. Furthermore, the chapter indicates some important positive and feasible key application aspects related to the various end products, required properties, and their unique processing attributes.

# 1.1 Introduction to Biodegradable Polymers and Biodegradability

#### 1.1.1 Defining Biodegradable Polymers and Biodegradability

The American Society for Testing and Materials (currently known as ASTM International), the European Committee for Standardization (CEN), the International Organization for Standardization (ISO), the German Institute for Standardization (DIN), and the Organic Reclamation and Composting Association (ORCA) are all actively involved in trying to develop definitions and testing methods for both biodegradability and compostability. Biodegradable polymers constitute only one subcategory of degradable polymers. Degradable polymers are broadly defined as polymers designed to undergo a physical or chemical change under specific conditions, resulting in a loss of some properties. Biodegradable polymers are designed to degrade by the action of living organisms such as bacteria, fungi, and algae. ASTM, ISO, CEN, and others have drafted a definition of compostability based on a respirometry test that measures carbon dioxide generated from biodegradation in a "compost-like" environment [1].

The ASTM definition, updated in 2000 by the ASTM Standard D883 and in 2023 by ASTM 6400-23, describes a *biodegradable plastic* as "a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae."

In essence, biodegradable plastics should degrade, in a defined period, into carbon dioxide and water. Biodegradation rates are dependent on the thickness and geometry of the tested articles. Rapid breakdown rates are often quoted for thin films. Thick articles such as plates, food trays, and cutlery can take up to a year to degrade biologically.

### 1.1.2 Fundamental Mechanisms of Degradation

Microbes catalyze the degradation of organic molecules and are greatly affected by the type, location, and number of functional groups. The ease of degradation in relation to the functional group follows the sequence:

 $OH > COOH > NH_2 > SH > CH_3 > CI$ 

Compounds with OH substitutions are most easily degraded, while those with halogen substitutions (Br, Cl, I) are the most difficult to degrade, and compounds with more substitutions are more difficult to degrade. Generally, polymers containing double bonds or ether, ester, and peptide bonds in the backbone, such as natural rubber, polyethers, polyesters, and polyamides, are biodegradable. Since only the polymer structure and not the source of the monomeric building blocks is responsible for biodegradability, the presence of hydrolytic linkages along the polymer chain susceptible to enzymatic cleavage is essential. The interaction of the active site of the enzyme with the polymer must also be possible, in addition to the degree of crystallinity and the molecular weight being favorable. Biodegradability is generally favored by hydrophilic and hydrolytic backbone and end groups, lower crystallinity, porosity, and thinness.

# 1.1.3 Composting

Composting is currently the most acceptable disposal method for biodegradable polymers. It requires collection systems and composting facilities. Compostable plastics are a subgroup of biodegradable plastics [2].

The ASTM definition, updated in 2000 by the ASTM Standard D883 and in 2023 by ASTM 6400-23, describes a *compostable plastic* as "a plastic that undergoes degradation by biological processes during composting to yield  $CO_2$ , water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leaves no visible, distinguishable or toxic residue."

# 1.2 Biodegradable Polymers' Composition, Processing, and Properties

Aliphatic polyesters play a dominant role in biodegradable plastics due to their hydrolyzable ester bonds. Biodegradable polyesters, which have been developed commercially, are [1]: PLA – poly(lactic acid) or polylactide, PBS – polybutylene succinate, PTMAT – polytetramethylene adipate/terephthalate, PHA – polyhydroxy-alkanoate, PHB – poly(3-hydroxybutyrate), PHH – polyhydroxyhexanoate, PHV – poly(3-hydroxyvalerate), PCL – polycaprolactone, PBSA – polybutylene succinate adipate, AAC – aliphatic-aromatic copolyesters, and PBAT – polybutylene adipate/ terephthalate.

Generally, polyesters degrade eventually, with hydrolysis (degradation induced by water) being the dominant mechanism. Synthetic aliphatic polyesters are synthesized from diols and dicarboxylic acids via condensation polymerization. These polyesters can be blended with starch-based polymers for cost-competitive biode-gradable plastics applications. The rates of degradation of PBSA, PHB/PHV, and PCL are similar, with the rate of PBS and PLA being respectively slower [1].

#### 1.2.1 Poly(lactic acid) (PLA)

#### 1.2.1.1 Composition and Properties

Poly(lactic acid) (PLA) is a linear aliphatic polyester made by polycondensation of naturally produced lactic acid or by catalyzed ring opening of the lactide moiety. Lactic acid is prepared (via starch fermentation) as a coproduct of wet corn milling. The ester linkages in PLA are prone to hydrolysis and enzymatic chain scission. PLA is often blended with starch to enhance biodegradation and decrease costs. However, the brittleness of the starch/PLA blend is a major shortcoming in many applications. Several low-molecular-weight plasticizers such as glycerol, sorbitol, and triethyl citrate are used to remedy this limitation. PLA does not have food contact approval due to its bacteria-based manufacturing method [1].

Lactide is a cyclic dimer of lactic acid possessing two optical isomers, D and L. L-lactide is the natural isomer and DL-lactide is a synthetic blend of D-lactide and L-lactide. The L-lactide (LPLA) homopolymer is a semicrystalline polymer. These materials exhibit high tensile strength and low elongation and consequently have a high modulus, making them suitable for load-bearing applications like orthopedic fixation and sutures. Poly(DL-lactide) (DLPLA) is amorphous as a result of a random distribution of D and L isomeric forms of lactic acid. The amorphous material has lower tensile strength, higher elongation, and enhanced degradation time, making it more suitable for drug delivery. Poly(L-lactide) has a crystallinity of 37%, with a melting point of 175–178 °C and a glass transition temperature  $(T_{a})$  of 60-65 °C. The degradation time of LPLA is significantly longer than that of DLPLA, requiring more than 2 years to degrade completely. Copolymers of L-lactide and DL-lactide disrupt the crystallinity of L-lactide and accelerate the degradation process. A unique advantage of PLA is that the basic raw ingredient comes from corn, a very abundant crop and a renewable resource. Cornstarch is first converted to dextrose, which is fermented to lactic acid. Wheat, maize, sugar beet, and agricultural wastes have also been used as the starting feedstock. The composition of lactic acid is depicted in Figure 1.1.

Polylactide molecular structure







a) L-lactide

b) meso-lactide

c) D-lactide

Different compositions of lactic acid

In many respects, PLA is analogous to polyethylene terephthalate. Both can be oriented, strain crystallized, and heat set to produce tough, solid, and transparent fibers or films. They both can reach levels of crystallinity of approximately 37%. Both polymers can be copolymerized to control the ultimate level of crystallinity achieved by annealing or orienting and heat setting. The significant difference is that polyethylene terephthalate has a glass transition temperature of 70-80 °C and a melting point of 255 °C. The control of the crystallinity of PLA is essential not only to maximize the service temperature of the polymer but also in regard to its degradation time. Crystalline poly(L-lactide) is more resistant to hydrolytic degradation than the amorphous random L - D copolymer form. Suture materials requiring long holding times are typically higher in L content than those intended for rapid absorption. Molecular weight is also a significant factor in the durability of the polymer. The composition of the copolymer ratios also results in different mechanical properties when processed by different methods. PLA can be processed much like polyolefins and can be extruded. It has low melt strength, but processors can work around this shortcoming. However, PLA crystallization rates are slow, resulting in longer injection molding cycles. This is shown clearly in Table 1.1 [3].

The poor thermal and hydrolytic stability of PLA-based materials, which limits their potential for durable applications, can be overcome using stereo-complex crystallization of enantiomeric poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA). Stereo-complex crystallization provides a significant enhancement in thermal stability and biocompatibility through strong intermolecular interactions between L-lactyl and D-lactyl units. Stereo-complex crystallization is obtained using enantiomeric pairs of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) from both melt and solution states. A blend of PLLA and PDLA enables hydrogen bonding interactions, leading to a helical chains arrangement between L-lactyl and D-lactyl units with opposite chiral conformation for PLA stereo-complexation (SC). SC increases the melting temperature by 50 °C compared to neat PLLA or PDLA [4].

(L-)/(D,L) Copolymer Ratio	Process Condition <sup>a</sup>	Physical Condition <sup>ь</sup>	Tensile Strength, MPa	Tensile Modulus, GPa	Elongation at Break, %
100/0	IM	С	64.8	4.00	-
90/10	IM	А	53.4	1.03	4.6
90/10	IM	С	58.6	1.29	5.1
90/10	EX, BO	SC	80.9	3.41	41.2
90/10	EX, BO, HS	SC	70.1	2.76	20.7
95/5	EX, BO	SC	68.6	1.88	56.7
95/5	EX, BO, HS	SC	60.7	1.63	63.8
80/20	IM	А	51.7	2.10	5.7

 Table 1.1
 Mechanical Properties of PLA [3]

(L-)/(D,L) Copolymer Ratio	Process Condition <sup>a</sup>	Physical Condition <sup>ь</sup>	Tensile Strength, MPa	Tensile Modulus, GPa	Elongation at Break, %
80/20	EX, BO	SC	84.1	2.94	18.2
80/20	EX, BO, HS	SC	80.1	2.66	32.3
Polystyrene	IM	А	48.3	3.10	2.0

 Table 1.1 Mechanical Properties of PLA [3] (continuation)

a. IM - injection molded, EX - extruded, BO - biaxially oriented (3X), HS - heat set at 110C

b. A - amorphous, C - crystalline, SC - strain crystallized

### 1.2.1.2 Biodegradation Mechanisms

PLA is biodegradable by composting at temperatures above 60 °C. The first two weeks of degradation are by hydrolysis of water-soluble compounds and lactic acid. The rapid metabolization of these products into  $CO_2$ , water, and biomass by various microorganisms occurs following hydrolysis. An important feature in using polylactide polymers is the ability of the polymers to maintain their base properties until discarded and then degrade as rapidly as possible [1].

It has been reported that PLAs are biodegradable by combining hydrolysis and microbial metabolism. Few studies have dealt with the degradation of PLAs in natural soil. In general, crystalline LPLA is more resistant to hydrolytic degradation than the amorphous DL form. The biodegradation rate of copolymers depends on the molar ratio of lactide/glycolide, the molecular weight of the polymers, the degree of crystallinity, and the  $T_{\rm g}$  of the polymers. The possible approaches to controlling the rate and occurrence of degradation include adding an activator or a water absorber, coating the part with either a hydrophobic or a hydrophilic material, copolymerizing the PLA, and controlling crystallinity. The hydrolytic degradation of PLA-SC is slower than that of neat PLLA or PDLA, due to the high degree of crystallinity.

The hydrolytic degradation of polyesters depends on their chemical composition, molecular weight and molecular weight distribution, pH, ionic strength, temperature, crystallinity, glass transition temperature, dimensions, hydrolysis mechanism (autocatalytic, noncatalytic, enzymatic), and processing history (injection molding, extrusion, sterilization) [5].

### 1.2.1.3 Processability

Lactide polymers are subjected to degradation during melt processing due to hydrolysis, which results in lactide formation and decreases the molecular weight of the polymer. Furthermore, as processing temperatures are increased above about 230 °C, lactide polymer degradation is substantially accelerated. During melt processing operations, the linear polylactide exhibits necking under tension. This leads to problems with maintaining consistency in film thickness. Linear polymers, such as PLA, exhibit hydrodynamic instability or draw resonance at high draw ratios. This can cause a periodic variation in a film width and gauge. The low melt strength of PLA can be enhanced by an increase in molecular weight average, branching, and increased bridging by free radical reaction and a polydispersity of at least about 2.5.

Polylactide copolymerized with epoxidized linseed oil has generated a polymer with reduced necking using low power consumption. Under similar extrusion temperatures, the control of polylactide could not be run because the power consumption exceeded the maximum levels (> 15 A). The results show that polylactide copolymerized with epoxidized linseed oil has the benefit of processing at lower temperatures and generates a polymer with increased melt strength, less necking, and a film of lower thickness [2].

# 1.2.2 Polybutylene Succinate (PBS)

Polybutylene succinate (PBS) is a synthetic aliphatic biodegradable polyester that has similar properties to those of PET. PBS is generally blended with other biodegradable materials, such as thermoplastic starch (TPS) and adipate copolymers (to form PBSA), to make its use economical [1]. PBS is a semicrystalline polymer with a  $T_{\rm m}$  of 65 °C.

#### **Degradation Mechanisms and Properties**

PBS begins to biodegrade via a hydrolysis mechanism. Hydrolysis occurs at the ester linkages, which lowers the polymer's molecular weight, allowing for further degradation by microorganisms. Data based on SK Chemicals (Korea) PBS indicates a degradation rate of one month for 50% degradation, for a 40-micron-thick film in garden soil [47].

Polyester amides containing four-carbon diacid units tend to degrade through a mechanism implying cyclization to imides, probably by an intramolecular amidolysis reaction. Several researchers suggest that incorporating small amounts of ester groups into polyamide has enhanced degradability without losing most of their physical properties.

The hydrolytic degradability of the PBS series increases as a consequence of increasing the amide composition. Since amide groups are polar, their incorporation into the main ester chain increases hydrophilicity. The enhanced hydrophilicity increases the amount of water sorption during hydrolysis. Consequently, as a result of this increase in water sorption in the amorphous region, the hydrolytic degradation rate seems to be accelerated with increasing amide content. When the amount of the amide group is over 10%, the crystallinity dramatically decreases below 20% [6].

# 1.2.3 Modified PET

Modified PET (polyethylene terephthalate) contains comonomers, such as ether, amide, or aliphatic monomers, which provide "weak" linkages susceptible to biodegradation through hydrolysis. Typical modified PETs include PBAT (polybutylene adipate/terephthalate) and PTMAT (polytetramethylene adipate/terephthalate). PTMAT is an aliphatic-aromatic copolyester designed to perform in service and then completely degrade in a composting environment. It is a random copolymer derived from aliphatic acid, terephthalic acid (aromatic), and butanediol, resulting in polytetramethylene adipate-coterephthalate – PTMAT. This biodegradable polymer is commercially available. For instance, two commercial PTMAT polymers are Eastman's Eastar<sup>™</sup> Bio and BASF's ecoflex<sup>®</sup>, composed of aromatic-aliphatic copolyesters based on butanediol, adipic acid, and terephthalic acid. Eastman's version is a highly linear polymer; BASF's polymers contain long-chain branching.

Eastman's PTMATs have a density of 1.21 g/cm<sup>3</sup>, a melting point of 108 °C, and exhibit good clarity, adhesion, and elongation (up to 800%). They have high humidity and oil resistance and process much like LDPE. Eastar<sup>TM</sup> Bio is used in lawn-and-garden bags, agricultural films, netting, and paper coatings.

ecoflex<sup>®</sup> polymer processes efficiently and has a melting point of 110–115 °C and other properties that resemble those of LDPE. The film version demonstrates high elongation and dart impact and transparency with good welding and printability. Special additives can change the feel of ecoflex<sup>®</sup> from soft to stiff. ecoflex<sup>®</sup> exhibits high toughness and good cling properties for the replacement of vinyl polymers in vegetable, fruit, and meat wraps, having a 50% lower MVTR (moisture vapor transmission rate) than other biodegradables.

DuPont offers a modified PET (Biomax<sup>®</sup> series) encompassing three aliphatic monomers. Biomax<sup>®</sup> has a 1.35 g/cm<sup>3</sup> density and a 195 °C melting point, resulting in higher service temperature and faster processing rates than those of other biodegradable polymers. Furthermore, it offers high stiffness and 40% to 500% elongation. Biomax<sup>®</sup> has targeted disposable fast-food packaging, yard-waste bags, diaper backing, agricultural film, flowerpots, and bottles.

#### **Degradation Mechanisms**

Modified PET is hydro-biodegradable, with biodegradation following initial hydrolysis. The mechanism combines hydrolysis of the ester linkages and enzymatic attack on the ether and amide bonds. It is possible to control the degradation rates with modified PET by varying the comonomers used. Eastar<sup>TM</sup> Bio copolyester fully degrades to  $CO_2$ ,  $H_2O$ , and biomass in a time frame comparable to that of paper, within 12 weeks in an active microbial environment such as a commercial composting site. In six months, the polymer will biodegrade completely [7]. PTMAT is designed to perform during its service life and then fully degrade in a composting environment. A 5-mil PTMAT film typically becomes invisible within 12 weeks of composting. Fibers have a greater surface area than films of the same weight and their biodegradation rate likely exceeds that of films. In Europe, the PTMAT copolyester is certified to be compostable. It is known that the degradation decreases as the amount of aromatic content increases [8]. Thus, in the range of high-aromatic-content polymers, they remain undegraded [9]. PTMAT ecoflex<sup>®</sup> contains approximately 9% w/w of aromatic moieties. It was also demonstrated that during the depolymerization of the polymer chains, either the aromatic sequences built water-soluble aromatic oligomers (e.g., if acid terminated) or the polymer chains are cleaved into smaller parts by the microbial enzymes. However, the short soluble oligomeric intermediates are hydrolyzed within three weeks into monomers, which are easily metabolized when a mixed microbial population from compost is present [9]. BASF commercialized a blend of PBAT and PLA under the trade name of ecovio<sup>®</sup>, as a partially biobased, compostable material.

# 1.2.4 Polyhydroxyalkanoate (PHA)

#### 1.2.4.1 Composition and Properties

Polyhydroxyalkanoates (PHAs) are aliphatic polyesters produced via a microbial process using a sugar-based medium, serving as carbon and energy storage material for the bacteria. The two main polymers of the PHA family are poly(3-hydroxybutvrate) (PHB) and poly(3-hydroxyvalerate) (PHV). PHBs were the first biodegradable polyesters to be commercialized. Aliphatic polyesters, such as PHAs, are copolymers of hydroxybutyric acid and hydroxyvaleric acid and have been proven readily biodegradable. The most common commercial PHA is composed of a copolymer PHB/PHV, a plasticizer/softener (e.g., triacetin), and inorganic additives such as titanium dioxide and calcium carbonate. Production costs are a significant factor in the competition between PHAs and petroleum-based plastics. Lower-cost nutrient materials include corn liquor, molasses, and even activated sludge. The PHB homopolymer is a stiff and somewhat brittle polymer of high crystallinity. PHB copolymers are preferred for general purpose, as the degradation rate of PHB homopolymers is high at its normal melt processing temperature. PHB and its copolymers with PHV are melt-processable semicrystalline thermoplastics made by biofermentation from carbohydrates [1].

Depending on the carbon numbers in the monomeric constituents, PHAs can be classified as short-chain-length PHAs (SCL PHAs, C3–C5), which consist of 3–5 carbon monomers, or medium-chain-length PHAs (MCL PHAs, C6–C14), which consist of 6–14 carbon monomers in the 3-hydroxyalkanoate units. For example, PHB, PHV, and their copolymer poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)

(PHBV) are typical examples of SCL PHAs, whereas poly(3-hydroxyoctanoate) (PHO) and poly(3-hydroxynonanoate) (PHN), which are primarily formed as copolymers with 3-hydroxyhexanoate (HHx), 3-hydroxyheptanoate (HH), and/or 3-hydroxydecanoate (HD), are typical examples of MCL PHAs. More than 150 different PHA monomers have been identified, making them the largest group of natural polyesters [10]. This creates the possibility of producing biodegradable polymers with a wide range of properties. PHB is the best characterized PHA. It has the lowest molecular weight and is most common in nature. Its molecular weight can be up to two million (i.e., 20,000 monomers per polymer molecule). The monomer units of PHA are all in D configuration owing to the stereospecificity of the biosynthetic enzymes. Side chains comprise hydrogen or hydrocarbon up to C13 in length, and the repeating unit can range from 1 to 3 or more. These two parameters affect the hydrophobicity,  $T_{a}$ ,  $T_{m}$ , and level of crystallinity. There are a variety of PHA homopolymers, copolymers, and terpolymers, obtained using high-productivity microbial biofactories. Copolymers vary in the type and proportion of monomers and are typically random in sequence. PHAs are available in molecular weights ranging from around 1000 to over two million [11, 12].

#### 1.2.4.2 PHA Stabilization

The use of biodegradable aliphatic polyesters is limited due to their thermal degradation and low crystallization rate during melt processing and low toughness following solidification to room temperature. To remedy these shortcomings, the effects of hyperbranched polyesters (HBPs) and plasticizers were studied in the case of biodegradable PHA [13]. Results have shown that a synergistic effect takes place when a liquid HBP has been combined with a plasticizer based on citrate oil (CO), having a combined content of only 5%. In the optimized case, the molecular weight increased by 20% compared to the processed neat PHA. This is attributed to the reduction in viscous heating of the composite phase-separated melt. Furthermore, the crystallization rate constant increases 200-fold, while the total crystallinity is raised from 20% for the neat PHA to 40% for the composite PHA, and the crystallization temperature increases from 65 °C to 90 °C, respectively. This has been attributed to heterogeneous nucleation of the HBP and CO phase. As for the mechanical properties, the elongation at break was enhanced from a low level of 12% for the neat PHA to the level of 26% in the case of the composite PHA. This increase in toughness was accompanied with a moderate decrease of the modulus from 740 MPa to 570 MPa. The formation of a separated phase containing HBP and CO and its effect on the plasticization, nucleation, and mechanical properties was studied and verified by scanning electron microscopy (SEM) [14].

#### 1.2.4.3 Branched PHA

Branched PHA (PBHB) copolymers (Nodax<sup>TM</sup>) make them unique. Carbon side chains of C6 to C24 in length are grafted from the C4 backbone, with a comonomer content ranging from 2% to 20%. As in the case of the conventional LDPE copolymer, PBHB's long-chain branching allows a considerable range for tailoring crystallinity, melting point, stiffness, and toughness. Nodax<sup>TM</sup> C4/C6 is said to be fit for injection molding and extrusion of sheet or film. The polymer exhibits mechanical properties similar to those of a polyolefin and surface properties much like those of a PET – including high receptivity to printing inks and dyes. Adhesion to LDPE and PP is good enough to avoid tie layers in multilayer structures. Remarkably, Nodax<sup>TM</sup>'s oxygen barrier approaches that of EVOH [15].

#### 1.2.4.4 Properties of PHB

The comparison of properties between PHB and PP is summarized in Table 1.2. As is evident, PHB is water-insoluble and relatively resistant to hydrolytic degradation. This differentiates PHB from most other currently available biodegradable plastics, which are either water-soluble or moisture-sensitive. Furthermore, PHB has a melting point of 175 °C, a glass transition temperature of 15 °C, and a tensile strength of 40 MPa, which is close to that of polypropylene.

PHB exhibits good oxygen barrier properties and ultraviolet resistance and is nontoxic and biocompatible. However, it has poor resistance to acids and bases and is soluble in chloroform and other chlorinated hydrocarbons.

Property	Polypropylene (PP)	РНВ
Melting point $T_{m}$ [°C]	171-186	171-182
Glass transition temperature $T_{g}$ [°C]	-5 to -15	5-15
Crystallinity [%]	65-70	65-80
Density [g·cm <sup>-3</sup> ]	0.905-0.94	1.23-1.25
Molecular weight (× 10 <sup>5</sup> )	2.2-7	1-8
Molecular weight distribution	5-12	2.2-3
Flexural modulus [GPa]	1.7	3.5-4
Tensile strength [MPa]	39	40
Elongation at break [%]	400	6-8
UV resistance	poor	good
Solvent resistance	good	poor
Oxygen permeability $[cm^3 \cdot m^{-2} \cdot atm^{-1} \cdot d^{-1}]$	1700	45
Biodegradability	-	good
Other	due to low density, floats in aquatic system	due to high density, sinks in aquatic system

Table 1.2 PHB Properties Compared to those of PP

#### 1.2.4.5 Biodegradability

PHAs are biodegradable via composting. The optimum conditions for the commercially available PHA (Biopol<sup>™</sup>) are a 10-week composting period at 60 °C and 55% moisture to achieve 100% degradation. These aliphatic polymers are suited for short-duration applications and high-degradation-rate requirements. It was found [16] that bacterial PHB/PHV (92/8 w/w) degraded nearly to completion within 20 days in anaerobic conditions, while synthetic aliphatic polyesters such as PLA, PBS, and PBSA did not degrade in 100 days. Cellophane, which was used as a control polymer, possessed a similar degradation rate as the PHB/PHV blend. Under landfill conditions, PHB/PHV degraded within 6 months [2].

PHAs offer a unique combination of biodegradability and hydrolytic stability under normal service conditions. Since carbon dioxide and water are the raw materials used to make PHAs, the PHA life cycle is a closed-loop process. For the first time, there is now a solution to the accumulation of plastics in the marine environment, which makes up the more significant part of the Earth's surface and is a source of much of the world's food [17].

The anaerobic decomposition is significant, for example, concerning biodegradation in landfills (where anoxic conditions exist) and anaerobic waste treatment processes. The natural polyhydroxyalkanoates PHB and PHBV were previously reported to be biodegradable under anaerobic conditions.

Thus, it can be stated that for PHB and PHBV, as well as PCL, a definite anaerobic attack was shown within the incubation period of 7 or 14 weeks. PHB and PHBV films, for example, were already wholly disintegrated at the sampling time in wastewater sludge and the anaerobic river sediment after 14 weeks of incubation. Increasing the degradation temperature may have a positive effect on biodegradability.

#### 1.2.4.6 Processability

PHB can be processed in a narrow window, as it is susceptible to thermal degradation above its melting temperature, resulting in decreased molecular weight and poorer mechanical properties. As a result, PHB has been processed in solution [2]. This problem might be overcome by melting point reduction below the processing temperature or cross-linking. The melting point of PHB was reduced by copolymerizing 3-hydroxybutyrate with either 3-hydroxyvalerate or 4-hydroxybutyrate. Another approach is blending with various additives or cross-linkers, which can repolymerize fragmented polymer chains. Accordingly, some attempts to improve the melt stability of PHB have been made with additives, including various organic and inorganic compounds. A recent study found that polyhydroxyalkanoate with pendant epoxide groups has a higher thermal stability due to cross-linking reactions of pendant epoxide groups with fragmented carboxyl chain ends [1]. Blending 10% to 20% PLA into PHB resulted in upgraded processability, and PHV contents of 5–20% give a good range of properties broadly similar to those of the polyolefins (polyethylene and polypropylene). They have lower melt temperatures than the homopolymer, improving melt processing, and their other properties are close to those of PHB.

# 1.2.5 PHBH Polyester

Polyhydroxybutyrate-*co*-polyhydroxyhexanoates (PHBHs) resins are the newest types of naturally produced biodegradable polyesters. The PHBH resin is derived from fermentation of carbon sources such as sucrose, fatty acids, or molasses. These are aliphatic-aliphatic copolyesters, distinct from aliphatic-aromatic copolyesters. Besides being completely biodegradable, they exhibit barrier properties similar to those of ethylene vinyl alcohol. The commercial polymer Nodax<sup>™</sup> was cast-extruded or blown to manufacture films. Potential applications are mono/multilayer film and nonwoven paper packaging at costs comparable to those of traditional materials such as EVOH.

PHBH resins biodegrade under aerobic and anaerobic conditions and are digestible in hot water under alkaline conditions [1].

# 1.2.6 Water-Soluble, Biodegradable Polymers

#### 1.2.6.1 Starch

Starch is a food source produced and stored in most plants. It is a linear polymer (polysaccharide) made up of repeating glucose groups linked by glucoside linkages in the 1-4 carbon positions. The length of the starch chains varies with the plant source and generally has between 500 and 2000 glucose units. Amylose and amylopectin are the two major molecules of starch. The alpha linkage of amylose starch makes it flexible and degradable. Starch-based polymers are based on crops of corn (maize), wheat, or potatoes having a starch content exceeding 60% before significant material degradation occurs. Starch is available in abundant quantities at a very low cost.

Starch itself is very brittle and has poor mechanical properties for real applications. However, its elongation can improve significantly by blending it with plasticizers, such as water, amino acids, or glycerol, but the tensile strength is negatively impacted. Often, starch-based polymers are blended with aliphatic polyesters and polyvinyl alcohols to achieve the desired performance for various applications. Biodegradation of starch-based polymers results from an enzymatic action at the glucoside linkages between the sugar groups leading to a degradation in the chain length and the splitting off of sugar units readily utilized in biochemical degradation. At starch contents lower than 60%, the starch particles act as weak links in the polymer matrix and are sites for a biological attack. This results in the polymer matrix disintegrating into small fragments but not biodegrading.

There are several variants of biodegradable starch-based polymers, including thermoplastic starch (TPS) products, starch/aliphatic polyester blends, starch/PBS/ PBSA polyester blends, and starch/PVOH blends.

Biodegradable TPSs have a starch (amylose) content greater than 70% and incorporate specific plasticizing additives that can produce thermoplastic materials with suitable properties and inherent biodegradability properties. Notably, such TPS compounds can be processed on existing plastics processing equipment. Highstarch-content plastics are highly hydrophilic and readily disintegrate in contact with water. This can be overcome through blending and reacting with hydroxyl groups, which readily undergo acetylation, esterification, and etherification.

Polyvinyl alcohol (PVOH) is blended with starch to produce readily biodegradable plastics. An Australian company (Propak) produces loose-fill peanuts from a starch/PVOH blend (a grade of Mater-Bi<sup>TM</sup>) that exhibits water-solubility in approximately 3 minutes. These expanded products have a closed-cell pore structure and densities ranging from 0.01 g/cm<sup>3</sup> to 0.1 g/cm<sup>3</sup>.

PVOH is readily water-soluble, and the starch/PVOH blends are degraded via hydrolysis and biodegradation of the sugar molecules [7].

### 1.2.6.2 Polyvinyl Alcohol (PVOH)

PVOH is a readily biodegradable, not compostable, water-soluble polymer. Traditional extrusion technologies cannot process conventional PVOH since it decomposes close to its melting point of 230 °C. Even partially hydrolyzed grades, which melt at 180–190 °C, undergo some decomposition during melt processing.

Until recently, PVOH films were prepared by casting from an aqueous solution. Recently, however, new grades of PVOH have been commercialized, incorporating plasticizers to allow extrusion.

The degradation of PVOH is influenced by its crystallinity and molecular weight. Testing has shown that PVOH does not biodegrade but simply dissolves in water. Literature from PVOH manufacturers indicates that PVOH can be biodegradable by activated sludge treatment. Blends of PVOH with starch, glycerol, and chitosan exhibit degradation of the second constituents, with the PVOH almost intact. Some evidence of oxidation and possibly biodegradation of the amorphous phase of PVOH has been noticed [11, 17]. The poor mineralization of PVOH in the soil is attributed to the absence of PVOH-degrading microorganisms in the soil. However, PVOH has been shown to degrade quickly in an aqueous medium enriched with

PVOH-degrading microbes [18]. Interactions with solid substrates have been claimed responsible for the limited biodegradability of microbial polysaccharides and proteins. Their presence seems restricted to specific environments, such as PVOH-polluted textile or paper mill effluents.

#### 1.2.6.3 Cellulose Ether

Cellulose ethers are high-molecular-weight compounds produced by replacing the hydrogen atoms of hydroxyl groups in the anhydroglucose units of cellulose with alkyl or substituted alkyl groups.

Cellulose ethers are water-soluble. The FDA (U.S. Food and Drug Administration) approved methylcellulose and hydroxypropyl methylcellulose as acceptable food additives. The maximum concentration is limited only by the solution viscosity. Cellulose ethers form clear, tough, and flexible films. Cellulose ethers are used as dispersing agents in agricultural fields, as suspending and dispersing aids for pesticide and fertilizer powders. They provide high wet tack and adhesion to waxy plant surfaces. Chemically inert and nonionic, cellulose ether is compatible with many active ingredients [19].

Despite their prolonged biodegradation rate, cellulose ether products should not pose any waste-/soil-recycling hazard. They are similar in behavior to wheat flour or sawdust. Because cellulose ether products and their aqueous solutions present no significant ecological problems, they can be disposed of by industrial incineration or in an approved landfill.

#### 1.2.6.4 Polyethylene Glycol (PEG)

Polyethylene glycol is a water-soluble, waxy solid used in the cosmetic industry. As the molecular weight of PEG is raised, the viscosity and the freezing point increase as well.

Polyethylene glycol is obtained by condensation of ethylene oxide and water, having a general formula of  $H(OCH_2CH_2)_nOH$ , where *n* designates the number of oxyethylene groups, typically from 4 to about 180. The low-molecular-weight materials from *n* = 2 to *n* = 4 are diethylene glycol, triethylene glycol, and tetraethylene glycol, respectively. The materials with a low molecular weight up to 700 are colorless, odorless, viscous liquids with a freezing point of -10 °C (diethylene glycol). In comparison, polymerized compounds with a molecular weight higher than 1000 are waxlike solids with a melting point up to 670 °C for *n* = 180. PEG is also soluble in many organic solvents, including aromatic hydrocarbons (not aliphatic). It is nontoxic, odorless, neutral, lubricative, nonvolatile, and nonirritating, and is used in a variety of pharmaceuticals and medications as a solvent, dispersing agent, ointment and suppository base, vehicle, and tablet excipient.

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