Polymers, Biodegradable

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1. Introduction

Biodegradable polymers have been around on an industrial scale since the end of the 1990s.

In contrast to biobased polymers, which are by definition made partially or completely of renewable raw materials, biodegradable polymers are not defined in terms of their

raw-material basis. After all, biodegradability means that a given substance can be completely converted into water, CO_2, and biomass through the action of microorganisms such as fungi and bacteria. This property is not dependent on the origin of the raw materials, but only on the chemical composition of the polymers [1].

A distinction has to be made between degradability (mechanical disintegration) and *bio*degradability (metabolism): not every polymer that can no longer be seen after a few weeks because it has disintegrated into small pieces has actually been biologically degraded. Biodegradability is a certified performance characteristic (ISO 17088, EN 13432 in EU, ASTM D 6400 in North America, GreenPla in Japan). To fulfill, e.g., the EN 13432 norm, the polymer has to be converted to CO_2 by over 90% within 180 d under defined conditions of humidity, temperature, and oxygen level.

Biodegradability is primarily a specific functionality which, like other properties, gives a product additional value. Three major areas of application can be defined:

1. Biodegradable waste bags for organic waste management. Approximately 30–40% of the household waste is organic waste, which can be converted to energy and to valuable compost. To enable this organic recycling in a hygienic and efficient way, biodegradable organic waste bags have been developed.

   Biodegradable carrier bags (e.g., for fruit and vegetables) fall in the same class of application.
2. Biodegradable packaging materials: flexible packaging (e.g., shrink film) and rigid packaging (e.g., trays, foams).
3. Biodegradable agricultural mulch film. Mulch film offers the opportunity to increase crop yield by reducing water consumption, improving microclimate and preventing growth of weeds. Biodegradable mulch film is plowed in the soil after harvest thus reducing the number of working steps.

Synthetic biodegradable polymers [2] and biotechnologically based polymers (PHA) [3] are produced and used in the applications mentioned above.

The following Chapter 2–4 will describe in more detail the key prerequisite for biodegradability followed by a description of the synthesis properties and processing of the various biodegradable polymers. Both structural and functional biodegradable polymers will be addressed. Value of biodegradability with respect to sustainability including life-cycle assessment (LCA) will be addressed in Chapter 6. The significant growth of the market (including legislative changes), the various market applications and the corresponding development of production capacities are reviewed in Section 5.7 and Chapter 8.

2. Biodegradability and Toxicology

The property of biodegradability is not dependent on the origin of the raw materials but only on the chemical composition of the polymers. A polymer is biodegradable if it is metabolized by microorganisms (bacteria, yeasts, algae, filamentous fungi) in their natural environment (e.g., surface or sea water, soil or compost) to energy, biomass, water, and carbon dioxide or methane within a given time period (e.g., in composting standards: six months).

Biodegradation is related to either aerobic or anaerobic processes. In an aerobic process, organic matter is transformed to carbon dioxide, water, energy, and biomass by microorganisms in the presence of oxygen. Aerobic biodegradation of polymers occurs in soil or in compost with a variety of microorganisms [4]. In anaerobic biodegradation, organic matter is metabolized by microorganisms in the absence of oxygen. In this process, organic matter is converted to methane, carbon dioxide, water, energy, and biomass.

2.1. Mechanism of Biodegradation

Most of the biodegradable polymers are insoluble in water. They are too big to pass the cellular membrane of microorganisms. Therefore, biodegradation of these polymers begins with chain cleavage by enzymes (e.g., lipases and esterases) secreted by the microorganism in the natural environment [5–7].
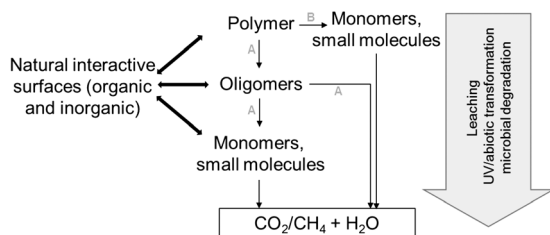
Figure 1. Mechanism of biodegradation

The polymer chains are cleaved to smaller fractions which can be absorbed and metabolized by microorganisms (Fig. 1). The cleavage can either be endolytic (Route A) resulting in oligomers and subsequently in monomers, or exolytic, which directly leads to monomers (Route B). The cells of the microorganism gain energy from the mineralization process producing water, biomass, carbon dioxide, or methane. Biodegradation is a surface erosion process because enzymes are too large to diffuse into the biodegradable polymer [8]. The microbial degradation is influenced by humidity, oxygen level, light, and temperature. At all steps of the degradation process intermediates interact with surfaces of the natural environment (e.g., soil organic matter, clay minerals, or mineral oxides). This permanent or reversible binding can lead to bound residues [9, 10]. The magnitude of this effect is of course highly dependent on the amount of potentially interacting surfaces. Due to potential formation of bound residues, the investigation of the toxicity of intermediates formed during the degradation process and their potential of bioaccumulation is of very high importance to secure environmental safety. Besides the biodegradation, leaching and abiotic factors such as UV radiation or hydrolytic degradation can influence the transformation of the polymer.

The enzymatic degradation of a polymer chain depends on the following factors:

- The polymer chains have to be flexible enough to enter the catalytic center of enzymes
- The presence of chemical bonds (e.g., ester bonds) that can be cleaved by enzymes

As the degradation is catalyzed by enzymes, the microbial community present at the site and habitat of interest define the degradation potential. The microbiome itself is strongly dependent on many factors such as temperature, humidity, nutrients, and gases (e.g., oxygen in aerobic biodegradation) [11]. In the last few years, some of the primary degrading organisms have been identified. A broad range of organisms from a variety of habitats have been shown to degrade aliphatic polymers like PBS, PHA, and PBSA. The degradation of aliphatic–aromatic copolyesters is slower in comparison to aliphatic polymers and the knowledge about the degradation process is limited. Nevertheless some primary degrading organisms from different environmental conditions have been described in the recent years shedding light on the degradation process [6, 7, 12].

As an example for the class of biodegradable polymers, the aliphatic aromatic polyester poly [(butylene adipate)-*co*-(butylene terephthalate)] (PBAT, Ecoflex), will be used to describe the different test procedures and standards. Laboratory tests have been performed with PBAT to monitor the biodegradation of polymers with respect to the formation of intermediates. It has been shown by interrupting the biodegradation process that Ecoflex was degraded to oligomers and to the monomers used to synthesize the polymer. The residual polymer, oligomers, and monomers could at any stage be metabolized by > 99% in an inoculum prepared from compost (Table 1) [12]. No accumulation of residues has been found.

2.2. Toxicity of Biodegradable Polymers

To prevent any negative impact of polymers which are designed for applications ending up in the environment, it is important to provide adequate information for comprehensive assessment of the environmental and toxicological safety of such a plastic. In general, this may be achieved by characterizing the raw materials, e.g., the polymer itself, and potentially resistant residues after biodegradation with respect to ecotoxicological and toxicological properties. As an example, results from laboratory tests are summarized in the following, which have been conducted with the polyester Ecoflex in order to identify toxic effects (see also → Ecotoxicology).

Table 1. Fragments of Ecoflex after degradation with isolated pure strain or pure strain and mixed cultures from compost (x = detected; n.d. = not detected)

	Monomers[*]			Aliphatic oligomers[*]		Aromatic oligomers[*]	
	B	A	T	BA	ABA	BT	BTB
Test 1	x	x	x	x	x	x	x
Test 2	x	x	x	x	x	n.d.	n.d.
Test 3	x	x	x	n.d.	n.d.	n.d.	n.d.
Test 4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

[*] A = adipic acid; B = 1,4-butanediol; T = terephthalic acid; BA and ABA = co-monomers from BDO and adipic acid; BT and BTB = comonomers from BDO and terephthalic acid. Test 1: 1750 mg polyester in 80 mL media. Intermediates from isolated pure culture after 21 d. Enzyme activity stopped by pH shift (in situ building of high amounts of acids during degradation).Test 2: 350 mg polyester in 80 mL media. Intermediates from isolated pure culture after 7 d.Test 3: 350 mg polyester in 80 mL media. Intermediates from isolated pure culture after 21 d. Test 4: Residues after a 7 d inoculation by isolated pure culture and a 14-d inoculation with compost eluate. No intermediates were detected by GC analysis.

Water-Soluble Intermediates - Daphnia Test. In the toxicity tests, the toxicity of the water-soluble intermediates is particularly important because they can easily enter groundwater or be more readily absorbed by the organism.

Testing was carried out in accordance with DIN 38412 Part 30. In this test, the pollutant-dependent immobilization of daphnia in solution of different concentrations (series of dilutions) is used. The control solution contains micro-organisms that biodegrade Ecoflex enzymatically. The stock solution at the end of the test also contains the degradation intermediates of Ecoflex.

The polymer was successively diluted and for each concentration 10 daphnia were placed in the test solution (20 °C, pH 7.0). After 24 h, the number of daphnia still swimming was counted. Even with a low dilution (Stage 2) as in the control solution, there were still nine daphnia swimming. The test was therefore passed.

Plant Growth Test. The ecotoxicity of composted biodegradable polyester (Ecoflex) was studied in a plant growth test following the EN 13432, Annex E, which is based on the OECD guideline 208. In this test, effects on seedling emergence and early plant growth are investigated with different higher plant species exposed to treated compost. Seeds are placed in contact with treated and control soil. Four plant species covering the three categories outlined in OECD guidance 208 were introduced in the test, namely wheat (*Triticum sativum*), summer barley (*Hordeum vulgare*), mustard (*Sinapis alba/Brassica alba*), and the mung bean (*Phaseolus aureus*).

The following samples were prepared and used for testing:

- Mixture of reference soil and 25% compost with addition of Ecoflex after 12 weeks composting
- Mixture of reference soil and 50% compost with addition of Ecoflex after 12 weeks composting.

The evaluation of the test results on seedling emergence and biomass showed no significant effects when treated soil was compared to control soil (Fig. 2). With all four plant species, both parameters reached at least 90% of the control level regardless of the test concentration.

An overview of the described and other tests is shown in Table 2 [13]. Biodegradation of PBAT (Ecoflex) causes no accumulation of environmentally dangerous compounds neither in organisms nor in the ecosystem.
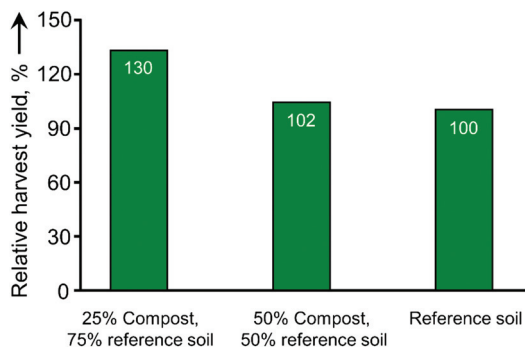

Figure 2. Result of plant growth test for PBAT (Ecoflex) according to OECD 208

Table 2. Ecotoxicological tests of PBAT (Ecoflex)

| Test	Result
Acute toxicity to daphnia DIN 38412 Part 30, fishes	passed
Terrestrial plant toxicity OECD 208	no effects at the highest concentration
Earth worm toxicity OECD 207	no effects at the highest concentration
Primary skin irritation rabbit OECD 404	nonirritant
Primary irritations of the mucus membrane rabbit OECD 405	nonirritant
Guinea pig OECD 406 (modified Buehler test)	nonsensitizing
LD_{50} rat (oral) OECD 423	> 4000 mg/kg, virtually nontoxic after a single ingestion
Ames test OECD 471	substance was not mutagenic

2.3. Standards for Biodegradable Polymers

2.3.1. Controlled Composting Test

Biodegradability of polymers is appropriately described by test and assessment methods in international standards. Industrial composting is today a well-established disposal process for organic waste materials. In order to adapt this industrial composting process, laboratory tests have been developed and certified in standards.

The most important proof of aerobic biodegradability is the controlled composting test according to ISO 14855, which is a central part of every standard for biodegradable polymers. In a composting vessel, the test polymer is incubated in a batch process—mixed with a defined, mature compost quality. The vessel is aerated continuously with carbon dioxide free air at 58 °C and at defined humidity. Thus, the composting process runs under optimum moisture and oxygen conditions. Simultaneously, a blank compost inoculum without additional carbon source is tested under the same conditions. The carbon dioxide content of the exhaust air of both vessels is compared. After subtracting the carbon dioxide evolution of the blank inoculum, the carbon dioxide evolution related to the test polymer is monitored as the biodegradation curve. Figure 3 shows that in a controlled composting test of Ecoflex more than 90% of the polymer was converted to carbon dioxide after 80 d.

The biodegradation curve shows the relative carbon dioxide evolution of the test inoculum with test polymer related to the theoretical carbon dioxide evolution of the test polymer. According to the ISO standard compostable polymers, ISO 17088, 90% of the theoretical carbon dioxide evolution of the test polymer has to be detected after 180 d. The activity of the compost inoculum in the controlled composting test is validated using a cellulose reference instead of the polymer. The strict requirements on the test result ensure that only compost with a defined degree of maturity is used to test the polymer.
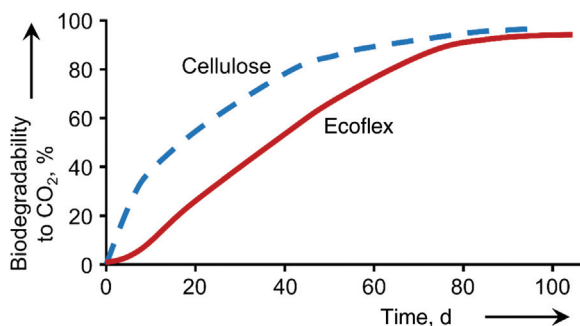
Figure 3. Controlled composting test of PBAT (Ecoflex) and cellulose

2.3.2. Controlled Test of Aerobic Biodegradation in Soil

In soil biodegradation is tested by simulating biodegradation in soil under optimum oxygen and humidity level at an ambient temperature of 20–25 °C $\pm$ 2 °C. The powder material is mixed in a concentration of 1% in test soil. As in the controlled composting test for industrial composting (see Section 3.3.1) the carbon dioxide production is continuously monitored against a cellulose reference and a sample of the inoculum without additional carbon source. The biodegradation test in soil has to be finished after 24 months. The test procedure is described in ASTM D5988, ISO 17556 and ISO 11266.

The certificate of biodegradation in soil can be obtained from Vincotte, Belgium, or DIN CERTCO, Germany. The certificate is required in Italy and Spain to obtain governmental support for biodegradable mulch film. A standard for biodegradability in soil is under development in France.

The results of the biodegradation test in soil are only accepted if the carbon dioxide curves of the three replicates achieve a minimum level of 90% relative to the cellulose reference and do not vary by more than 20%.

The test sequence in Table 3 only applies concerning the disclosure of the composition of the film material including the metal test as well as the plant toxicity test. Both test results are accepted if a certificate of industrial composting has been granted to the film material.

2.3.3. Home Composting

The controlled composting test under home composting conditions is used to determine the aerobic composting of biodegradable polyesters at ambient temperature. The test simulates an intensive aerobic composting process and determines biodegradability under optimum oxygen and dry conditions at 20–28 °C $\pm$ 2 °C. The polymer powder sample is mixed in a concentration of 6–8% with an inoculum—a compost quality with a defined maturity. As in the controlled composting test for industrial composting (see Section 3.3.1), carbon dioxide production is continuously monitored against a cellulose reference and a sample of the inoculum without additional carbon source. The biodegradation test under home composting conditions has to be finished after 12 month.
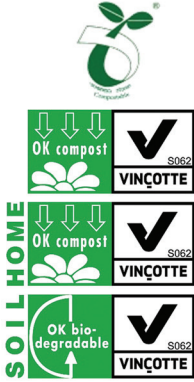
The certification process has been defined first by Vincotte, Belgium. The Australian standard AS5810 is the only applicable standard which is used for certification by the Australasian Bioplastics Association ABA, AUS, and DIN Certco, D. However, new standards are under development in several countries of the EU.

The test sequence described in Table 3 applies as well to the test scheme for home

Table 3. Registration scheme for biodegradable polymers

Test	Assessment
Declaration of polymer composition including metal (and fluorine) test (AS4736, ASTM D 6400, EN 13432, ISO 17088)	volatile solids > 50%; metal (and fluorine) content < limits
Biodegradation test (ISO 14855)	· EN 13432: > 90% of theoretical CO_2 evolution after 180 d · ASTM D 6400 (homopolymers): > 60% of theoretical CO_2 evolution after 180 d · ASTM D 6400 (heteropolymers): > 90% of theoretical CO_2 evolution after 180 d
Disintegration in pilot-scale composting test using specimen of maximum thickness (ISO 16929)	< 10% of the weight of the specimen shall fail to pass through a > 2 mm fraction sieve
Analysis of compost quality (ISO 16929)	density; dry solids; volatile solids; salt content; pH; content of elemental N, P, Mg, Ca
Plant toxicity test using minimum two species of plants (OECD 208)	rate of germination and biomass > 90% of blind value of compost without polymer
Only for AS 4736, AS 581 Earth worm toxicity test (ASTM E1676, OECD 207, ISO 11268)	>90% survival rates of earth worms in all tests with 30% and 50% compost from the disintegration test

Table 4. Logos of biodegradable polymers according to the standards [7]

Organisation	DIN-Certco	Vincotte	Jätelaito-syhdistys	BPI/USCC	BPS
Location	Germany	Belgium	Finland	North America	Japan
Logo					
Standard	EN 13432 ASTM D 6400	EN 13432	EN 13432	ASTM D 6400	GreenPLA certification scheme

composting to achieve, e.g., the label OK Compost Home, the ABA, and the DIN Certco certificate. The main difference to industrial composting is that only a qualitative disintegration test is required with a maximum duration of 12 months.

2.3.4. Standard Assessment of Biodegradable Polymers

Like the ISO 17088, the European standard 13432 and the American standard ASTM D 6400 define basic requirements for packaging and packaging materials to be considered as biodegradable and compostable in industrial composting facilities by addressing the scheme summarized in Table 3. The test results have to be certified by registered test institutes (e.g., DIN-Certco, D; Vincotte, B; Biodegradable Products Institute, USA).

The new ISO standard 17088 became effective in 2008 and is mainly based on EN 13432 and ASTM D 6400. This standard can be used worldwide. Additional tests may be necessary to obtain the product registration according to ISO 17088 based on a regional standard.

Registered biodegradable polymers are used to produce biodegradable finished products, e.g.,

bags, packaging, cutlery, plates, which have to be certified in the next step. This procedure at a certified test institute shall prevent the use of nonconforming additives, colors, and packaged goods. The certificate entitles the holder to use the regional symbol for biodegradable plastics on his packaging or article in combination with his certification number (Table 4).

Until now, standardized processes for degradation testing have not been available for all natural environments. The development of reliable, worldwide-comparable test systems is an ongoing challenge.

3. Biodegradable Polymers: Synthesis, Properties, and Suppliers

3.1. Raw Materials

Biodegradability is a functional performance characteristic of the polymer backbone, which can be achieved with renewable as well as fossil-based raw materials.

Fossil-Based Raw Materials. Major fossil-based monomers are 1,4-butanediol (BDO) and the dicarboxylic acids adipic acid,

terephthalic acid, and succinic acid (SA). BDO is produced in world-scale plants with different processes and feedstocks (acetylene by Reppe process, butane, butadiene). Compared to BDO, SA is produced on a smaller scale based on maleic acid anhydride. Adipic acid is based on cyclohexane derived from benzene, and terephthalic acid is based on *p*-xylol.

Renewable raw materials are used as

- feedstock for monomer production (e.g., lactic acid) or polymer production (polyhydroxyalkanoates, PHA)
- structural material (e.g., cellulose) and as a compound ingredient (e.g., starch) for biodegradable polyesters

Feedstocks for Monomer or Polymer Production. Starch (from corn, wheat, etc.) → Starch is transformed to glucose, which is further used as fermentation feedstock for monomers (e.g., lactic acid) or PHA production. Other feedstocks for fermentative monomer production are sucrose, glycerol, or plant oils [8]. Intensive work is underway to use cellulose raw materials (C_6 and C_5 sugars) not only for bioethanol production but as well for different chemical intermediates and monomers like lactic acid (LA) and SA [14].
   → Lactic Acid
   Besides the indirect use of feedstocks for monomer production via fermentation, the direct access to monomers via extraction and processing of renewable feedstocks (e.g., sebacic acid, azelaic acid, biorefinery → Biorefineries–Industrial Processes and Products) is intensively elaborated and being commercialized. For example, Novamont plans to install a biorefinery process for the production of biodegradable polyesters using local feedstocks [15].
   The most established monomer production via fermentation for biodegradable polymers is the production of LA [16] whereas commercial SA and BDO production via fermentation is starting soon [17–20]. Ethylen glycol is also produced from fermentative bioethanol via ethylene on large scale.

Structural Materials and Compound Ingredients. Through the Viscose process, highly transparent cellulose films are produced, which can be used as a basic material for coating and/or lamination with biodegradable polyesters. Starch (from corn, wheat, potato) is used as a compound ingredient for biodegradable polyesters to produce film materials (see Section 4.2). The biodegradable polyester is needed as an "enabler" to improve the properties and processability of the starch.

3.2. Starch

→ Starch

Starch is a naturally occurring polysaccharide and is used either in its native form as granules or modified as so-called thermoplastic starch.

Pure starch can be successfully formulated only for a limited number of plastic applications such as foam, e.g., for loose fill. Pure starch films and sheets are brittle and moisture-sensitive and disintegrate in the presence of water. Additionally, the temperature window for processing is very small because of the limited temperature stability of natural starch of about 170–180 °C. Chemical modification of starch by partial substitution of hydroxyl groups (e.g., with esters or ethers) can significantly improve hydrophobicity and the rheological properties. Cross-linking of the starch chains improves stability against acids, heat treatment, and shear forces [15]. However, the high requirements of film applications are not fulfilled by modified starch alone. Compounds with biodegradable polyesters as enablers are therefore the appropriate solution (see Section 4.6).

3.3. Poly(Lactic Acid) (Polylactide, PLA)

→ Lactic Acid

Synthesis. PLA is a melt-processible thermoplastic polymer completely based on renewable resources. The manufacture of PLA includes one fermentative step followed by several chemical transformations [21, 22]. The typical annually renewable raw material source is corn starch, which is broken down to unrefined dextrose, i.e., glucose. This sugar is subjected to a fermentative transformation to lactic acid
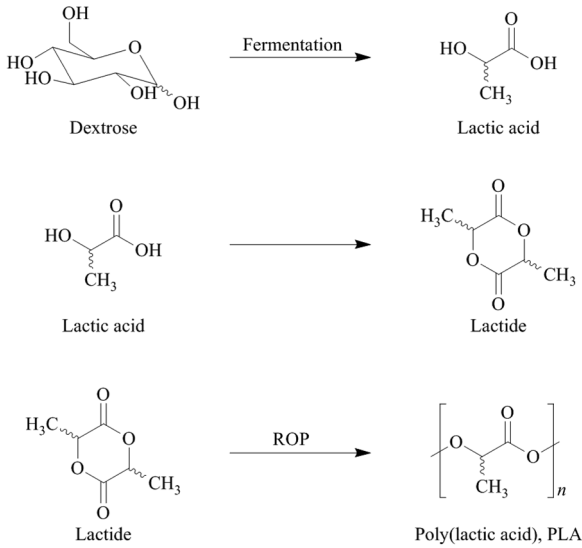
Figure 4. Production process for PLA

(LA). Direct polycondensation of LA is possible [23, 24], but usually LA is first chemically converted to lactide, a cyclic dimer of LA. This currently requires a two-step process, in which initially a low-molecular-mass PLA prepolymer is produced from LA, which is subsequently depolymerized to form lactide [25]. Only recently a selective direct lactide formation starting from LA by using zeolith catalysts has been reported [26]. Finally, after purification by either distillation or melt crystallization, lactide is converted via a ring-opening polymerization (ROP) to PLA [27] (Fig. 4).

Figure 5. Lactic acid and lactides

Properties and Applications. Due to its stereogenic center, lactic acid exists in two enantiomeric forms (D- and L-lactic acid) leading to three different lactide stereoisomers (D-, L-, and *meso*-lactide, Fig. 5). Depending on the relative amounts of the different stereoisomers in the final polyester, the crystallinity and crystallization speed of the resulting PLA is heavily influenced and in this way the properties of the polymer can be adjusted to satisfy the needs of different applications [27, 28].

PLA shows properties similar to polystyrene. Its high stiffness and transparency in its amorphous state makes it a suitable material for applications such as plastic bottles, cups for cold drinks, stiff packages like clamshells as well as degradable films. PLA is completely nontoxic and classified in the USA as generally recognized as safe (GRAS) [29]. PLA can be processed on standard equipment and used in injection molding, injection stretch blow molding, fiber spinning, and for the production of blown and cast films, biaxially oriented films, or transformed to extrusion paper-coating compounds, etc. Although PLA is a compostable material, it is also more and more used in durable applications because of its biogenic origin and its sustainable image.
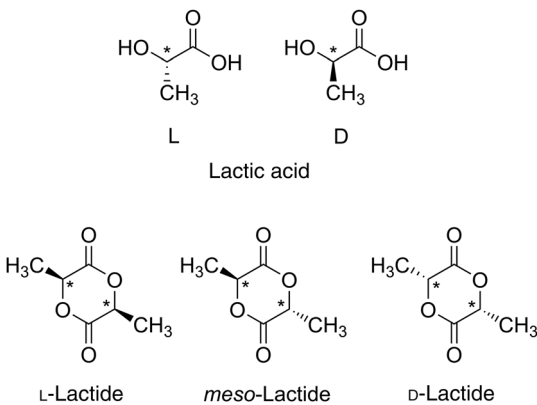
Limitations and Technical Developments. Nevertheless, PLA still suffers from several drawbacks like its low impact strength, its poor barrier properties and especially its low heat resistance in its amorphous state. A lot of research activities are currently in process to overcome these drawbacks. For example, by using crystalline PLA (cPLA) or stereocomplex PLA (scPLA) [30], the heat distortion temperature can be raised above 100 °C. In addition more and more companies offer solutions to the problems based on masterbatches of PLA copolymers or compounds.

Biodegradation. Chemical hydrolysis is considered to be the main degradation route for PLA [22]. This hydrolysis process takes place at high humidity and at elevated temperatures, which, for example, are found in industrial composting facilities. The fragments that result from the hydrolysis process, i.e., short oligomers and monomers, can then be consumed by microorganisms. Therefore, PLA articles can be certified to be compostable under these conditions but will not quickly degrade in home composting piles because of the fact that temperatures are typically much lower. Apart from composting (or incineration), PLA can be recycled like other plastic materials. Even chemical recycling by conversion of the used polymer back to the monomers followed by repolymerization has been proven.

Producers. The leading producer of PLA is NatureWorks LLC based in the US with a nominal production capacity of 150 000 t/a (see Chap. 8). NatureWorks LLC sells PLA resins for packaging and fiber applications under the trade name Ingeo. Recently Purac has announced to build a 75×10^3 t PLA facility in Thailand next to its existing lactide monomer plant, which has been in operation since 2012 [31].

3.4. Polyhydroxyalkanoates (PHA)

Structurally related to PLA are the polyhydroxyalkanoates (PHA), a class of polyesters derived from hydroxyalkanoic acids, which can differ in chain lengths and in the positions of their hydroxyl groups (Fig. 6). The most common representatives among this class of biodegradable polymers are poly(3-hydroxybutyrate) (PHB), poly(4-hydroxybutyrate) (P(4-HB)), poly(3-hydroxybutyrate-*co*-valerate) (PHBV) poly(3-hydroxybutyrate-*co*-hexanoate) (PHBH) and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P(3-HB-*co*-4HB).

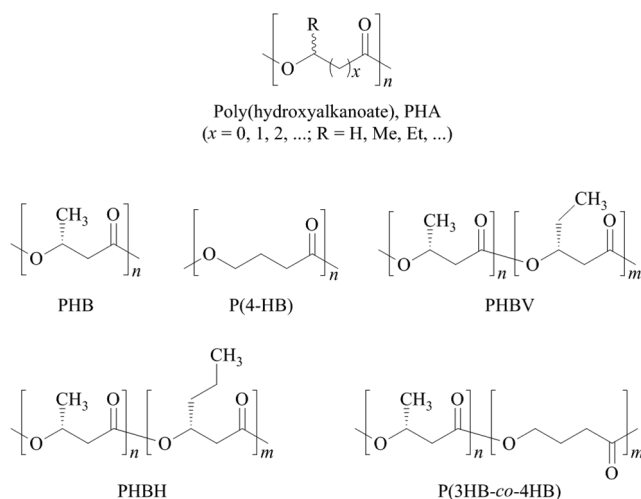
Poly(hydroxyalkanoate), PHA
(*x* = 0, 1, 2, ...; R = H, Me, Et, ...)

PHB   P(4-HB)   PHBV

PHBH   P(3HB-*co*-4HB)

Figure 6. Polyhydroxyalkanoates, general structure and most important derivatives
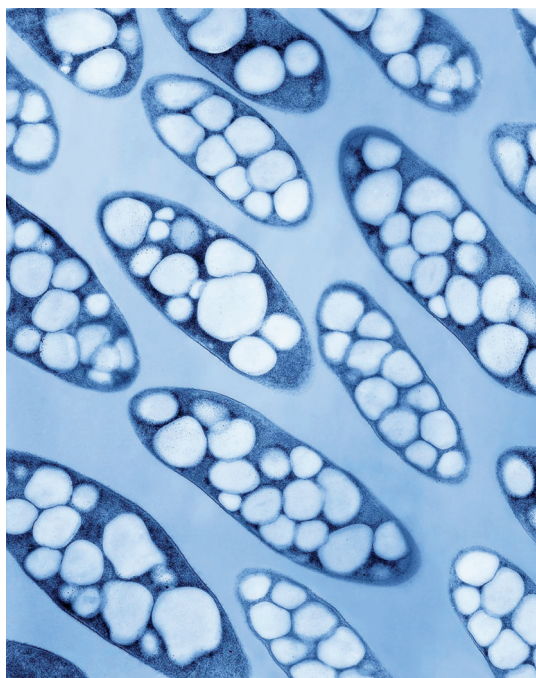
Figure 7. Polyhydroxyalkanoate particles in microorganism (photograph provided by former Telles, USA)

Synthesis. PHAs are the only thermoplastic polyesters which are derived from annually renewable resources like sugars, starch, or fatty acids through a single fermentative step. In addition, also hydrocarbons like methane have recently been described to be used for the fermentative synthesis of PHB by methanotrophic bacteria [32]. The polymer itself is made by various microorganisms as a carbon- and energy-storing substance (Fig. 7) [33, 34]. The mass of the polymer in the microorganism can reach up to 90% of the dry weight of the cell mass. The chemical structure of the resulting PHA depends on the bacterial species and the composition of the carbon source on which the microorganisms are grown [35]. After fermentation and cell lysis, high-purity PHA can be isolated by either solvent extraction or water based purification processes. Leading companies today are using genetically modified microorganisms in order to optimize the space–time yield of the fermentation and to develop more efficient recovery processes for improved economics [33, 34, 36–38].

Properties and Applications. The great structural variety of PHAs (see Fig. 6) gives rise to a multitude of different property profiles and different possible applications including injection-molded articles for bioresorbable medical and nonmedical applications such as fishing nets, degradable films, etc. [3, 36–38]. However, besides high costs, PHAs suffer from several drawbacks, which have prevented the commercial success until today. The two most important ones are the thermally induced fast polymer chain degradation in the melt and the very low melt strength of PHAs, which both makes processing very challenging [39].

Biodegradation. As PHAs are direct metabolites of microorganisms found in natural environments, they are accepted as food sources by many abundant microbe species, which break the polymer down by extracellular poly(hydroxyalkanoic acid) depolymerases [38]. This is the reason why PHAs are quickly biodegraded both under aerobic conditions (e.g., composting, soil) and in environments where anaerobic degradation takes place (e.g., marine environment, biogas plant).

Producers. Although fermentative PHB has been known since 1926 [40], commercial interest occurred not earlier than in the fourth quarter of the 20th century. Companies active in the area of PHAs are Kaneka (Aonilex), Metabolix (Mirel), Tianan (Enmat), and Meredian. The production capacities of PHAs are still modest after the joint venture between ADM and Metabolix dissolved in 2012 and the respective 50×10^3 t PHA plant has been shut down (see Chap. 9).

3.5. Synthetic Structural Polyesters

3.5.1. Aliphatic Polyesters

Introduction. It is not the origin of the raw materials used in the manufacture of a polymeric material that renders it biodegradable: It is the chemical structure that allows enzymatic attack and enzymatic hydrolysis of the polymer chain followed by complete digestion of the fragments by microorganisms (see Chap. 3) [41]. With this knowledge, polymers can be specifically designed and produced from existing fossil-based monomeric building blocks in
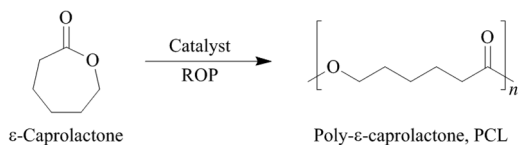
Figure 8. ROP polymerization for PCL production

existing production plants. These polymers are then not only biodegradable but also exhibit beneficial mechanical properties. Aliphatic polyesters were the first completely fossil-based polymers which combined both the biodegradability of polymers found in nature as well as the useful mechanical properties of modern plastics.

Structure and Synthesis. There are two fundamentally different structures of synthetic polyesters. One of them is closely related to fermentative PHAs (Section 3.4) and is derived from hydroxyalkanoic acids or their intramolecular cyclic condensates, lactones. The most common derivative is poly-ε-caprolactone, which is produced in by ROP from ε-caprolactone (Fig. 8) [42, 43]:

The other type of polyester is based on a direct condensation reaction of aliphatic dicarboxylic acids and aliphatic glycols [44]. The most important derivatives are polycondensates from 1,2-ethylene glycol or 1,4-butanediol with succinic acid, adipic acid, or combinations of both (poly(ethylene succinate) (PES), poly(butylene succinate) (PBS), and poly[(butylene succinate)-*co*-(butylene adipate)] (PBSA), Fig. 9).

Properties and Applications. Due to the broad spectrum of different monomers that can be used for the synthesis of these polymers, the properties can be adjusted to a certain degree. While PBS is a relatively stiff polyester, other combinations with longer dicarboxylic acids lead to more flexible materials. Generally, aliphatic polyesters are low-melting, flexible plastic materials which are used for mulch films and monofilament fibers. They are also used for rather soft and flexible foams and injection-molded parts. Processing on conventional polyolefin equipment is typically possible [44]. A drawback of succinic acid based aliphatic polyesters is the fact that they are prone to chemical hydrolysis leading to limitations in shelf life and transportation.

Biodegradation. In microbially active environments like soil and compost, aliphatic polyesters are degraded in a combination of chemical and enzymatic hydrolysis and the fragments are ultimately degraded to carbon dioxide and water [44].

Producers. High-molecular-mass PCL is produced by Perstop (Capa). Due to the low melting point, low modulus and 100% fossil origin of PCL, this biodegradable polymer is mostly used as a component in blends with other biopolymers (see Section 3.6). PBS and PBSA are produced by the Japanese companies Showa Denko (Bionolle) [44] and Mitsubishi Chemicals (GS Pla™). Both companies have announced to switch from fossil to biobased SA in the near future. Production capacities have been significantly increased recently since PTT MCC Biochem. Co. (a joint venture

Figure 9. Most important biodegradable aliphatic polyesters

Figure 10. Aliphatic/aromatic copolyester PBAT (Ecoflex)

between Mitsubishi Chemicals and PTT from Thailand) will start up its recently built new 20 000 t-polyesters plant located in Thailand.

3.5.2. Aliphatic-Aromatic Polyesters

Synthesis. The good biodegradability of aliphatic polyesters can be combined with the good mechanical properties of aromatic polyesters to some extent by copolycondensation of aliphatic and aromatic monomers togeth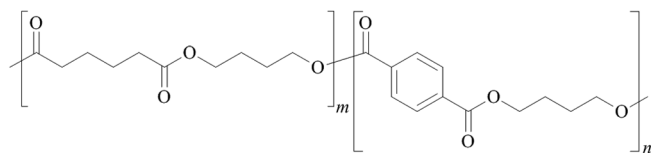er with aliphatic diols [45]. The best known aliphatic–aromatic polyester is Ecoflex by BASF which has been introduced into the market in the late 1990s (Fig. 10). The standard grade Ecoflex F is produced from the readily available fossil monomers adipic acid, terephthalic acid and 1,4-butandiol (generic name: poly[(butylene adipate)-*co*-(butylene terephthalate)], PBAT). Through the incorporation of a biobased monomer made from plant oil, a partly biobased variant has been commercialized in 2009 under the trade name Ecoflex FS.

Properties and Applications. Ecoflex is designed to be a strong and flexible material with mechanical properties similar to PE-LD [46]. Therefore, Ecoflex can be melt-processed on standard polyolefin equipment and is mainly used in film applications like organic waste bags, mulch films, shopping bags, and cling films.

Due to its beneficial properties and its complete biodegradability as well as to a clear trend to renewable raw materials, Ecoflex is used as an "enabler" for renewable biopolymers like starch, PLA, PHAs, lignin, and cellulose. Ecoflex/starch as well as Ecoflex/PLA blends (e.g., Ecovio by BASF) are the most common renewable and biodegradable plastic materials for film applications in the market.

Biodegradation. Although fully aromatic polyesters like poly(butylene terephthalate) are not prone to microbial attack, copolyesters of aliphatic and aromatic monomers are completely biodegradable, if the aromatic content does not exceed a certain limit [45–48]. Similar to aliphatic polyesters, these mixed structures also degrade in microbially active environments, mainly by enzymatic hydrolysis, followed by complete mineralization of the fragments [12].

Producers. Ecoflex from BASF is the most important aliphatic–aromatic polyester sold to the market with a current production capacity of 74 000 t/a. Novamont from Italy produces aliphatic–aromatic polyesters under the trade name Origo-Bi for captive use in its blends. Several Asian companies have announced to also start production of PBAT, e.g., Junhui Zhalong from JinHui group.

3.6. Compounds

Biodegradable polymers have defined property profiles (Table 5) as explained in the previous chapters, which limit their application range to a certain extent. If the market demands biodegradable polymer solutions using renewable resources, a compound can be developed by using a combination of rigid polymers like PLA or PHA and soft and impact-resistant synthetic biodegradable polymers like PBAT. Such a compound can be precisely adjusted to the application requirements (Fig. 11). One example is the Ecoflex/PLA compounds Ecovio F2224, which enables the production of film products similar to PE-HD.

3.6.1. Compounds of Starch and Biodegradable Polyesters

Based on the experience in extruder cooking of starch for products like peanut flips and dry pet food, compounding equipment for compounds

Table 5. Properties of biodegradable polyesters and reference polymers[*]

Test	Standard	PET	PLA	PHB	PBAT	PBS	PE-LD
Transparency		transparent	transparent	opaque	translucent	translucent	transparent
Density, g/cm^3	ISO 1183	1.35	1.25	1.25	1.25	1.26	0.92
Melting point, ℃	DSC	245	140–175	175	115–120	115	105–115
Glass transition temp. T_g, ℃	DSC	75	58	−4	−33	−32	−100
Vicat A, ℃	ISO 306	75	56	96	91	93	90
Mechanics MD/CD[**]							
Module of elasticity, MPa	ISO 527	3100	3600	1900	80	645	250
Tensile stress, MPa	ISO 527	58	70	27	23	35	20
Ultimate elongation, %	ISO 527	50	3	8	470	47	500
Barrier properties							
Oxygen transmission rate, mL m^{-2} d^{-1} bar^{-1}	ASTM D 3985	15		45	600	100	1500
Water absorption, %		0.15	0.3	0.5	0.5	0.4	
Food contact	2002/72/EC	o.k.	o.k.	o.k.	o.k.	no	o.k.
Biodegradability	EN 13432	no	yes	yes	yes	yes	no

[*] Injection-molded specimen, 4 mm, barrier values: blown film: 100 µm.
[**] MD = machine direction = direction of extrusion of blown film, CD = cross direction = perpendicular to direction of extrusion of blown film.

of biodegradable plastics has been developed. Corotating, intermeshing, and self-cleaning twin-screw extruder concepts are available from machinery suppliers like Coperion, Clextral, Extricom, Leistritz, Krauss Maffei Berstorff, and others. These extruder concepts prevent caking and charring of the dew during starch cooking.

Starch compounds with polyesters are used to enhance hydrophobicity as well as mechanical and thermal properties of compounded products and in order to increase the biobased content of the compounds while maintaining complete biodegradability. The crystalline structure of starch granules has preferably to be disintegrated prior to its use in applications (e.g., production of thin films and bags) because starch granules as large as the film thickness reduce the mechanical properties. High shear forces, heat, and/or plasticizers (e.g., moisture, glycerol) are used in a separate compounding step to turn granular starch into thermoplastic starch.
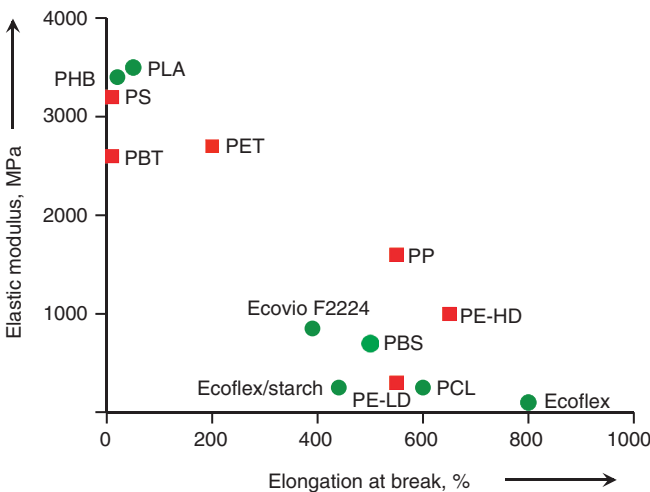

Figure 11. Stiffness versus flexibility for typical standard and biodegradable plastics, ISO 527
Ecoflex = PBAT; Ecovio F2224 = compound containing 45% PLA, about 55% Ecoflex and compatibilizers

Compounding of starch and biodegradable polyesters can be efficiently performed in a four-stage process:

1. Starch is destructurized by temperature, pressure, and plasticizer (e.g., water, glycerol).
2. The biodegradable polyester (e.g., PCL, PBAT, PVOH) is added.
3. The melt has to be degassed by an effective vacuum, leaving only a few percent of moisture in the compound.
4. The compound is granulated under water or air and subsequently dried in a vacuum drier.

Film products with good mechanical characteristics are only obtained if thermoplastic, plasticized starch has been used. Another condition is that the biodegradable "enabling polyester" forms the coherent phase [49]. If no plasticizer is used, biodegradable polymers with merely limited mechanical properties will be obtained.

In Table 6, most of the mechanical properties of average PE-LD carrier bags from blown film, 30 μm, are close to the PBAT–starch compounds containing thermoplastic starch. The reduction in stiffness by 20–25% compared to that of PE-LD is lower than for PBAT–starch compounds with granular starch, which amounts to 50–55%. The reduction in tensile strength is similar for both starch compounds: 10–35%. If granular starch is used, the film samples exhibit a rough surface. Thus printability and mechanical properties (stiffness and

puncture resistance) of PBAT compounds with granular starch are inferior to PBAT/starch compounds with thermoplastic starch by about 30–55%.

3.6.2. Compounds of PLA and Biodegradable Polyesters

PLA is a transparent, stiff polyester (see Section 3.3). It can also be transformed into transparent flexible films with properties close to cellophane using biaxial orientation technology and into fibers using standard production process of fiber spinning and subsequent orientation and fixation. However, for most of the flexible-film applications the stiffness of PLA (3600 MPa) is too high. Therefore, compounds of PLA and soft biodegradable polyesters like PBAT are used in order to reduce the stiffness efficiently [50].

The addition of 20% PBAT (e.g., Ecoflex) in PLA already reduces the stiffness of PLA by 25% (Fig. 12), keeping the impact strength (e.g., Charpy, unnotched, according to ISO 179/1eU at $-20\,°C$) at 22 kJ/m^2, which is above the level of high-impact polystyrene. Containers produced from this compound are resistant even to sudden impact - they deform without brittle failure at room temperature ($23\,°C$).

Flexible-film applications are much more demanding regarding the stiffness/toughness ratio of the PBAT–PLA compound. Usually, polypropylene with a stiffness of 1600 MPa is

Table 6. Examples for blown films, 30 μm

Test	Standard	PE–LD carrier bags (mean)	PBAT	PBAT + granular starch compound	PBAT + thermoplastic starch compound
Transparency		opaque	translucent	opaque	opaque
Printability		8 colors flexoprint	8 colors flexoprint	poor printability	8 colors flexoprint
Mechanics MD/CD[*]					
Modul. of elasticity, MPa	ISO 527	330/270	110/100	150/140	270/205
Tensile stress, MPa	ISO 527	32/25	35/40	23/22	21/20
Ultimate elongation, %	ISO 527	460/640	640/750	390/590	490/540
Puncture resistance, J/mm	DIN 53373	17	26	9	19
Barrier properties					
Oxygen transmission rate, mL m^{-2} d^{-1} bar^{-1}	ASTM D 3985	4800	2000		
Water vapor transmission rate, g m^{-2} d^{-1}	ASTM F 1249	3	240		
Food contact	2002/72/EC	not limited	not limited	dry food	dry food
Biodegradability	EN 13432	no	yes	yes	yes

[*] MD = machine direction = direction of extrusion of blown film, CD = cross direction = perpendicular to direction of extrusion of blown film.
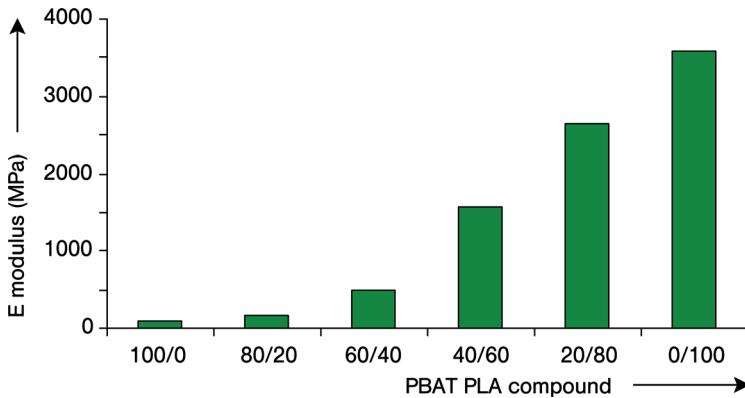
Figure 12. Stiffness of injection-molded specimen from PBAT–PLA compounds with varying PLA content according to ISO 527

the stiffest product to be used in blown-film extrusion. But most blown-film lines for stiff products can only handle conventional PE-HD with a stiffness of 600–1200 MPa. Moreover, high requirements have to be fulfilled concerning the bubble stability at lower film thicknesses, e.g., at 10–15 µm or below.

Corotating, intermeshing, and self-cleaning twin-screw extruder concepts (e.g., from machinery suppliers like Coperion, Clextral, Leistritz, Kraus Maffei Berstdorf, Extricom) as being employed for starch compounds can be modified for the compounding of PBAT and PLA. The volume elements for deaeration of starch powder have to be changed to elements for conveying and

melting of granulates. Adapted shear mixing devices are used to blend the melts at low shear energy to avoid high temperatures causing pronounced hydrolysis of the PLA phase. A thorough venting in one or two steps as needed for starch compounds is not necessary for PBAT–PLA compounds. It is frequently possible to achieve higher output rates with PBAT–PLA compounds than with PE–LD.

Good performance characteristics are obtained for PBAT–PLA compounds with PBAT as the continuous phase and PLA as the discontinuous phase. Examples are given in Table 7 for a blend with 45% PLA (PLA as discontinuous phase, PBAT as continuous phase) and a blend with

Table 7. Characteristics of blown films, 30 µm, from PE-HD and compounds with PBAT

Test	Standard	PE-HD[a]	PBAT/PLA 55/45 dryblend[b]	PBAT/PLA 55/45 compound[c]	PBAT/PLA 40/60 compound[d]
Transparency		opaque	opaque	opaque	translucent
Printability		8 colors flexoprint	8 colors flexoprint	8 colors flexoprint	8 colors flexoprint
Mechanics MD/CD[e]					
Modul. of elasticity, MPa	ISO 527	650/630	1180/490	1020/440	1560/1080
Tensile stress, MPa	ISO 527	45/42	39/21	50/32	47/30
Ultimate elongation, %	ISO 527	640/520	360/170	430/360	160/160
Puncture resistance, J/mm	DIN 53373	42	19	31	31
Barrier properties					
Oxygen transmission rate, mL m^{-2} d^{-1} bar^{-1}	ASTM D 3985	2000		1400	
Water vapor transmission rate, g m^{-2} d^{-1}	ASTM F 1249	1.3		160	
Food contact	2002/72/EC	not limited	not limited	not limited	not limited
Biodegradability	EN 13432	no	yes	yes	yes

[a] Average values for carrier bags.
[b] Dryblend of 55% PBAT and 45% PLA.
[c] Compound of approx. 55% PBAT and 45% PLA.
[d] Compound approx. 40% PBAT and 60% PLA.
[e] MD = machine direction = direction of extrusion of blown film, CD = cross direction = perpendicular to direction of extrusion of blown film.

60% PLA (PLA as continuous phase, PBAT as discontinuous phase), compared to PE-HD.

Table 7 shows that a compound with 45% PLA and PBAT can achieve about 70–75% of the mechanical properties of an average PE-HD carrier bag at 30 µm thickness. The values of a PE-LD compound (see Table 6) are reached or exceeded. The 45% PLA compound (Ecovio F2224) yields a biodegradable film that comes closest to the properties of PE-HD films on the market.

In order to mimic PE-LD, compounds with a higher ratio of PBAT over PLA are used to increase the flexibility and tear resistance of the films. Thus, PE-HD-like or PE-LD-like properties can be achieved by using an appropriate combination of PBAT and PLA in the compound [51].

Another important aspect of biodegradable PBAT–PLA blends is their shelf life under regular storage conditions. Because standard climate is used to condition plastic specimens prior to test, standard room climate (23 °C, 50% relative humidity) has been used to store film samples from PBAT and PBAT–PLA compounds. After three years of storage under these conditions, biodegradable films from PBAT (Ecoflex F C1200) achieve or exceed the mechanical properties of PE-LD carrier bags except for stiffness. Films from PBAT–PLA compounds (e.g., Ecovio F2224) maintain the property level of PE-LD carrier bags during two years of storage for stiffness, tensile strength, and puncture resistance.

3.7. Cellulose Derivatives

→ Cellulose
Cellulose esters (e.g., with acetic acid or propanoic acid) are well-known amorphous plastics which are used for injection molding of transparent articles. Thus, there are compounds for injection-molded products on the market, e.g., for candle housings in cemeteries or as disposable cutlery. However, only cellulose acetate with a degree of substitution of not more than 2.5 is biodegradable. Biodegradability certificates according to EN 13432 are difficult to achieve because the biodegradation of cellulose derivatives is a very slow process.

Cellulose films (e.g., cellophane) are very transparent and exhibit an excellent barrier against oxygen and aroma if the moisture level is kept below 50% relative humidity. When a coating based on natural waxes is used, a high water-vapor barrier can be achieved, which makes these films applicable for packaging of food, e.g., cereals, pasta, cheese, fruit, and vegetables.

3.8. Biodegradable Functional Polymers

Besides the well-known structural polymers described above, which are used as shaped article based on thermoplastic or thermosetting materials, there is the class of water-soluble macromolecules which are referred to as functional polymers. These materials are usually not perceived as typical "plastics", but they are used to evoke a specific physical effect in solution. Most prominent examples are thickeners, dispersants (→ Disperse Systems and Dispersants), and flocculants (→ Flocculants). Therefore, these polymers are used in many day-to-day applications [52]. The most prominent functional biopolymer occurring in nature is DNA, which, however, has not made its way into technical applications.

The global water soluble polymers market value is projected to reach approx. 39.5×10^6 \$ by 2019 [53]. This market as such is extremely diverse. The share of biodegradable polymers within the segments differs strongly. In some segments, e.g., the food sector, biodegradable polymers, in particular polysaccharides, strongly dominate the market, whereas in other areas, e.g., water treatment, nonbiodegradable polymers such as polyacrylamide prevail. In addition, the substitution pressure to replace nonbiodegradable polymers is different for each application and each region. Therefore, the overall market share for biodegradable functional polymers and in particular the expected development over the next years is difficult to estimate across all segments.

An important class of functional polymers are the well-established polysaccharide derivatives such as methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, and carboxymethyl cellulose (→ Cellulose Ethers). Together with (optionally modified) starches
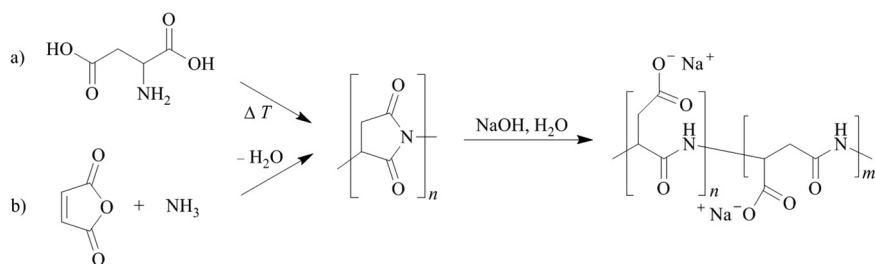
Figure 13. Two different routes to produce poly(aspartic acid)
a) Polycondensation of aspartic acid; b) Polycondensation of maleic anhydride and ammonia

and maltodextrins, these materials find widespread applications as dispersants, binders and/or thickeners in construction chemicals, food, as well as home and personal care applications. Also, other polysaccharides such as guar gum and its derivatives can be used as functional polymers, e.g., in cosmetics and oilfield applications. However, as mentioned above, it needs to be pointed out clearly that, although these polymers are (at least to a wide extent) biobased, biodegradation significantly decreases if the extent of chemical modification, expressed by the degree of substitution of the individual sugar units, exceeds a critical value. Therefore, many of these biobased functional polymers are not biodegradable according to the standards described above.

Proteins are abundant in nature, and like all biopolymers produced by nature, they are generally biodegradable (although some of them may not meet the standards outlined above). However, most natural proteins have not found use as functional polymer due to inherent storage ability issues. Most proteins are not long-time stable and require addition of a biocide to the final product; moreover, degradation of proteins often leads to smelling volatile degradation products which, in many cases, are undesired.

An important exception is gelatin (→ Gelatin). Gelatin is produced in large quantities by partial hydrolysis of collagen, a byproduct of meat production. Gelatin is used in feed and food applications as gelling agent or protective colloid. Other applications are in the field of pharmaceutical formulations (gelatin capsules) and in cosmetic products.

Polyaspartate. The homopeptide polyaspartate (→ Polyaspartates and Polysuccinimide) is a synthetic analogue to naturally occurring peptides. It is synthesized in a polycondensation reaction of aspartic acid via polysuccinimide, which is hydrolyzed to polyaspartate (Fig. 13). As indicated by the name of the polymer, it can be prepared from the corresponding amino acid. However, there is an alternative route to this polymer based on fossil resources, i.e., maleic anhydride and ammonia. Both routes proceed through polysuccinimide as an intermediate. The polymer comprises a mixture of two different forms in which the monomeric building block can be incorporated into the polymer chain, namely the α and β form.

This water-soluble and biodegradable polyamide is commercialized by Lanxess under the trade name Baypure. Often, polyaspartate is used as a biodegradable alternative to replace the nondegradable poly(acrylic acid) [49].

Applications of Polyaspartates. Polyaspartates are of interest in application fields like water treatment and detergents and cleaners. In terms of water treatment, polyaspartate shows features like scale inhibition effects towards calcium carbonate, which in fact is the main scale-forming species in cooling and process water application. Besides its good corrosion inhibiting effect, especially in combination with phosphonates or metal salts [54], an advantage of polyaspartate in water treatment is its outstanding calcium tolerance.

In terms of detergents and cleaners, polyaspartate functions as a co-builder and thereby allowing the formulation of a modern detergent with fully degradable structures [49, 55]. Polyaspartates are also suitable for the builder system of automatic dishwashing detergents with a good primary and secondary detergency [56].

In addition modified polyaspartate has been proposed for better detergency and improved whiteness to the fabric [57] as well as a carrier material in laundry detergents [58].

Other fields of applications could be pigments, colorants, and coatings, in which poly(aspartic acid) might function as dispersion of organic pigments.

Poly(ethylene Oxide) (PEO) (→ Polyoxyalkylenes) is a water-soluble polyether mainly used in detergents and shampoos. It is produced via ROP of ethylene oxide. If desired, other alkylene oxides can be copolymerized to fine-tune the product properties. PEO is both aerobically and anaerobically biodegradable if the molecular mass is not too high [59–62].

Many commonly used surfactants can also be considered as oligomers of ethylene oxide or other alkylene oxides such as propylene oxide. Two predominant architectural principles can be distinguished:

- Alkoxylated long-chain fatty acids or alcohols; these amphiphilic molecules have a relatively low molar mass and are typical nonionic surfactants used in all kinds of cleaning applications; and
- Block copolymers of ethylene oxide and propylene oxide. These polymers are often referred to as Polyoxamers or Pluronics. They are also used as compatibilizer and solubilizer in cosmetic and pharmaceutical applications.

Poly(Vinyl Alcohol). The only existing biodegradable polymer with an all-carbon backbone is poly(vinyl alcohol) (PVOH). PVOH is synthesized by (partial) hydrolysis of poly(vinyl acetate) and shows a solubility in water which depends on the degree of hydrolysis. PVOH can be processed into films by solution casting or by thermoplastic melt processing [63]. The films are biodegraded in wastewater treatment or in composting facilities.

The main application of PVOH as biodegradable polymer is in flushable items. The mechanism of biodegradation is different from the ones discussed for polycondensates: it includes oxidation of the alcohol functionalities followed by enzymatic chain scission to smaller fragments which can finally be mineralized [64].

Major suppliers of PVOH are Kuraray (Poval, Mowiol), Nippon Gosei (Hi-Selon), and Indroplast (Hydrolene).

4. Processing and Additives

(→ Plastics, Processing; → Films, Section 6.10)

4.1. Introduction

Biodegradable polyesters for film extrusion are designed for processing on regular equipment for standard polymers. Nevertheless, the equipment has been originally designed according to the property profiles of standard polymers. Therefore, the following limitations have to be taken into account if a conversion process is adapted for a biodegradable polyester.

1. Limited compatibility of biodegradable polymers to standard polymers. Biodegradable polyesters are incompatible to standard polymers like PE, PP, PS, and PVC. Nonetheless standard polymers can be flushed out in most instances using appropriate processing conditions or a purging aid [65].
2. Sensitivity to moisture. Biodegradable polyesters can be degraded by chain cleavage caused by hydrolysis depends on the type of polyester, the moisture level, and the processing temperature and time [66–68].
3. Reduced thermostability at higher melt temperatures. Natural polymers like starch, cellulose and polyhydroxyalkanoates are temperature sensitive. At processing temperatures above 170–180 °C, decomposition and charring occurs depending on the processing time. Synthetic biopolymers like PBAT, PCL, and PBS are more stable without significant changes of viscosity until 200 °C. For example, a significant change in melt viscosity is only observed at a melt temperature above 230 °C for PBAT [46].

Biopolymers are mainly used for blown-film applications, e.g., for mulch film, organic waste bags, and shopping bags that are designed to serve as organic waste bags in their second life. Thus blown-film extrusion is the most important process for biopolymers.

Rigid packaging applications and food service ware requires the continuous processes:

- sheet extrusion and thermoforming [69, 70],
- extrusion blow molding [71, 72],
- foam extrusion and thermoforming,
- extrusion coating of paper and card board [73],

and the discontinuous processes:

- injection molding [71, 72],
- injection blow molding [72],
- molding of particle foam [73].

Melt spinning of fibers and nonwovens from biodegradable polymers are important conversion processes for wipes, tea bags and textile applications.

Blown-Film Extrusion, Bag Making, and Recycling. Basically, biodegradable polyesters are designed to run on existing extruders for polyolefins, PS, PVC, or PET. To achieve high output rates, an appropriate extruder screw design has to be selected. Major manufacturers of extrusion equipment provide special screws, e.g., for PLA and PLA compounds.

Because of the incompatibility of most standard polymers to biodegradable polyesters, an appropriate purging procedure has to be employed changing from a standard polymer, e.g., PE-LD to a biopolymer. A purging aid containing PCL that is compatible with a lot of standard polymers [65, 74] and inorganic fillers like chalk can be used at standard polyolefin temperature to purge out the standard resin. Afterwards the biodegradable polyester (e.g., compounds from PBAT and PLA) can be introduced and the melt temperature can be lowered to the processing temperature of the compound.

In general, mechanical properties of polymers are improved by orientation processes [50, 66, 68, 75]. Because of the biaxial orientation, films from blown-film lines exhibit a high puncture resistance. Blown-film lines are designed to produce flexible PE-LD or PE-HD films ranging from 5–200 μm [76].

Biodegradable polyesters like PBAT, PBS, PBSA, PCL and their respective compounds for film extrusion run well on extrusion lines for PE-LD. Branching and chain extension, e.g., of PBAT leads to a good bubble stability even at low thickness of about 8–12 μm, which is a standard film thickness, e.g., for mulch film.

Low melt temperatures, e.g., 140–170 °C for PBAT and PBAT–starch compounds and 165–190 °C for PBAT–PLA compounds can be achieved, which are beneficial for blown-film stability and in order to minimize thermal degradation.

PCL, PBAT and its compounds can be welded, e.g., by contact heating, on existing bag-making machines for PE-LD und PE-HD at lower welding temperatures of e.g., 90–100 °C for PBAT. PBAT and their compounds with PLA exhibit the same weld strength as LDPE at about 40 °C lower sealing temperatures. As the crystallization process is slower than with PE-LD, the welding line can stick to the surface, if direct surface contact is possible. Therefore, the welding machine has to allow for extra cooling of the weld lines.

Scrap from extrusion as well as from bag making can be recycled into the same application in an agglomeration or under water pelletizing process using recycling machines from, e.g., Munch or Erema. Being common practice in PE conversion, the recycled pellets can be added in film production again after appropriate drying.

4.2. Modification of Biodegradable Polyester Films

Additives. To improve processing and performance of films made of biodegradable polyesters, film qualities can be modified by using additives in the form of masterbatches.

Slip agents are used to reduce the coefficient of friction of the final film as well as the adhesion of the film to metal parts or to itself during processing. Biodegradable amides of fatty acids, e.g., oleamide, erucamide, ethylene-bis-stearylamide, fatty acid esters like glycerol oleates or glycerol stearates, as well as saponified fatty acids, e.g., stearates are typically used as slip agents for biodegradable polyesters.

Antibloc agents like talc, chalk, or silica can be used in form of masterbatches, e.g., based on PBAT and compounds of PBAT–PLA [46, 77].

Pigment masterbatches can be used to achieve specific colors in film applications. The use of pigment masterbatches is limited by the requirements on heavy metal content by the standards for biodegradability, e.g., EN 13432 [78]. Examples for heavy-metal-free pigments are carbon black and titanium dioxide. Carbon black pigment is used to make black films, which are applied as mulch film to increase the soil temperature in spring. Coated titanium dioxide pigments allow the production of white films, e.g., for carrier bags or for white mulch films, which reflect infrared radiation to reduce the soil temperature. The maximum loading with titanium dioxide is limited by the standards that have to be met.

Antifog agents like fatty acid esters are used to avoid the formation of water droplets on the film under condensation conditions, e.g., in cling film applications at the transition from room temperature to a refrigerated warehouse. The antifog agent is hydrophilic. It reduces the surface tension of droplets so that a uniform water film does not impair the clarity of the cling film [77].

Additives can be minimized using multilayer films. Surface active additives like slip, antibloc, or antifog agents are used only in the outer layers of a multilayer film. The migration of the organic additives and their solubility in the polymers has to be considered.

Printing of Biodegradable Plastics. In general, PBAT and PBAT–PLA can be printed and welded on standard equipment for PE-LD. Both alcohol-based and water-based inks can be used after testing. Prior to printing, the material has to be corona-treated if the surface tension is $< 38 \times 10^{-5}$ N. The drying temperatures should be kept below PE-LD conditions, depending on the content of PLA in the compound. As drying conditions depend very much on the machine design, they should be determined during production trials [77].

Metallization of Biodegradable Plastics. Depositing of a thin metal layer under a high vacuum using a plasma process is one of the most efficient production processes for high-barrier films. Slip and antibloc agents in the film have to be avoided, because surface defects reduce the barrier properties of the coating. Biodegradable polyesters like PLA and PBAT/PLA compounds, and cellulose derivatives like cellophane can be metallized on standard equipment [78].

Film properties of different polymers can also be combined to meet barrier requirements, e.g., of pouches for coffee, cosmetics, detergents etc. In a lamination process, films of different materials are bonded using heat and/or biodegradable adhesives [79]. A metallized film, e.g., from PBAT–PLA compounds with flexibility and high barrier to oxygen and water vapor can be laminated onto a PBAT–PLA compound with good welding performance.

5. Market Overview and Growth Drivers

Compared to the global market for PE film applications (approx. $35\,000 \times 10^3$ t in 2015), the market for biodegradable polymers (663×10^3 t production capacity in 2014 [80]) represents a small niche segment, which is going to show double digit growth in the coming decade, based on the following product and market drivers of biodegradable polymers in specific applications:

- legislative frameworks to enhance the use of biodegradable products in the food chain; examples are:
  - fruit and vegetable bags in France, Spain, Italy, UK
  - organic waste bags in both Europe and the USA
  - agricultural mulch films in China, USA, and Southern Europe
- superior life-cycle ecological efficiency (e.g., for garden waste bags)
- changing consumer behavior based on higher sensitivity for environmental issues and an increased interest in environmentally friendly products
- increased interest of retailers to differentiate in the market
- support by municipal authorities (providing a composting infrastructure)
- technology progress including access to new applications (e.g. home compostability, marine degradation)
- larger production plants and increasing production capacities

The authors expect the market (production capacity) for biodegradable polymers to grow from 663×10^3 t (2014) to 1287×10^3 t (2019), which means an average annual growth rate of 14%. Depending on the development of the above-mentioned factors and technology progress, the market growth for biodegradable polymers may be influenced significantly.

Biodegradable Polymers versus Feeding the World. In contrast to fuels and energy, the much lower amount of renewable resources needed for the production of biodegradable polymers does not and should not lead to a competition to global food production. Assuming a 14% annual growth rate of the biodegradable polymer market and a 100% raw material sourcing via agricultural feedstock, this would demand only 0.02% of the arable land [81]. This shows that there is no competition between biomass use for food and feed and biomass use for making biodegradable polymers. In addition, first generation feedstock bioplastics are an enabling technology that will facilitate the transition to later generations of feedstock [14].

6. Value of Biodegradability—Life-Cycle Assessment (LCA)

Biodegradable plastics are developed for applications where a possibility for a safe release into the environment is required. They are particularly attractive when economic and/or ecological benefits can be gained by leaving plastic products in the soil or organic waste stream.

To define the value of biodegradable polymers, the overall system costs and the environmental impact of individual products in their respective target applications have to be considered. To this end, comprehensive life-cycle assessments are an appropriate tool, especially when accompanied by cost evaluations that cover all phases from the cradle to the grave.

When looking at the life cycle of biodegradable plastics, two aspects are of particular importance: the end-of-life options and the use of renewable resources in the material production (the major part of the currently available biodegradable plastic products are made of blends of fossil-based polymers and polymers derived from biomass).

By using renewable carbon from biomass, an improvement in the CO_2 balance can be achieved. However, significant effects beyond the impacts on greenhouse gas emissions are possible, e.g., soil modification, eutrophication, impact on biodiversity, land requirements, and water consumption. These aspects depend on different factors like feedstock type, scale of production, cultivation and land-management practices, location, and downstream processing routes. Especially the environmental implications of agriculture are sometimes difficult to assess by the LCA methodology and require further research.

The functional value of biodegradable polymers can be decisive for their LCA in specific applications. Amongst the most important values of biodegradable polymers is the contribution to organic waste diversion and avoidance of pollution from thin, nonbiodegradable films in agriculture.

Organic Waste Diversion. For the disposal of organic waste, different end-of-life options are possible: landfilling, incineration, and biological treatment.

Landfilling. This traditional way is still common in the EU. In landfills, biodegradable waste decomposes to produce landfill gas and leachate. The landfill gas consists mainly of methane and, if not captured, it contributes considerably to the greenhouse effect. For this reason, the diversion from landfill is an important part of the European Waste Framework Directive.

This directive requests that 50% of municipal waste in EU member states is recycled by 2020. As organic waste is the largest fraction of municipal waste in the EU (equaling approximately 30–40% of organic waste volumes), the organic recycling of organic wastes is the most important measure to achieve the directive targets.

Incineration. Organics waste is usually incinerated as part of the mixed municipal waste stream. Depending on the facility and the energy use, this process can be regarded as energy

recovery or as disposal. As the moisture content in organic kitchen waste is mostly very high (about 60%), this waste does not contribute significantly to energy recovery.

Biological Treatment. Composting is the most common biological treatment option. It may be considered as a recycling option when the resulting compost is used as fertilizer or soil improver. Effects like increased water retention capacity and improved soil structure are ecological benefits which are of particular importance when soil erosion is a serious problem (for example in some Southern European countries).

Anaerobic digestion is a method of producing biogas from organic waste for energy purposes and, thus, could be seen as energy recovery. This waste management option is especially suitable for treating wet organic waste. Since compost has a higher value as soil improver for farming than digestate, the dominant design is increasingly to combine anaerobic digestion plants with compost plants. As a result, digestate is transformed into compost before application onto the fields.

Value for Organic Waste Diversion. In applications such as organic waste bags and shopping bags, biodegradable polymers offer multiple values; these include:

- Increased volumes of organic waste diversion: The volumes of separately collected organic waste were shown to increase in households that use compostable bags in comparison to the volumes collected before the introduction of organic waste bags. The most probable reason is that the products facilitate a cleaner organic waste collection [82]. The increase of collected organic waste also results in an increased production of compost, which is a known source for nutritive substances such as phosphate [83].
- The specific biogas yield of organic waste increases by over 30% if it is collected in compostable bags. The low oxygen permeability by using an organic waste bag results in a silage effect that conserves the organic waste before its treatment in an anaerobic digestion plant.

Agricultural Applications of Biodegradable Polymers. A nonbiodegradable agricultural film has to be collected after use (labor costs) and disposed of (or recycled), which generates additional costs within the system. Thin mulch film hinders used film collection and eventually its recycling. Inefficient collection of PE mulch film leads to accumulation of plastic particles inside the soil [84]. These hinder nutrients to reach the plant root but also the overall circulation of water, air and microorganisms in the soil. For example, in Xinjiang province, long-term use of thin 10 μm PE mulch film resulted in a yield decrease of cotton of 11% over 10 years [85, 86]. A critical factor for collecting used mulch film is the film thickness. A comparative LCA study of conventional PE and Ecovio biodegradable mulch film concluded that viable collection and recycling of conventional film requires minimum thickness of 25 μm [86]. Thin, biodegradable mulch film is a stand-alone alternative solution which does not require the building of recycling infrastructure, collection equipment, and extra working time for farmers and also avoids soil pollution and its implications.

7. Applications

The following paragraphs describe the major applications today (loose-fill applications excluded) as well as emerging applications in packaging. An overview of applications and volumes for 2015 and 2020 is shown in Table 8.

Table 8. Development of applications for biodegradable polymers (selected)

Application	Volume 2015, 10^3 t	Volume 2020, 10^3 t
Organic waste bags	55	162
Shopping bags	24	45
T-shirt bags	22	50
Fruit and vegetables bags	0	20
Biodegradable mulch film	4	14

7.1. Organic Waste Bags (OWB)

As described in Chapter 2 and 6, industrial composting is the most favored method of recovery of post-consumer organic waste according to the European Waste Framework Directive 2008/98/EC. Industrial composting is already well-established in some European countries like Germany, Benelux, Northern Italy, Austria, and is being established in others, e.g., UK. The Netherlands and Germany are the leading countries in the development of a composting infrastructure. In these two countries, 95% and 60% of all households, respectively, have access to industrial composting plants. In the EU, organic matter accounts on average for 30–40% of total domestic refuse. With the expectation of continuous expansion of the composting infrastructure, a significant growth of OWB is expected.

From a technical point of view, OWB have to be biodegradable according to EN 13432. A certificate of the bag according to the certification scheme for biodegradable plastics [87, 88] on the bag level is the basic prerequisite for OWBs. According to the organic waste ordinance in Germany a biobased content of >50% is required based on the ^{14}C method (EN 16929) for the German market.

Beyond mechanical properties to carry the designated volume of 5–20 L of organic waste, it is necessary to down-gage the bags to 15–30 μm to obtain a cost-competitive bag. The temperature resistance should allow transport and storage at 60 °C. Breathability, i.e., low-barrier properties for water below <300 g/m^2 is required to reduce the formation of water in the waste collection bin.

Hygienic organic waste collection is still one of the most important issues to consumers [89]. An investigation of the amount of bacteria and fungi on the surface at organic waste handling biodegradable plastic bags showed that these are preferable over, e.g., paper bags without coating with biodegradable compounds [89].

PBAT–PLA compounds exhibit a natural barrier against oxygen and other gases at room temperature. The low oxygen availability within the bag leads to fermentation of the organic waste resulting in a drop of the pH value under five during storage (1–2 weeks). Due to these conditions the premature degradation of organic material during waste collection and storage is reduced. As a result, the overall methane production in anaerobic digestion is increased over other organic waste-collection methods if PBAT–PLA bags are used [90]. Besides the higher potential for biogas production, the impurity of organic waste was shown to decrease by the usage of OWB [90].

7.2. Shopping (Carrier) Bags

Legislative changes and an increased interest of consumers in environmental friendly products accompanied by an interest of retailers to differentiate are the major drivers for the market growth of biodegradable shopping bags. After shopping, these bags can be applied for the disposal of organic waste resulting in a double use of the material [91].

Thin biodegradable carrier bags have a property profile similar to that of compost bags:

- Good mechanical properties for loads of about 1000 times of their own weight
- Good puncture resistance, e.g., for liquid beverage cartons
- Down-gaging to 15–35 μm
- Good printability (eight-color flexo printing) for superior presentation
- Good welding performance for high-speed bag making
- Usefulness as compost bags after several services as a carrier bag

Except for the optical presentation and the resulting need for printability, biodegradable carrier bags have to fulfill the same requirements as biodegradable compost bags. Thus the material options are also the same. An LCA has been performed to show the better sustainability of shopping bags in double function as compost bags if compared to PE-LD-shopping bags and OWB from biodegradable polymers and compounds [91].

7.3. Mulch Film

Agricultural films are a well-established application in Japan and the EU. The regulations for

waste disposal of nonbiodegradable mulch film require either recycling or adequate treatment (e.g., incineration). If thin mulch films are concerned, the recovery of the film in the field is crop-dependent and difficult. Cleaning of the soil residues is cost-intensive. In this case it is frequently more cost-effective to use biodegradable mulch film of approximately 10 μm, which is adapted to the climate and the fruit application.

As the most important property of mulch film is the appropriate biodegradability, extensive experiments in each region are indispensable.

7.4. Horticulture and Formation of Landscape

Different horticultural items made of biodegradable polymers such as plant pots, seed/fertilizer tape and binding materials, foams, and nets for erosion control offer reduction of system complexity by reducing the number of work steps. These tapes are usually manufactured in a cast-film process producing a sheet which is slit into tapes. The tapes are oriented in a multistep process on a roller stack with a typical process orientation rate of 5:1 to 7:1 using PBAT–PLA-compounds without filler.

7.5. Packaging

The packaging market for biodegradable polyesters and compounds is under development. Especially the food packaging market offers large opportunities for biodegradable polymers in specific applications. In the following section, the focus will be on flexible food packaging, paper coating for food service ware, e.g., paper cups, and ridged packaging like foam and biodegradable coffee capsules.

7.5.1. Shrink Films

Shrink films are used to combine several sales items in one packaging—e.g., six bottles in a six-pack. The bottles are packed in a piece of film which is heated and shrunk in a heating tunnel above the melting point of the film for a short time. The shrink forces after relaxation have to stay high enough to store and carry the packaged goods along the logistic chain: Thus the requirements are:

- High shrink values in extrusion direction MD > 60%
- Low shrink values in cross direction CD < 20%
- High shrink rate during heating in the oven
- Welding of the loose end during shrink process
- High shrink forces after relaxation

Although the market is large, biodegradable shrink films are still under development. PBAT–PLA compounds have a good strength and an adequate heat resistance. Films thereof exhibit the necessary shrink values.

7.5.2. High-Heat Applications

Coated or laminated paper products represent another potential market for biodegradable polymers. At present, paper packaging such as disposable cups are extrusion coated with PE-LD to provide water and fat barrier to the paper, which restricts the biodegradation of the paper substrate because the PE-LD acts as an impervious barrier. By using biodegradable polymers instead of PE-LD, the complete cup is rendered biodegradable while maintaining the good barrier properties formerly provided by the PE-LD.

New solutions for high-heat applications like coffee capsules have been developed over the past years, which use for example cPLA- or PBS-based compounds to achieve the desired temperature stability against hot water.

7.5.3. Shock Absorber from Biodegradable Particle Foam

For loose-fill applications, foamed biodegradable polymers based on starch have been used for more than one decade (not addressed in detail in the text and excluded in Table 8). A new generation of biodegradable foams for food packaging applications is under development (BASF, consortium PURAC/Synbra/Sulzer). The foams have the potential to replace EPS–EPP foams currently used for food and protective packaging. The new particle

foams feature a similar density to EPS–EPP, which is much lower than that of corrugated board designs.

8. Production Capacity

After one decade of market development, production capacities will be increased significantly by the end of the 2010s (see Chap. 6). This increase is dominated by PLA expansion plans. NatureWorks LLC (US capacity 150 000 t/a) plans to build a 75 000 t/a PLA plant in Asia. Corbion intends to build a 75×10^3 t PLA plant in Thailand as well. There are no capacity expansion plans in PBAT polyester published. PHA will continue to be a small but promising 100% biobased polyester, marketed by Kaneka (Japan), Meredian (USA), and other smaller players. A summary of existing and planned capacities is shown in Table 9.

9. Outlook

Biodegradable polymers are specialty plastics for selected applications where biodegradability adds value. The market for biodegradable polymers (650×10^3 t in 2104 production capacity; excluding loose fill) represents a small niche segment compared to the global market for PE film (approx. $35\,000 \times 10^3$ t in 2015) or to the global polymer market (approx. $300\,000 \times 10^3$ t in 2014). Based on different market drivers (legislative frameworks and requirements, brand owner engagement, changing consumer behavior, improved composting infrastructure, technology,application, and capacity development), the expected growth rate of approximately 15% per year can be influenced significantly. Biodegradable polymers combine different chemical and biotechnological steps in their synthesis and biodegradation and thus are an excellent example of a symbiosis between these disciplines.

Glossary and Abbreviations Terms for Carbon Origin and Degradation

Biobased	Refers to the origin of the raw materials. Only significant if the carbon content of annually renewable raw materials is given as the share of the total carbon content.
Renewable	Refers to renewable (annually or otherwise renewable) raw materials such as corn, wheat, paper, wood, etc.
Fossil (nonrenewable) or fossil-based	Refers to raw materials not considered to be renewable, such as gas, crude oil, coal, which are organic in origin.
Fragmentable (degradable)	Certain materials containing special metal additives as decomposition aids to obtain fragments under the effect of time, heat, and stress. Not fully biodegradable according to current scientific standards.
Biodegradable	Microorganisms such as bacteria, fungi, or algae metabolize these materials completely, giving off CO_2, water, energy, and biomass (aerobic process). In anaerobic biodegradation, also methane is produced.
Compostable	Fully biodegradable under composting conditions, as defined by current standards, i.e., ISO 17088, EN 13432, ASTM D 6400, Japanese GreenPla.

Table 9. Expected development of production capacities of biodegradable polyesters and compounds

	Manufacturers	Product	Capacity 2014, t/a	Capacity 2018, t/a	Country
PLA	NatureWorks LLC	Ingeo	150 000	225 000	USA, Asia
	Corbion Purac		0	75 000	Thailand
PHA	Kaneka	Aonilex	1000	5000	Japan
	Meredian		1000	5000	USA
Aliphatic/aromatic polyesters	BASF	Ecoflex	74 000	74 000	Germany
	Novamont	Origo-Bi	70 000	70 000	Italy
	JinhuiZhaolong High Tech. Co.		20 000	20 000	China
Aliphatic polyesters	Showa Denko	Bionolle	3000	3000	Japan
	Mitsubishi Chemicals & PTT MCC	GS-PLA	6000	20 000	Japan

Abbreviations

BDO	1,4-butanediol
LA	lactic acid
LCA	life-cycle assessment
OWB	organic waste bag
PBAT	poly[(butylene adipate)-*co*-(butylene terephthalate)]
PBS	poly(butylene succinate)
PBSA	poly[(butylene succinate)-*co*-(butylene adipate)]
PBT	poly(butylene terephthalate)
PC	polycarbonate
PCL	polycaprolactone
PE	polyethylene
PE-HD	high-density polyethylene
PE-LD	low-density polyethylene
PEO	poly(ethylene oxide) (also poly(ethylene glycol), PEG)
PES	poly(ethylene succinate)
PET	poly(ethylene terephthalate)
PHA	polyhydroxyalkanoate
PHB	poly(3-hydroxybutyrate) (also P(3-HB))
PHBH	poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)
PHBV	poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)
P(3HB-*co*-4HB)	poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate)
P(4-HB)	poly(4-hydroxybutyrate)
PLA	poly(lactic acid) (also polylactide when prepared through ROP of lactide)
PLLA	poly (L-lactic acid) or poly(L-lactide)
PDLA	poly (D-lactic acid) or poly(D-lactide)
cPLA	crystalline PLA
scPLA	stereocomplex PLA
ROP	ring-opening polymerization
PP	polypropylene
PS	polystyrene
PVC	poly(vinyl chloride)
PVOH	poly(vinyl alcohol)
SA	succinic acid

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