1

An Overview of Methods and Standards

Biocomposites are considered the next-generation materials as they can be made using natural/green ingredients to offer sustainability, eco-efficiency, and green chemistry (1–3). Nowadays, biocomposites are being utilized by numerous sectors, which include automobile, biomedical, energy, toys, sports, and others.

An effort has been made to provide a comprehensive assessment of the available green composites and their commonly used in order to make materials capable of meeting present and future demands. Various types of natural fibers have been investigated with polymer matrixes for the production of composite materials that are on par with the synthetic fiber composite. Also, the requirements for green composites in various applications from the viewpoint of variability of fibers available and their processing techniques have been detailed (4).

1.1 History of Biodegradable Plastics

In the late 1980s, biodegradable plastics came into use. However, these came to be misapplied in a number of situations. The misapplication of inappropriate or incompletely developed technology led to products which often did not meet performance claims and expectations. The so-called *first generation technologies* often lacked one or more of the following issues (5):

- Rate or extent of biodegradation, primarily due to limitations of starch incorporation,
- Necessary physical properties and related characteristics
- An economical means to effectively and efficiently manufacture starch-based blends,
- Intermediate product compatibility with conventional plastics product conversion processes, and
- Lower limits on film thickness caused by the use of non-gelatinized starch materials.

The synthesis, processing, and technology of renewable polymers has been reviewed (6–27). Furthermore, the state-of-the-art for food packaging applications has been reviewed (28–32). Using biomass for the production of new polymers can have both economic and environmental benefits (33).

Biomass-derived monomers can be classified into four major categories according to their natural resource origins (34):

1. Oxygen-rich monomers including carboxylic acids, e.g., lactic acid succinic acid, itaconic acid, and levulinic acid, but also ethers, such as furan,
2. Hydrocarbon-rich monomers including vegetable oils, fatty acids, terpenes, terpenoids and resin acids,
3. Hydrocarbon monomers, i.e., bio-olefins, and
4. Non-hydrocarbon monomers such as carbon dioxide.

Carbon dioxide is an interesting synthetic feedstock, which can be copolymerized with heterocycles such as epoxides, aziridines, and episulfides. In 1969, *Inoue* reported the zinc catalyzed sequential copolymerization of carbon dioxide and epoxides as a new route to poly(carbonate)s (9, 35). The reaction is shown in Figure 1.1.

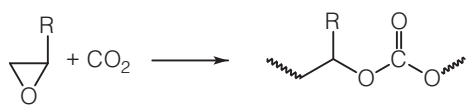


Figure 1.1 Reaction of carbon dioxide with epoxides (35).

Plants produce a wide range of biopolymers for purposes such as maintenance of structural integrity, carbon storage, and defense

against pathogens as well as desiccation. Several of these natural polymers can be used by humans as food and materials, and increasingly as an energy carrier. Plant biopolymers can also be used as materials in certain bulk applications such as plastics and elastomers (36).

Lignin, suberin, vegetable oils, tannins, natural monomers like terpenes, and monomers derived from sugars are typically natural precursors for bio-based industrial polymers. Glycerol and ethanol also play a potential role as future precursors to monomers (37).

1.2 Green Chemistry

The principles and concepts of green chemistry are the subjects of several monographs (38–47). Recent progress in enzyme-driven green syntheses of industrially important molecules has been summarized (48). Studies in biotechnological production of pharmaceuticals, flavors, fragrance and cosmetics, fine chemicals, as well as polymeric materials (49) have been documented. Biocatalysis is a transformational technology uniquely suited to delivering green chemistry solutions for safer, efficient, and more cost-effective chemical synthesis.

The different catalytic processes for the conversion of terpenes, triglycerides and carbohydrates to valuable chemicals and polymers have been reviewed (50).

A basic task of green chemistry is to design chemical products and processes that use and produce less hazardous materials. The term *hazardous* covers several aspects, including toxicity, flammability, explosion potential and environmental persistence (51).

The synthesis of maleic anhydride illuminates a possibility of multiple pathways. Maleic anhydride can be synthesized both from benzene and from butene by oxidation. In the first route, a lot of carbon dioxide is formed as an undesirable byproduct. Thus, the first route is addressed as *atom uneconomic*. In Table 1.1, some uneconomic and economic reaction types in organic chemistry are opposed.

There were in total 12 basic principles in green chemistry (52–55). These principles are summarized in Table 1.2.

Table 1.1 Atom uneconomic and economic reaction types.

Economic	Uneconomic
Rearrangement reaction	Substitution reaction
Addition reaction	Elimination reaction
Diels-Alder reaction	Wittig reaction
Claisen reaction	Grignard reaction

Table 1.2 Basic principles of green chemistry (53).

Principle
Ensure that all material and energy inputs and outputs are as inherently nonhazardous as possible.
Better prevent waste than cleanup.
Minimize energy consumption and materials.
Maximize efficiency of mass, energy, space, and time.
Products, processes, and systems should be *output pulled* rather than *input pushed*.
Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition.
The design goal should be targeted durability.
Unnecessary capacity or capability is not desirable.
Material diversity in multicomponent products should be minimized.
Development of products, processes, and systems must consider energy and materials flows.
The design should consider a commercial *afterlife*.
Material and energy inputs should be renewable.

Recently, the above-mentioned concept was extended (56). The special volume on green and sustainable chemistry and engineering has fourteen papers that were considered relevant to the present day issues and discussion, such as adequate use of raw materials and efficient energy, besides considering renewable sources for materials and energy; and changing economical canons towards circular economy. Businesses, governments and societies are facing a number of challenges along the pathway to sustainability for the well-being of future generations. Chemicals are ubiquitous in everyday activities. Their widespread presence provides benefits to societies' well-being, but can have some deleterious effects. To counteract such effects, green engineering and sustainable assessment in industrial processes have been gathering momentum in the last thirty years. Green chemistry, green engineering, eco-efficiency, and sustainability are becoming a necessity for assessing and managing products and processes in the chemical industry. Fourteen articles have been discussed, related to sustainable resource and energy use (five articles), circular economy (one article), cleaner production and sustainable process assessment (five articles), and innovation in chemical products (three articles) (56).

Catalytic processes from the viewpoint of green chemistry include catalytic reductions and oxidations methods, solid-acid and solid-base catalysis, as well as carbon-carbon bond formation reactions (57).

Novel concepts and techniques such as *bio-inspired* polymer design, *synthetically-inspired* material development are now considered to contribute to the development of natural monomers and polymers as a sustainable resource. These concepts and techniques that integrate materials synthesis, process and manufacturing options with eco-efficiency have been documented (58–62).

1.2.1 Genetic Engineering

The direct production of novel compounds in biomass crops in order to produce bioenergy as a coproduct seems to be a promising way to improve the economics of transgenic plants as biofactories (63).

Genetic engineering of plants may be used for the production of novel polymers and basic chemicals. These methods may help to

alleviate the demands for limited resources and provide a platform to produce some desired compounds in bulk quantities.

Recent advances in enhancing the production of novel compounds in transgenic plants consist of a multigene transformation and the direction of the biosynthetic pathways to specific intracellular compartments.

Basically it appears feasible to produce interesting proteins, such as spider silk or collagen, novel carbohydrates, and biopolymers using transgenic plants. These compounds could replace petroleum-based plastics (63). However, there are pro and con arguments. For example, if transgenic plant factories should compete with conventional production processes, economic efficiency and sustainability are important. These factors depend on the future development of oil and energy prices.

On the other hand, societal factors such as the public acceptance of transgenic plants are also key factors (63). Chemicals that may be produced from biomass or in transgenic plants are listed in Table 1.3.

Cyanophycin is an attractive biopolymer with chemical and material properties that are suitable for industrial applications in the fields of food, medicine, cosmetics, nutrition, and agriculture (65). For the efficient production of cyanophycin, cyanophycin synthetases have been investigated and also fermentations and downstream processes have been elucidated.

The strategies for cyanophycin production in microbial strains, including *Escherichia coli, Pseudomonas putida, Ralstonia eutropha, Rhizopus oryzae*, and *Saccharomyces cerevisiae*, heterologously expressing different cyanophycin synthetase genes have been reviewed.

Also, the chemical and material properties of cyanophycin and its derivatives produced through biological or chemical modifications were addressed in the context of their industrial applications (65).

The biochemical pathways for producing 2(E)-heptenedioyl-CoA methyl ester have been described (66). Also, methods for enzymatically converting hept-2-enedioyl-CoA methyl ester to pimeloyl-CoA using a polypeptide have been shown.

Table 1.3 Chemicals from biomass or occurring in transgenic plants (64).

Compound	Remark
Succinic acid	Natural substances in plants
Fumaric acid	Natural substances in plants
Malic acid	Natural substances in plants
2,5-Furandicarboxylic acid	Oxidative dehydration of C6 sugars
3-Hydroxypropionic acid	Fermentation from sugar
Aspartic acid	Amination of fumaric acid
Glucaric acid	Oxidation of starch
Glutamic acid	Byproduct of sucrose production
Itaconic acid	Conversion of aconitic acid
Levulinic acid	Acid-catalyzed dehydration of cellulose
3-Hydroxybutyrolactone	Oxidation of starch
Glycerol	In plant oil
Sorbitol	Hydrogenation of sugars
Xylitol	Hydrogenation of sugars
Lysine	Fermentation
Proline	Fermentation
Arginine	A component of cyanophycin
Isomaltulose	From sucrose
Inulin	From chicory

1.3 Commercial Situation

The chemistry, important applications, and the market potential of intrinsically biodegradable polymers have been reviewed (67). One method for evaluating the potential demand for biodegradable polymers is to review the applications and necessary pricing to penetrate various end uses. Each application end use has a price hurdle associated with it.

However, the true market potential for biodegradable plastics will depend on:

- The selling price of the material,
- Environmental pressure,
- Legislation,
- Establishment of standards for degradability,
- The development of composting infrastructure, and
- The ability to overcome the problem of potentially contaminating the pool of recyclable materials.

These factors are difficult to predict since there are external forces that may not be universally applied in the same manner. The interest in biodegradable plastics has continuously grown as the conventional resources based on petroleum are beginning to decrease. The last two decades of the twentieth century saw a paradigm shift from biostable to biodegradable materials.

For example, in the next couple of years, many of the permanent prosthetic devices used for temporary therapeutic applications will be replaced by biodegradable devices that could help the body to repair and regenerate the damaged tissues (68).

Finding applications for renewable polymers that lead to mass production and price reduction poses a major contemporary challenge. This can be attained by improving the end performance of the biodegradable polymers (69).

The complexities of renewable supply chains have been elucidated (70). In particular, polymers manufactured from renewable feedstocks will augment various industrial markets such as plant material used as a renewable ingredient in paint manufacture, partially substituting for crude oil derivative ingredients. Polymer industrial supply chains have been identified and the market opportunity for renewable polymers has been estimated.

The developments in the field of renewable polymers illustrate how business models can link producers and customers through the development of new technologies and products (71). Initially, the companies assumed that reducing the costs and increasing the production will guarantee success of biopolymers in the market. However, some unconventional hurdles emerged. Companies have build markets for biopolymers and to assure customers that biopolymers are in fact produced sustainably.

Several companies have identified new market opportunities for biopolymers, designed distinctive types of business models to seize these opportunities, and developed ways to create an increased value by communicating performance advantages and the reduction of the environmental impact to downstream entities.

However, because they did not include societal factors in their efforts to define the term *sustainable*, a significant risk emerges that their sustainable value propositions may not endure without further refinements (71).

1.4 Environmental Situation

Polymer waste management options are shown in Figure 1.2. The utilization of waste polymers by mechanical recycling and incineration has ecological limitations.

The impact of biodegradable polymers on the environment and on the society has been detailed (72).

Landfills contain a tremendous amount of plastic waste. As the plastics degrade, pollutants leach into the soil and gases escape into the air. In response to this issue, the concept of recycling has been introduced into the consumption cycle. Recycling generally involves processing of the used materials into new products. However, the processing of waste can be economically ineffective, as it entails various mechanisms, such as:

- Collecting the waste,
- Sorting the waste according to provided specifications, and
- Processing the waste into materials that can be used in new products in the final stage.

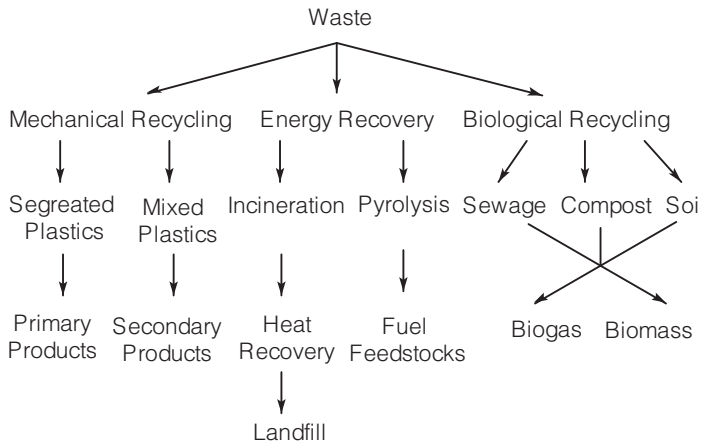


Figure 1.2 Polymer waste management options (73, 74).

Aside from the ineffective processes, recycling is not widely available in all communities and if available, often is not mandatory. Thus, many individuals either do not have a convenient venue for recycling or simply choose not to recycle (75).

Recycling has its disadvantages as well. The sorting and shipping of the plastic waste to the appropriate recycling facility is costly, both monetarily and environmentally. Different types of plastics must be recycled separately because they do not cooperate to form a stable reusable plastic. In addition, many plastics have a limited recyclable life. For example, recycling plastic water bottles can result in a lower grade plastic that cannot be converted into a new plastic water bottle.

Other methods of preventing this pollution include the partial use of biodegradable materials in plastic products. Certain auxiliary elements, made of biodegradable material, are then incorporated within the container. However, the remainder of the container is substantially plastic based on petroleum. If these mixed products are included with other plastics for recycling, they can contaminate the product and render it unusable (75).

Materials such as paper, paperboard, plastics, and even metals are presently used in enormous quantities in the manufacture of articles such as containers, separators, dividers, lids, tops, cans, and other packaging materials.

Most of the currently used food packaging materials are non-degradable and are creating serious environmental problems. New technologies are being explored and developed to study the complex interaction between the food packaging materials and food (76). For example, a nanocomposite of cellulose constitutes environmentally friendly packaging, which is easily recycled by combustion and requires low power consumption in production.

There are several such biodegradable materials which are available at a low price, have good mechanical properties and allow disposal in the soil. This is advantageous because biological degradation produces only carbon dioxide, water, and inorganic compounds. Also, it has been discovered that biodegradable plastics made of such materials can be disposed of together with organic waste. The widespread use of biopolymers in the place of standard plastics would help to reduce the weight of waste. Therefore, biodegradable materials take part in the natural cycle *from nature to nature* and play an important role for environmental sustainability (76).

Modern processing and packaging technology allows a wide range of liquid and solid goods to be stored, packaged, and shipped in packaging materials while being protected from harmful elements such as gases, moisture, light, microorganisms, vermin, physical shock, crushing forces, vibration, leaking, or spilling. Many of these materials are characterized as being disposable, but actually have little, if any, functional biodegradability. For many of these products, the time for degradation in the environment can span decades or even centuries (77).

Each year, over 100 billion aluminum cans, billions of glass bottles, and thousands of tons of paper and plastic are used in storing and dispensing soft drinks, juices, processed foods, grains, beer and other products. In the United States approximately 5.5 million tons of paper are consumed each year in packaging materials, which represents about 15% of the total annual domestic paper production.

Packaging materials are all, to varying extents, damaging to the environment. For example, the manufacture of poly(styrene) (PS) products involves the use of a variety of hazardous chemicals and starting materials, such as benzene, a known mutagen and a probable carcinogen. Chlorofluorocarbons have also been used in the manufacture of blown or expanded PS prod-

ucts. Chlorofluorocarbons have been linked to the destruction of the ozone layer.

Due to widespread environmental concerns, there has been significant pressure on companies to discontinue the use of PS products in favor of more environmentally safe materials. Some groups have favored the use of products such as paper or other products made from wood pulp. However, there remain drawbacks to the sole use of paper due to the tremendous amount of energy that is required to produce it. A strong need to find new, easily degradable materials that meet necessary performance standards remains (77).

The concept of sustainable bio-based products is as follows (78): A bio-based product derived from renewable resources should have a recycling capability and a triggered biodegradability. This means that it is stable in the course of service time. However, it should biodegrade after disposal under the specific conditions of composting. This composting procedure should also be commercially viable.

The general situation of compostable polymer materials has been described in detail in a monograph (79).

From a waste management perspective, high-barrier, multilayer, biodegradable food packaging could be a useful replacement for current multilayered packaging that is non-recyclable and non-degradable (80).

It has been envisioned that a biodegradable thermoplastic starch and poly(β-hydroxyalkanoate) (PHA) layered material could be a promising target. In a study an attempt was made to quantify the greenhouse gas trade-offs associated with using the proposed biodegradable packaging and identify the important design considerations (80).

The study also considered the impacts of landfill methane capture efficiency, which is an important aspect as biodegradable packaging may release methane when disposed of in a landfill whereas non-biodegradable packaging is inert (80). However, a key result is that when food waste is included in the system boundaries, it contributes over 50% of the greenhouse gas emissions associated with the system, regardless of whether the package is biodegradable or not.

This shows that even for biodegradable packaging, reducing food waste is a key design consideration. In fact, the negative environmental impacts associated with disposal of a PHA-biodegradable

thermoplastic starch packaging in landfill with low gas capture rates can actually be offset if the package reduces food wastage (beef) by approximately 6%. The overarching result is that a PHA-biodegradable thermoplastic starch food packaging only delivers positive greenhouse gas outcomes if it reduces food wastage or increases the viability of biological food waste processing (80).

1.4.1 Problems with Bio-based Composites

Bio-based composites often exhibit unsatisfactory properties, such as, or resulting from (81):

- Inadequate processing conditions, resulting in filler agglomeration and poor filler dispersion within the matrix,
- Variations in natural fiber properties, often due to geographical and seasonal variability,
- Anisotropy of the natural fibers themselves,
- High linear coefficient of thermal expansion for natural fibers, and
- Incompatibility between typically hydrophilic natural fibers and hydrophobic polymer matrices, resulting in poor interfacial adhesion between the phases.

The chemical modification of a natural fiber is often performed in order to enhance the properties of the interface between fiber and matrix. A more recent method of modification involves the deposition of a coating of nanosized cellulose onto the natural fibers or dispersing a nanosized cellulose in natural fiber reinforced composites. This method has been shown to improve the fiber-matrix interface and the overall mechanical performances. Such composites have been addressed as hierarchical, multiscale, nanoengineered, or nanostructured composites. The state-of-the-art in this field has been reviewed (81).

Natural polymer blends and nanocomposites as well as natural fiber reinforced composites and other aspects have been reviewed in a monograph (82).

1.4.2 Biodegradation

Biodegradable polymers are commonly those that undergo a microbially induced degradation, i.e., a chain scission. This will result in mineralization, photodegradation, oxidation, and hydrolysis. In this way, the polymer is altered in the course of the degradation process (83).

Biodegradation reactions are typically enzyme catalyzed and occur in aqueous media. Natural macromolecules containing hydrolyzable linkages, such as protein, cellulose and starch, are generally susceptible to biodegradation by the hydrolytic enzymes of microorganisms.

A few man-made polymers, however, are also biodegradable. The hydrophilic character of the polymers greatly affects their biodegradability. A general rule is that polar polymers are more readily biodegradable. Other important polymer characteristics that affect the biodegradability include crystallinity and chain flexibility.

Besides being able to biodegrade, it is often important for a polymer to exhibit certain physical properties such as stiffness, flexibility, water resistance, strength, elongation, temperature stability, or gas permeability (84).

The intended application often dictates the necessary properties. For example, in the case of sheets and films for usage as packaging materials, the desired criteria of performance include elongation, printability, imperviousness to liquids, temperature stability, etc.

Since the number of biodegradable polymers is limited, it is often difficult, or impossible, to select a single polymer or copolymer that meets all the desired performance criteria.

Polymers that have a high glass transition temperature (T_g) are difficult to be blown into films or are too brittle for use as a packaging material. In contrast, polymers with a low glass transition temperature show low softening and melting temperatures. This makes the fabrication of sheets and films difficult without self- adhesion. In addition, such sheets may lack adequate water permeation, which is necessary for packaging applications (84).

1.4.2.1 Details of the Mechanism of Degradation

In general, biodegradable plastics are believed to undergo enzymatic biodegradation through the following processes (85):

- A polymer degrading enzyme is first adsorbed onto the surface of the polymer material. This enzyme is a substance secreted extracellularly by a certain kind of microorganism.
- The enzyme then breaks down chemical bonds in polymer chains, such as ester, glycosidic, and peptide bonds, by a hydrolysis reaction.
- As a result, the polymer material is reduced in molecular weight and even decomposes to a low molecular weight compound unit by the degrading enzyme.
- Finally, decomposed products are further metabolized and utilized by various microorganisms and converted into carbon dioxide, water, and bacterial cell components.

1.4.2.2 Controlling the Rate of Biodegradation

The rate of biodegradation can be controlled. The essential ingredients for such a composition are a biodegradable polymer, a carbodiimide compound, an ultraviolet ray absorbent, and an antioxidant (85).

Examples of carbodiimide compounds are summarized in Table 1.4.

N,*N*´-Dicyclohexylcarbodiimide and *N*,*N*´-diisopropylcarbodiimide are particularly preferable because of their industrial availability. Polycarbodiimides can be synthesized from isocyanates by conventional methods (86). As carbodiimidization catalyst, 3-methyl-1-phenyl-2-phospholene-1-oxide is used.

Antioxidants are collected in Table 1.5 and examples of ultraviolet absorbers are summarized in Table 1.6. Some ultraviolet absorbers are also shown in Figure 1.3.

These compounds can be used as additives to tailor the properties of the polymers if desired.

Table 1.4 Carbodiimides (85).

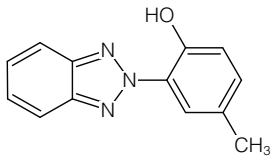
Monocarbodiimides
N,*N*´-dicyclohexylcarbodiimide
N,*N*´-Diisopropylcarbodiimide
Dimethylcarbodiimide
Diisobutylcarbodiimide
dioctylcarbodiimide
tert-Butylisopropylcarbodiimide
Diphenylcarbodiimide
Di-*tert*-butylcarbodiimide
Di-*β*-naphthylcarbodiimide
Isocycanate Monomers for Polycarbodiimides
4,4´-Dicyclohexylmethane diisocyanate
Isophorone diisocyanate
Tetramethylxylylene diisocyanate

Table 1.5 Antioxidants (85).

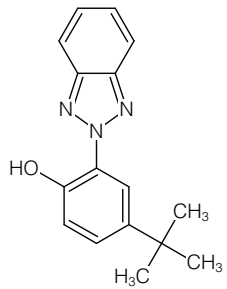
Hindered Phenol-based Antioxidants
4,4´-Methylene-bis-(2,6-di-*tert*-butylphenol)
Octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate
Phosphite-based Antioxidants
Tris-(2,4-di-*tert*-butylphenyl)phosphite
Bis-(2,4,di-*tert*-butylphenyl)pentaerythritol-diphosphite
Bis-(2,6-di-*tert*-butyl-4-methylphenyl)pentaerythritol-diphosphite

Table 1.6 Ultraviolet absorbers (85).

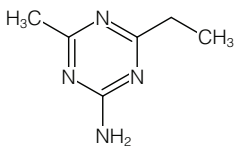
Benzotriazole-based Compounds
2-(2´-Hydroxy-5´-methylphenyl)benzotriazole
2-(2´-Hydroxy-5´-*tert*-butylphenyl)benzotriazole
2-(2´-Hydroxy-3´-*tert*-butyl-5´-methylphenyl)-5-chlorobenzotriazole
2-(3,5-Di-*tert*-butyl-2-hydroxyphenyl)-5-chlorobenzotriazole
2-[2´-Hydroxy-3´,5´-bis(α,α-dimethylbenzyl)phenyl]benzotriazole
Triazine-based Compounds
2-(4,6-Diphenyl-1,3,5-triazine-2-yl)-5-[(hexyl)oxy]phenol
2-[4,6-Bis(2,4-dimethylphenyl)-1,3,5-triazine-2-yl]-5-[(octyl)oxy]phenol
2,4,6-Triamino-1,3,5-triazine
2,4-Diamino-6-phenyl-1,3,5-triazine
2,4-Diamino-6-methyl-1,3,5-triazine
2,4-Diamino-6-(2-(dodecasylamino)ethyl)-1,3,5-triazine
2,4-Diamino-6-(o-methoxyphenyl)-1,3,5-triazine
4,6-Diamino-1,2-dihydro-2,2-dimethyl-1-(2,6-xylyl)-1,3,5-triazine
2,4-Diamino-6-(2-methoxyethyl)-1,3,5-triazine
2-Amino-4-ethyl-1,3,5-triazine
2-Amino-4-phenyl-1,3,5-triazine
2-Amino-4-ethyl-6-methyl-1,3,5-triazine



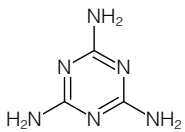
2-(2´-Hydroxy-5´-methyl phenyl)benzotriazole



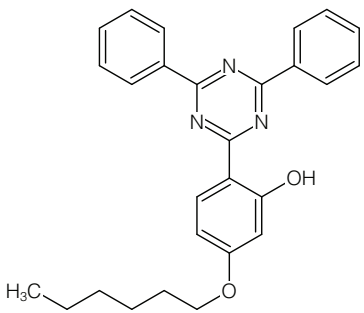
2-(2´-Hydroxy-5´-*tert*-butyl phenyl)benzotriazole



2-Amino-4-ethyl-6-methyl-1,3,5-triazine



2,4,6-Triamino-1,3,5-triazine



2-(4,6-Diphenyl-1,3,5-triazine-2-yl)-5-[(hexyl)oxy]phenol

Figure 1.3 Ultraviolet absorbers.

1.5 Properties of Biodegradable Polymers

Biopolymers are polymers that degrade through the action of living organisms. Such polymers include a range of synthetic polymers such as poly(ester)s, poly(ester amide)s, poly(carbonate)s, and others (84). In Table 1.7 the mechanical properties of E-glass and some natural fibers are compared.

Table 1.7 Mechanical properties (78).

Material	Density /[$g\,cm^{-3}$]	E-Modulus /[$G\,Pa$]
E-glass	2.55	73
Hemp	1.48	70
Flax	1.4	60–80
Jute	1.46	10–30
Sisal	1.33	38
Coir	1.25	6
Cotton	1.51	12

As can be seen from Table 1.7, in the case of hemp and flax, the elastic modulus is comparable to E-glass and the density is even smaller than that of E-glass.

1.6 Special Methods of Synthesis

The methods of synthesis of biodegradable polymers can be subdivided into conventional methods, click chemistry, enzymatic polymerization and polycondensation, chemoenzymatic polymerization, vine-twining polymerization, and bacterial synthesis. These methods will be detailed subsequently.

1.6.1 Conventional Methods

Biodegradable polymers can be synthesized using renewable resources by conventional methods (33). The recent advances in the synthesis of polymers from renewable resources have been shown (87).

For example, yttrium complexes are suitable compounds for the synthesis of poly(lactide)s (33).

Also, a chiral Schiff base/aluminium alkoxide can be used as initiator for the stereoelective polymerization of *rac*-(*D*,*L*)-lactide (88). The compound is shown in Figure 1.4.

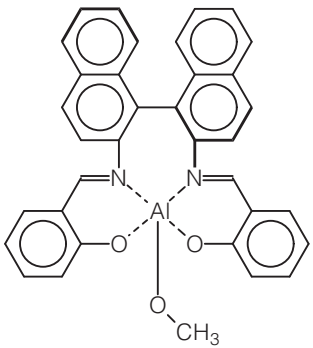


Figure 1.4 Chiral Schiff base (88).

A rather high stereoelectivity is observed, as a polymer with an 88% enantiomeric enrichment in the *D* units can be isolated at 19% conversion. At higher conversions a stereo-complex from *D*- and *L*-enriched stereocopolymers is formed. A narrow molecular weight distribution of M_w/M_n in the range of 1.05–1.30 is observed even at very high conversions. Thus, the polymerization reaction shows living type features (88).

1.6.2 Click Chemistry

Click chemistry is a powerful strategy that relies mainly on the construction of carbon-heteroatom bonds. It has been described in the present meaning in 2001 (89).

Applications are found in a wide variety of methods in modern chemistry, including biocompatible synthesis (90). For example, adhesive polymers can be formed when polyvalent azides and alkynes are assembled into crosslinked polymer networks by copper-catalyzed 1,3-dipolar cycloaddition (91). The polycondensation is efficiently promoted by copper ions.

As another example, poly(glycolide)s have been described that include a polymeric alkynyl-substituted glycolide (92). The alkynyl groups provide reactive sites for further functionalization of the

polymer, for example, by reaction with azide derivatives. The alkynyl and azide groups react via the click chemistry mechanism to form functional groups covalently bonded to the polymer via a triazole link. The polymers are biodegradable and can be used to deliver drugs or other therapeutic substances at controlled release rates.

The thiol-ene click reactions are considered a versatile and broadly applicable tool in polymer science (93). This reaction can be used as a click reaction for the synthesis of monomers as well as of dendrimers. Also, polysaccharides can be derivatized via a click reaction (94).

1.6.3 Enzymatic Polymerization

The field of enzymatic polymerization has been reviewed in detail (95–97). Enzymes have been industrially established in large-scale synthesis and degradation, such as the use of:

- Glucose isomerase in food industry,
- Cellulase for textile finishing,
- Lipase, protease, and cellulase in detergents, and
- Catalysts in chemical and pharmaceutical industries.

Enzymatic polymerization is an important issue for green polymer chemistry to save energy in production processes and to reduce the formation of undesired byproducts since the reaction is mostly selective. In general, an enzyme catalyzed reaction proceeds much faster than a conventional reaction, by lowering the activation energy.

Typical polymers that can be synthesized by an *in-vitro* enzymatic catalysis are summarized in Table 1.8. The basic concept of the

Table 1.8 Polymers by *in-vitro* enzymatic catalysis.

Enzyme types	Polymers
Oxidoreductases	Polyphenols, polyanilines, vinyl polymers
Transferases	Polysaccharides, cyclic oligosaccharides, polyesters
Hydrolases	Polysaccharides, polyesters, poly(carbonate)s, polyamides, polyphosphates, polythioesters

in-vitro enzymatic polymerization can be explained as follows: In the course of an *in-vitro* enzymatic polymerization, a monomer is treated by the catalyst enzyme as an unnatural or artificial substrate. But the substrate must be recognized and form a complex with the enzyme in order to allow a reaction.

The polymerization of catechol under high-pressure homogenization was catalyzed by laccase from *Myceliophthora thermophila* (98). This polymer was used for the green coloration of textile substrates.

The oxidation reactions were conducted using different forms of laccase, i.e., native laccase, PEGylated laccase and PEGylated laccase immobilized onto an epoxy resin. These three enzyme forms were deposited inside a polyester fabric bag during the experiments. The amount of polymer obtained was similar when using the three enzyme forms and its dispersion in a water/dimethyl sulfoxide mixture led to powder particles of about 30–60 *nm*.

It could be shown that the oxidation of catechol conducted under high-pressure homogenization can be an efficient methodology for the *in-situ* coloration of textiles. The polymers produced by this methodology strongly stained the textile container, revealing this experimental setup as a promising greener coloration/coating methodology involving milder conditions than that normally used in textile processes (98).

2,5-Furandicarboxylic acid-based semi-aromatic poly(amide)s were synthesized using enzymatic polymerization (99). These polymers are bio-based alternatives to poly(phthalamide)s, which are petrol-based semi-aromatic polyamides. From a commercial perspective, they have interesting properties as high-performance materials and engineering thermoplastics. It is even more appealing to explore novel 2,5-furandicarboxylic acid-based polyamides with added functionality for the development of sustainable functional materials.

Here, a set of 2,5-furandicarboxylic acid-based heteroatom polyamides have been successfully produced via a Novozyme 435 (N435)-catalyzed polymerization of bio-based dimethyl 2,5-furandicarboxylate with potentially heteroatom diamines, i.e., 4,9-dioxa-1,12-dodecanediamine, diethylenetriamine, and 3,3-ethylenediiminopropylamine (99). The enzymatic polymerization reactions were performed both in solution and in bulk. The latter approach is more sustainable and results in high-

er molecular weight products. Among the tested heteroatom diamines, N435 showed the highest catalytic activity toward 4,9-dioxa-1,12-dodecanediamine. Furthermore, it was found that all obtained 2,5-furandicarboxylic acid-based heteroatom polyamides are amorphous materials with a relatively high thermal stability. These heteroatom polyamides show glass transition temperatures ranging from 41°C to 107°C (99).

Enzymatic ring-opening polymerization is an appealing method for the preparation of poly(lactide)s and poly(lactone)s (100). These reactions are typically carried out at relatively high temperatures of 60–130°C.

However, there is a deficiency of enzyme-compatible solvents for such thermally demanding biocatalytic processes. A series of short-chained glycol-grafted ionic liquids were prepared based on a phosphonium, imidazolium, pyridinium, ammonium, or piperidinium cationic headgroup.

Most of these glycol-grafted ionic liquids exhibit relatively low dynamic viscosities (33–123 $mPa\,s$ at 30°C), coupled with excellent short-term thermal stabilities with decomposition temperatures in the 318°C–403°C range (100). Significantly, the long-term thermal stability under conditions matching those for enzymatic ring-opening polymerization synthesis (130°C for 7 d) is excellent for several of these task-specific ionic liquids.

Using a Novozym 435-catalyzed ring-opening polymerization, these ionic liquids were demonstrated to be viable solvents for the enzymatic production of reasonable yields (30–48%) of high molecular mass ($M_w \sim 20\ kDa$) poly(*L*-lactide) and poly(ε-caprolactone) compared to solventless conditions (12–14 kDa) (100).

1.6.3.1 Polycondensation

The recent developments in lipase-catalyzed synthesis of polyesters have been reviewed (101). A series of diacids, such as succinic acid, glutaric acid, adipic acid, and sebacic acid, and diols, such as 1,4-butanediol, 1,6-hexanediol, and 1,8-octanediol have been polymerized in solution and in bulk using lipase as a catalyst (102, 103).

Polymerization reactions with longer chain length monomers show a higher reactivity than reactions of shorter chain length

monomers (103). The lipase-catalyzed reaction of an alcohol with a vinyl ester proceeds much faster than with an alkyl ester (104).

The dependence of the origin of the particular lipase on the conversion in the ring-opening polymerization of 15-pentadecanolactone is shown in Table 1.9.

Table 1.9 Origin of lipase and conversion of 15-pentadecanolactone (101).

Lipase Type	Conversion/[%]
None	0
Rhizopus japanicus (lipase RJ)	<5
Hog liver (HLE)	<5
Penicillium roqueforti (lipase PR)	12
Aspergillus niger (lipase A)	16
Candida rugosa (lipase CR)	21
PPL	27
Lipase CC	54
Pseudomonas cepacia (lipase PC)	90
Lipase PF	97

1.6.4 Chemoenzymatic Polymerization

The mechanism of catalysis of green biocatalysts and metal catalysts is quite different, but if both are mutually compatible, then it allows the application concurrently in the same reaction system. The combination of these different types of catalysts is also known as chemoenzymatic method. Utilizing the advantages of enzymes, the chemoenzymatic method has been developed for the synthesis of various block copolymers, which are otherwise difficult to prepare.

The combination of the lipase-catalyzed ring-opening polymerization of lactones and the atom transfer radical polymerization allows a versatile synthesis of block copolymers consisting of a polyester chain and a vinyl polymer chain (105). Also, branched polymers have been produced by the chemoenzymatic technique (106).

1.6.4.1 Cyclodextrins

Cyclodextrins can polymerize cyclic esters such as lactones and lactides (107). They can initiate the polymerization of cyclic esters in bulk without any solvents to give products in high yields.

Cyclodextrins are cyclic oligosaccharides. α-Cyclodextrin is a 6-membered ring, β-cyclodextrin is a 7-membered ring, and γ-cyclodextrin is an 8-membered ring. The structure of α-cyclodextrin is shown in Figure 1.5.

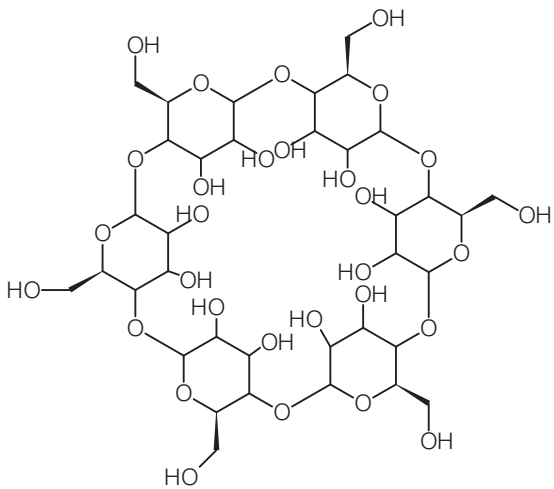


Figure 1.5 α-Cyclodextrin.

It has been found that cyclodextrins are active not only as initiators and catalysts but also support certain architectures of the final product similar to chaperone proteins.

Chaperones are proteins that assist the folding or unfolding process and thus the assembly or disassembly of other macromolecular structures. However, they do not appear in those macromolecular structures (108).

The cyclodextrin may encircle a linear polymer chain so that the chain assumes the proper conformation and avoids coagulation. So, a cyclodextrin mimics the strategy that a living system uses to form polymers. It is believed that such a system could provide an

environmentally friendly route to produce biodegradable functional polymers (107).

Multi-responsive cyclodextrin vesicles have been prepared and shown to be self-assembled by supramolecular bola-amphiphiles, consisting of (*N*,*N*´-bis(ferrocenylmethylene)-diaminohexane a guest, and as host, i.e., γ-hydroxybutyric-β-cyclodextrin (109). The vesicles may serve as redox-responsive systems.

Bola-amphiphiles are amphiphilic molecules that have hydrophilic groups at both ends of a sufficiently long hydrophobic hydrocarbon chain. Basically, a bola-amphiphile looks like the schematic shown in Figure 1.6.

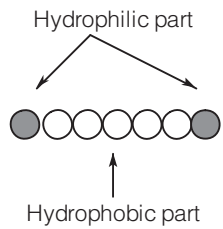


Figure 1.6 Schematic illustration of a bola-amphiphile.

1.6.5 Vine-Twining Polymerization

The Vine-twining polymerization is a method for the preparation of well-defined supramolecules, which are amylose polymer inclusion complexes (110). The method consists of the enzymatic polymerization of α-*D*-glucose-1-phosphate catalyzed by phosphorylase in the presence of various synthetic polymers such as poly(ether)s, poly(ester)s, poly(ester ether)s, and amphiphilic block copolymers. The 1H-NMR spectra of the polymers indicated structures composed from amylose and guest polymers.

The preparation of inclusion complexes composed of amylose and hydrophobic poly(carbonate)s have been achieved by vine-twining polymerization (111, 112). The structure of such complexes is shown in Figure 1.7.

This is a phosphorylase-catalyzed enzymatic polymerization of an α-*D*-glucose-1-phosphate from a maltoheptose in the presence of poly(carbonate)s. Poly(carbonate)s with a shorter methylene chain

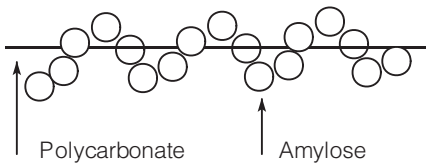


Figure 1.7 Inclusion complexes (112).

length, such as poly(tetramethylene carbonate), is more favorable as the guest polymer to form the inclusion complex with amylose.

It has been shown that amylose selectively includes poly(tetrahydrofuran) or poly(δ-valerolactone) from a mixture of two resemblant poly(ether)s, i.e., poly(oxetane) and poly(tetrahydrofuran), or also a mixture of two resemblant polyesters in vine-twining polymerization (113). The highest priority on the inclusion of amylose showed poly(tetrahydrofuran). Also, a selective inclusion according to the molecular weight of a poly(tetrahydrofuran) was demonstrated (114).

The enzymatic polymerization was investigated at 80°C using a primer-grafted poly(γ-glutamic acid) in the presence or absence of poly(*L*-lactic acid) as a guest polymer for the inclusion by amylose (115). The produced amylose-grafted poly(γ-glutamic acid)s formed microparticles by cooling the mixtures at room temperature after the enzymatic polymerization in either the presence or absence of poly(*L*-lactic acid). The particle sizes, which were evaluated by scanning electron microscopy (SEM), were dependent on the feed ratios of poly(*L*-lactic acid) (115).

It has been found that amylosic inclusion complexes, which were obtained by vine-twining polymerization using a designed guest polymer, i.e., an amphiphilic triblock copolymer poly(2-methyl-2-oxazoline-block-tetrahydrofuran-block-2-methyl-2-oxazoline), exhibited gel and film formation properties (116).

The characterization of the products suggested that enzymatically elongated amylose chains were complexed with the poly(tetrahydrofuran) block in the triblock copolymer (116).

Here, the outer poly(2-methyl-2-oxazoline) blocks constructed hydrophilic spaces among the inclusion complex segments. Furthermore, the presence of such outer blocks affected the low-

er regularity of crystalline alignment among the inclusion complex segments in the products. Probably, such higher-order structures induced the formation of supramolecular soft materials such as gels and films (116).

1.6.6 Bacterial Synthesis

Bacteria can synthesize a wide range of biopolymers. The key aspects of the production of bacterial biopolymers have been reviewed (117, 118). It is expected that a better understanding of polymer biosynthesis and material properties can lead to an increased use of bacterial biopolymers.

PHAs are biopolymers that can be synthesized by microorganisms such as the bacterium *Burkholderia xenovorans* LB400 (119). In particular, LB400 cells are capable of synthesizing poly(3-hydroxybutyrate) (PHB) from glucose.

An attempt has made to produce and characterize electrospun fibers obtained from bacterial PHB (119). Here, the bacterial strain LB400 was grown in M9 minimal medium using xylose and mannitol (10 $g\,l^{-1}$) as the sole carbon sources and NH_4Cl (1 $g\,l^{-1}$) as the sole nitrogen source.

The so-obtained biopolymer-based films were used to produce fibers by electrospinning. The diameter and the morphology of the microfibers were analyzed by SEM and also their thermogravimetric properties were investigated. Bead-free fibers using both PHBs were obtained with diameters of less than 3 μm. The surface morphology of the microfibers based on PHBs obtained from both carbon sources was different, even though their thermogravimetric properties were found to be similar. These results indicate that the carbon source may determine the fiber structure and properties (119).

1.7 Biodegradability Standards

There are several standards available in order to determine the biodegradability of plastic materials. Technical reports have been given that analyze a set of standards, documents and other reports, related to bio-based products (120, 121). The report is limited to matters concerning bio-based products, and hence excludes traditional products, energy applications and food.

In January 2018, the European Union released its strategy for a more sustainable plastics industry to be achieved by the year 2030 (122). Besides promoting plastic recycling, the strategy discusses the opportunities and the risks of biodegradable plastics.

These standards are summarized in Table 1.10. In addition, other certification schemes that are used in various other countries have been collected in the literature (123).

Table 1.10 Biodegradability Standards.

Number	Title
ISO 10210:2012	Plastics – Methods for the preparation of samples for biodegradation testing of plastic materials (124)
ISO 13975:2019	Plastics – Determination of the ultimate anaerobic biodegradation of plastic materials in controlled slurry digestion systems – Method by measurement of biogas production (125)
ISO 14851:2019	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium – Method by measuring the oxygen demand in a closed respirometer (126)
ISO 14852:2018	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium – Method by analysis of evolved carbon dioxide (127)
ISO 14853:2005	Plastics – Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system – Method by measurement of biogas production
ISO 16929:2018-04	Plastics – Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test (128)

1.7.1 Guidelines for the Development of Standards

There are guidelines for the recovery and recycling of plastics waste (145). The standard ISO 15270:2008 provides a guideline for the

Table 1.10 (contd.) Biodegradability Standards.

Number	Title
ISO 15270:2008	Plastics – Guidelines for the recovery and recycling of plastics waste
ISO 14855-1-2012	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions – Method by analysis of evolved carbon dioxide – Part 1: General method (129)
ISO 14855-2-2018	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions – Method by analysis of evolved carbon dioxide – Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test (130)
ISO 17556:2019	Plastics – Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved (131)
ISO 17088:2012	Specifications for compostable plastics (132)
ISO 23517	Plastics – Biodegradable mulch films for use in agriculture and horticulture – Requirements and test methods (133)
ISO 15985:2014	Plastics – Determination of the ultimate anaerobic biodegradation and disintegration under high-solids anaerobic digestion conditions – Method by analysis of released biogas (134)
ISO 18830:2016	Plastics – Determination of aerobic biodegradation of non-floating plastic materials in a seawater/sandy sediment interface – Method by measuring the oxygen demand in closed respirometer (135)
ISO 14852:2018-09	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium - Method by analysis of evolved carbon dioxide (136)

Table 1.10 (contd.) Biodegradability standards.

Number	Title
ASTM D5338-15	Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions (137)
ASTM D5511-18	Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic-Digestion Conditions (138)
ASTM D5526-18	Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under Accelerated Landfill Conditions (139)
ASTM D5929-18	Standard Test Method for Determining Biodegradability of Materials Exposed to Source-Separated Organic Municipal Solid Waste Mesophilic Composting Conditions by Respirometry (140)
ASTM D5988-18	Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in Soil (141)
ASTM D6400-04	Standard Specification for Compostable Plastics (142)
ASTM D6691-17	Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in the Marine Environment by a Defined Microbial Consortium or Natural Sea Water Inoculum (143)
ASTM D7475-11	Standard Test Method for Determining the Aerobic Degradation and Anaerobic Biodegradation of Plastic Materials under Accelerated Bioreactor Landfill Conditions (144)

Table 1.10 (contd.) Biodegradability Standards.

Number	Title
DIN EN 13432	Packaging – Requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation criteria for the final acceptance of packaging
DIN EN 14995	Plastics – Evaluation of compostability – Test scheme and specifications
OECD 306B	Biodegradability in seawater

development of standards and specifications covering plastics waste recovery, including recycling.

This standard establishes the different options for the recovery of plastics waste arising from pre-consumer and post-consumer sources. It also establishes the quality requirements that should be considered in all steps of the recovery process, and provides general recommendations for inclusion in material standards, test standards and product specifications. Consequently, the process stages, requirements, recommendations and terminology presented in the standard are intended to be of general applicability.

Proper methods for the preparation of test samples that can be used for the determination of the ultimate aerobic and anaerobic biodegradability of plastic materials in an aqueous medium, soil, controlled compost or anaerobic digesting sludge have been standardized. These should result in an improved reproducibility of the test results during the assessment of the biodegradability (124).

1.7.2 Specifications for Compostable Plastics

The ASTM D6400-04 specification covers plastics and products made from plastics that are designed to be composted in municipal and industrial aerobic composting facilities (142). Properties that are required to predict whether plastics products will compost satisfactorily, including biodegrading, are specified. In this way, products can be assessed that will compost satisfactorily in commercial and municipal composting facilities.

1.7.3 Ultimate Anaerobic Biodegradability

A method of the assessment of the ultimate anaerobic biodegradability of plastic materials in a controlled anaerobic slurry digestion system with a solids concentration of less than 15% has been described. Such a solid concentration is often present after the treatment of sewage sludge, livestock feces, or garbage. The rate of conversion of the organic carbon into carbon dioxide and methane, i.e., biogas, can be obtained (146).

On the other hand, the evaluation of the ultimate anaerobic biodegradability of plastics under high-solid content of more than 20% of total solids and static non-mixed conditions is available (147). This is based on the measurement of the evolved biogas and the degree of disintegration at the end of the test procedure. In particular, the method is designed to simulate typical anaerobic digestion conditions for the organic fraction of mixed municipal solid waste.

1.7.4 Aerobic Biodegradability

Biodegradation of a plastic within a composting unit is an important phenomenon because it may affect the decomposition of other materials enclosed by the plastic and the resulting quality and appearance of the composted material. Biodegradation of plastics will also allow the safe disposal of these plastics through large, professionally managed composting plants and well-run residential units, where thermophilic temperatures are achieved. A procedure, ASTM D5338-15, has been developed to permit the determination of the rate and degree of aerobic biodegradability of plastic products when placed in a controlled composting process (137).

1.7.4.1 Oxygen Control

The ultimate aerobic biodegradability of plastic materials in an aqueous medium can be controlled by measuring the oxygen demand in a closed respirometer (148).

ISO 18830:2016 specifies a test method to determine the degree and rate of aerobic biodegradation of plastic materials when settled on marine sandy sediment at the interface between seawater and the seafloor, by measuring the oxygen demand in a closed respirometer (135).

This test method is a simulation under laboratory conditions of the habitat found in different seawater/sediment-areas in the sea, e.g., in a benthic zone, where sunlight reaches the ocean floor (photic zone) that, in marine science, is called the sublittoral zone.

The determination of biodegradation of plastic materials buried in marine sediment is outside the scope of this International Standard. The conditions described in this International Standard may not always correspond to the optimum conditions for the maximum degree of biodegradation to occur.

The measurement of the aerobic biodegradation can also be obtained by monitoring the carbon dioxide evolution. This is not in the scope of this International Standard but of ISO 19679 (149). This test method is a simulation under laboratory conditions of the habitat found in different seawater/sediment-areas in the sea, e.g., in a benthic zone where sunlight reaches the ocean floor (photic zone) that, in marine science, is called the sublittoral zone.

Furthermore, the ultimate aerobic biodegradability of plastic materials in soil can be performed by measuring the oxygen demand in a closed respirometer or by the amount of carbon dioxide evolved. The method is designed to yield an optimum degree of biodegradation by adjusting the humidity of the test soil (150, 151). If a non-adapted soil is used as an inoculum, the test simulates the biodegradation processes which take place in a natural environment. If a pre-exposed soil is used, the method can be used to investigate the potential biodegradability of a test material.

The standard ASTM D6954-18 is used for the exposure of plastics that can degrade by a combination of oxidation and biodegradation (152). This standard should permit the comparison and ranking of the overall rate of the environmental degradation of plastics in the course of thermal or photo oxidation. Each degradation stage is independently evaluated to allow a combined evaluation of a polymer's environmental performance.

1.7.4.2 Carbon Dioxide Control

The ISO standards 14852 and 14855 (153, 154) have been recently revised in the form of ISO 14855-1:2012 (129). This standard describes a method for the determination of the ultimate aerobic biodegradability of organic plastics materials under controlled composting

conditions by the measurement of carbon dioxide evolved and the degree of disintegration of the plastic at the end of the test.

This method is designed to simulate the typical aerobic composting conditions for the organic fraction of solid mixed municipal waste. The test material is exposed to an inoculum which is derived from compost. The composting takes place in an environment wherein temperature, aeration and humidity are closely monitored and controlled. The test method is designed to yield the percentage conversion of the carbon in the test material to evolved carbon dioxide as well as the rate of conversion.

A variant of this method uses a mineral bed, i.e., vermiculite inoculated with thermophilic microorganisms obtained from compost with a specific activation phase, instead of a mature compost. This variant is designed to yield the percentage of carbon in the test substance converted to carbon dioxide and the rate of conversion.

Part 2 of this standard specifies a method for determining the ultimate aerobic biodegradability of plastic materials under controlled composting conditions by gravimetric measurement of the amount of carbon dioxide evolved. The method is designed to yield an optimum rate of biodegradation by adjusting the humidity, aeration and temperature of the composting vessel. This method applies to the following materials (155):

1. Natural or synthetic polymers and copolymers, and mixtures of these,
2. Plastic materials that contain additives such as plasticizers or colorants,
3. Water-soluble polymers, and
4. Materials that, under the test conditions, do not inhibit the activity of microorganisms present in the inoculum.

1.7.4.3 Measurement of Biogas

The ISO 14853:2005 Standard specifies a method for the determination of the ultimate anaerobic biodegradability of plastics by anaerobic microorganisms (156). The conditions described in the standard do not necessarily correspond to the optimum conditions for the maximum degree of biodegradation to occur. Instead, the test calls for exposure of the test material to sludge for a period of up to

60 *d*, which is longer than the normal sludge retention time (25–30 *d*) in anaerobic digesters, though digesters at industrial sites can have much longer retention times. The method applies to the same materials as in Standard ISO 14855-2-2018 (130).

1.7.5 Biodegradability of Plastics in Seawater

Many industrial wastewaters with a variety of chemicals are reaching the sea either by direct discharge or via estuaries and rivers in which the residence times are low compared with the period necessary for complete biodegradation. Because of the growing awareness of the need to protect the marine environment against increasing loads of chemicals and the need to estimate the probable concentration of chemicals in the sea, test methods for biodegradability in seawater have been developed.

In addition, the use of plastics aboard ships is on the rise and the use of the sea as a trash dumping site is no longer a possibility (143). Also, for this reason, the disposal of plastic materials while at sea has emerged as a major issue. Biodegradable plastics could help with regard to the safe disposal of plastic materials at sea.

The OECD 306B test deals with the biodegradability of plastics in seawater (157). This test is also known as the Zahn-Wellens/EVPA Test and is included in a series of standards. Here, the shake flask method is used.

The test substance is used in the test medium at a concentration of 5–40 $mg\,l^{-1}$ of total organic carbon dissolved. No inoculum is added in addition to the microorganisms already present in the seawater. Stock solutions for mineral nutrients are shown in Table 1.11.

A test medium is prepared by adding 1 *ml* of each of the stock solutions in Table 1.11 to 1 *l* of pretreated seawater. The solution of the test substance in the test medium is incubated under agitation in the dark or in diffuse light under aerobic conditions at 15–20°C. Five flasks should be used:

- Two for the test suspension,
- Two for the blank seawater, and
- One for procedure control.

Optionally, one additional flask is used containing a reference compound for procedure control and another containing the test

Table 1.11 Aqueous stock solutions for mineral nutrients.

Mineral	Amount/[$g\,l^{-1}$]
Solution A	
Potassium dihydrogen orthophosphate, KH_2PO_4	8.50
Dipotassium hydrogen orthophosphate, K_2HPO_4	21.75
Disodium hydrogen orthophosphate dihydrate, $Na_2HPO_4 \times 2H_2O$	33.30
Ammonium chloride, NH_4Cl	0.50
Solution B	
Calcium chloride, $CaCl_2$	27.50
Solution C	
Magnesium sulfate heptahydrate, $MgSO_4 \times 7H_2O$	22.50
Solution D	
Iron(III) chloride hexahydrate, $FeCl_3 \times 6H_2O$	0.25

substance and a sterilizing agent, e.g., mercury chloride, for abiotic sterile control. As reference compounds, sodium benzoate, sodium acetate or aniline may be used.

The recommended maximum test duration is around 60 *d*. The degradation is monitored by measurements of the total organic carbon content. A typical reaction curve is shown in Figure 1.8.

In addition, the closed bottle method has been described. This method uses similar conditions as the previously described method, but the experiments are performed in the dark. In addition, the degradation is followed by the change of oxygen by a chemical or electrochemical method. Here, many more test samples are used.

Another test method has been developed to assess the rate and degree of aerobic biodegradation of plastics exposed to marine microorganisms (143). Aerobic biodegradation is determined by measuring the amount of biogas produced during such an exposure. It has been stated that there is no similar or equivalent ISO standard.

Non-floating products made from biodegradable plastics, including packaging and coatings, can be tested under the conditions of the marine environment (158). In particular, environments are shallow and deep saltwater and brackish water. The products should exhibit satisfactory performances in terms of disintegration during

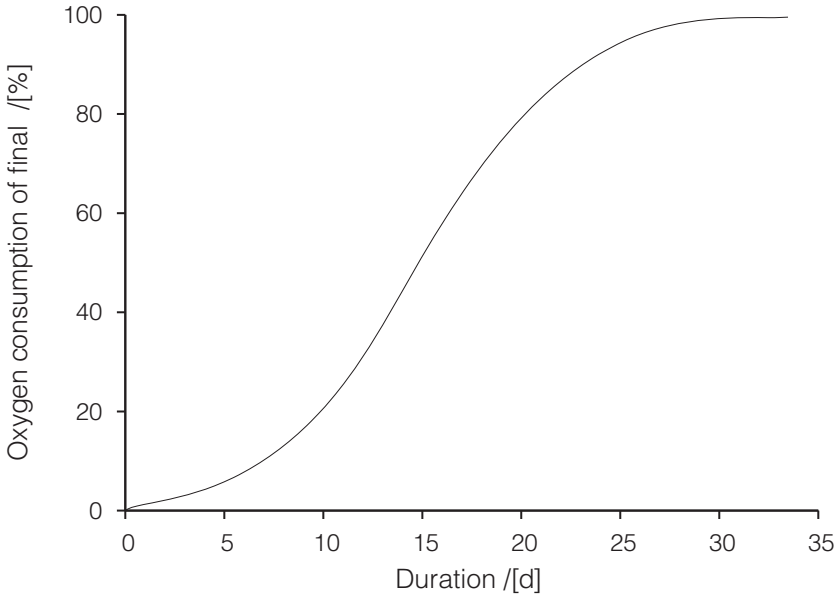


Figure 1.8 Typical reaction curve.

marine degradation, inherent biodegradation, and environmental toxicity.

1.8 Test of the Biological Origin

Biologically derived compounds may be distinguished from similar compounds produced from a petrochemical source or from fossil fuel carbon by dual carbon-isotopic fingerprinting. This method can distinguish chemically identical materials (159). In addition, such methods have gained some importance in discriminating between natural and industrial pollution (160).

The isotopes ^{14}C and ^{13}C give complementary information to this problem. The radiocarbon dating isotope ^{14}C with its nuclear half life of 5730 *y*, clearly allows differentiating between fossil and biospheric feedstocks (161).

The basic assumption in radiocarbon dating is that the constancy of the ^{14}C concentration in the atmosphere leads to the constancy of the concentration of ^{14}C in living organisms. When dealing with an

isolated sample, the age of a sample can be approximately deduced by the relationship (159)

$$t = -\frac{5730}{0.693}\ln(\frac{A}{A_0}) \quad . \tag{1.1}$$

Here, t is the age, 5730 years is the half lifetime of radiocarbon, and $\frac{A}{A_0}$ is the specific ^{14}C activity of the sample and of a modern standard (162).

However, because of atmospheric nuclear testing since 1950 and the burning of fossil fuel since 1850, ^{14}C has acquired a second, geochemical time characteristic. Its concentration in atmospheric CO_2, and thus in the living biosphere, approximately doubled at the peak of nuclear testing in the mid-1960s. Afterwards, it has gradually returned to the steady-state baseline isotope rate ^{14}C of ca. 1.2×10^{-12} (159).

The stable carbon isotope ratio $^{13}C/^{12}C$ is another route of checking the origin. This ratio in a biosourced material results from the $^{13}C/^{12}C$ ratio in atmospheric carbon dioxide at the time the carbon dioxide is fixed and also reflects the precise metabolic pathway. Regional variations may occur.

Terrestrial plants and marine carbonates show differences in the isotope ratio. Sometimes large variations due to isotopic fractionation effects are observed.

The major cause of differences in the carbon isotope ratio in plants is closely associated with differences in the pathway of photosynthetic carbon metabolism in the plants, particularly the reaction occurring during the primary carboxylation.

The most significant reaction type is the photosynthetic mechanism. There are two classes of the photosynthetic cycle, the Calvin-Benson photosynthetic cycle and the Hatch-Slack photosynthetic cycle.

The Calvin-Benson photosynthetic cycle is dominant in hardwoods and conifers. The primary CO_2 fixation or carboxylation reaction involves the enzyme ribulose-1,5-diphosphate carboxylase and the first stable product is a 3-carbon compound (163).

On the other hand, the Hatch-Slack photosynthetic cycle is important for tropical grasses, corn and sugarcane. Phosphenol-pyruvate carboxylase is responsible for the primary carboxylation reaction.

The first stable carbon compound is a C_4 acid, which is subsequently decarboxylated (164, 165). The fundamentals and systematics of the non-statistical distributions of isotopes in natural compounds have been reviewed (166).

The ^{13}C measurement scale was originally defined by a zero set by belemnite limestone. The values are given in parts per thousand deviations from this material. These values are calculated as follows:

$$\delta^{13}C = \frac{\left(^{13}C/^{12}C\right)_{sample} - \left(^{13}C/^{12}C\right)_{standard}}{\left(^{13}C/^{12}C\right)_{standard}} \times 1000 \qquad (1.2)$$

For example, biologically derived 1,3-propanediol, and compositions comprising biologically derived 1,3-propanediol, may be completely distinguished from their petrochemically derived counterparts on the basis of ^{13}C and dual carbon-isotopic fingerprinting (159).

Also, the average carbon isotope contents of a series of glycerol samples have been determined. The results indicated that it is possible to distinguish the glycerol obtained from the glycerides produced in plants following the C_3 and C_4 carbon fixation pathways (167). Natural ethyl butyrate can be differentiated from industrially manufactured ethyl butyrate by the content of ^{14}C (168).

Trade names appearing in the references are shown in Table 1.12.

Table 1.12 Trade names in references.

Trade name Description	Supplier
Acrawax® Amide wax (159)	Lonza Group AG, Basel, Switzerland
Acronal® 4F Poly(*n*-butylacrylate) (159)	BASF AG
Acronal® Acrylic resins (159)	BASF
Adcote® 313 Polyethyleneimine (159)	Morton International
Adcote® 50T4983 Ethylene acrylic acid dispersion (159)	Morton International
Adcote® 50T4990 Ethylene acrylic acid dispersion (159)	Morton International
Airflex® (Series) Vinyl acetate/ethylene copolymer emulsions (159)	Air Products and Chemicals, Inc.
Aquathane® 97949 Nonsulfonated urethane dispersion (159)	Reichhold
Aquathane® 97959 Nonsulfonated urethane dispersion (159)	Reichhold
Biolice® Biodegradable polymer (75)	Limagrain
Biomax® Sulfonated aliphatic-aromatic copolyesters (159)	DuPont
Bionolle® Poly(butylene succinate) (159)	Showa Highpolymer Co.
Biopol® Biodegradable hot melt adhesive (PHV/B) (159)	Zeneca
Bynel® (Series) Anhydride modified ethylene vinyl acetate resin, adhesion promoter (159)	DuPont
Carboset® CR-760 Anionic acrylate-styrene dispersion (159)	B.F. Goodrich Co.
Citroflex® A-4 Acetyltri-*n*-butyl citrate (159)	Morflex, Inc.
Cozeen™ 303N Natural coating (75)	Freeman Industries LLC

Table 1.12 (cont) Trade names in references.

Trade name Description	Supplier
Cymel® (Series) Amino resins (159)	Cytec
Devcon® Acrylic adhesive (91)	ITW Performance Polymers
Dispercoll® (Series) Sulfonated polyester urethane dispersions (159)	Bayer Corp.
Eastar® Bio Compostable copolyester (159)	Eastman Chemical Company
EcoFoam® Biodegradable materials for use in packaging (159)	National Starch and Chemical Co.
EcoPLA® Poly(lactide) (159)	Cargill Dow LLC
EnPol® Poly(1,4-butylene succinate) (159)	IRe Chemical Ltd.
EnviroFil® Modified starch (159)	ENPAC LLC.
Escorez® (Series) Tackifying resins (EVA) (159)	ExxonMobil Chemical Co.
Flexthane® (Series) Nonsulfonated urethane dispersions (159)	Air Products and Chemicals, Inc.
Hycar® (Series) Amine-terminated butadiene-acrylonitrile (159)	Lubrizol Advanced Materials Inc.; B.F. Goodrich Co.
Jagotex® KEA Acrylic dispersions (159)	Jager Co.
Kynar® Poly(vinylidene fluoride) (159)	Arkema Inc.
Luphen® D 200 A Nonsulfonated urethane dispersions (159)	BASF
MicroMid® (Series) Poly(amide) dispersions (159)	Union Camp Corp.
Myvacet® (Series) Acetylated monoglycerides of modified fats (159)	Kerry Group Services Ltd.
Myvaplex® 600 2,3-Dihydroxypropyl octadecanoate (glycerol monostearate) (159)	Kerry Group Services Ltd.
Myverol® Propylene glycol monostearate (159)	Kerry Group Services Ltd.

Table 1.12 (cont) Trade names in references.

Trade name Description	Supplier
NatureFlex™ NE 30 Heat-sealable compostable film (75)	Innovia Films Ltd.
NeoRez® (Series) Nonsulfonated urethane dispersions (159)	Zeneca Resins
Papermatch® Masterbatch to impart paper-like properties to polymer films (159)	A Shulman, Inc.
Piccotex® LC-55WK Styrene resin emulsion (159)	Hercules Inc.
Polectron® 430 Vinylpyrrolidone/styrene copolymer emulsion fluid (159)	ISP Corp.
Quilastic® (Series) Nonsulfonated urethane dispersions (159)	Merquinsa
Resyn® (Series) Vinyl acetate homopolymer dispersions (159)	ICI
Rhoplex® (Series) Acrylic latex (159)	Evonik, Rohm & Haas
Rucoflex® Polyester polyol (159)	Bayer
Sancure® Nonsulfonated urethane dispersions (159)	Lubrizol Advanced Materials Inc.
Synthemul® (Series) Carboxylated acrylic copolymer (159)	Reichhold
Tacolyn® 5001 Styrene resin dispersion (159)	Hercules Inc.
Tecoflex® (Series) Urethane elastomers (159)	Lubrizol Advanced Materials Inc.
Texigel® (Series) Silanated anionic acrylate-styrene polymer dispersions (159)	Scott Bader Inc.
Tronox® 470 Titanium dioxide pigment (159)	Tranox Ltd.
Tween® 20 Sorbitan monolaurate (159)	Uniqema
Tween® 40 Sorbitan monopalmitate (159)	Uniqema
Tween® 60 Sorbitan monostearate (159)	Uniqema

Table 1.12 (cont) Trade names in references.

Trade name Description	Supplier
Tween® 85 Sorbitan monooleate (159)	Uniqema
Vancryl® (Series) Anionic acrylate-styrene dispersions (159)	Air Products & Chemicals Inc.
Vycar® Poly(vinylidene chloride) emulsion (159)	Lubrizol
Weld-It® All purpose adhesive (91)	Devcon Inc.

References

1. V. Thakur, *Green Biorenewable Biocomposites: From Knowledge to Industrial Applications*, Apple Academic Press, Toronto, 2015.
2. P.M. Visakh and S. Lüftl, eds., *Polyethylene-Based Biocomposites and Bionanocomposites*, John Wiley & Sons, Hoboken, New Jersey; Scrivener Publishing, Beverly, Massachusetts, 2016.
3. P.M. Visakh and M. Poletto, *Polypropylene-Based Biocomposites and Bionanocomposites*, John Wiley & Sons, Hoboken, New Jersey; Scrivener Publishing, Beverly, Massachusetts, 2018.
4. G.S. Mann, L.P. Singh, P. Kumar, and S. Singh, *Journal of Thermoplastic Composite Materials*, Vol. in press, p. 0892705718816354, 2018.
5. D.C. Schiltz, Biodegradable starch-based polymer compositions, US Patent 5 449 708, September 12, 1995.
6. H. Chum, *Polymers from Biobased Materials*, Noyes Data Corp., Park Ridge, NJ, 1991.
7. U. Albertsson, ed., *Degradable Aliphatic Polyesters*, Vol. 157 of *Advances in Polymer Science*, Springer, Berlin, Heidelberg, 2001.
8. M.S. Lindblad, Y. Liu, A.-C. Albertsson, E. Ranucci, and S. Karlsson, Polymers from renewable resources in *Degradable Aliphatic Polyesters*, Vol. 157 of *Advances in Polymer Science*, pp. 139–161. Springer, Berlin, Heidelberg, 2001.
9. C. Williams and M. Hillmyer, *Polymer Reviews*, Vol. 48, p. 1, January 2008.
10. S. Pilla, ed., *Handbook of Bioplastics and Biocomposites Engineering Applications*, Wiley Scrivener, Hoboken, NJ, Salem, Mass, 2011.
11. V. Mittal, ed., *Renewable Polymers Synthesis, Processing, and Technology*, Scrivener Publishing LLC, Beverly, MA, 2012.
12. A. Morelli, D. Puppi, and F. Chiellini, *Journal of Renewable Materials*, Vol. 1, p. 83, April 2013.
13. S. Ebnesajjad, ed., *Handbook of Biopolymers and Biodegradable Plastics: Properties, Processing and Applications*, William Andrew, Oxford, 2013.
14. F. Flores, J.A. Dobado, J. Isac-García, and F.J. Martín-Martínez, *Lignin and Lignans as Renewable Raw Materials: Chemistry, Technology and Applications*, Vol. 1 of *Wiley Series in Renewable Resource*, Wiley, Hoboken, 2015.
15. A. Pandey, R. Höfer, M. Taherzadeh, M. Nampoothiri, and C. Larroche, eds., *Industrial Biorefineries and White Biotechnology*, Elsevier Ltd., Amsterdam, Netherlands, 2015.
16. S. Madbouly, C. Zhang, and M.R. Kessler, eds., *Bio-based Plant Oil Polymers and Composites*, William Andrew, an imprint of Elsevier, Kidlington, Oxford, UK, 2015.
17. M. Khalaf, ed., *Green Polymers and Environmental Pollution Control*, Apple Academic Press, Toronto, 2016.

18. K.M. Zia, A. Noreen, M. Zuber, S. Tabasum, and M. Mujahid, *International Journal of Biological Macromolecules*, Vol. 82, p. 1028, 2016.
19. F. Cavani, S. Albonetti, F. Basile, and A. Gandini, eds., *Chemicals and Fuels from Bio-based Building Blocks*, Wiley-VCH Verlag GmbH & Co, Weinheim, 2016.
20. S.E. Hosseini and M.A. Wahid, *Renewable and Sustainable Energy Reviews*, Vol. 57, p. 850, 2016.
21. Z. Fang and J. Smith, Richard L., eds., *Production of Biofuels and Chemicals from Lignin*, Biofuels and Biorefineries, Springer, Berlin, 2016.
22. S.A. Ashter, *Introduction to Bioplastics Engineering*, William Andrew, an imprint of Elsevier, Oxford, UK, 2016.
23. R. Łukasik, ed., *High Pressure Technologies in Biomass Conversion*, Royal Society of Chemistry, United Kingdom, 2017.
24. V.K. Thakur, M.K. Thakur, and M.R. Kessler, eds., *Structure and Chemistry*, Vol. 1 of *Handbook of Composites from Renewable Materials. Advanced Applications*, John Wiley & Sons,, Hoboken, NJ; Scrivener Publishing LLC, Beverly, MA, 2017, 2017.
25. V.K. Thakur, M.K. Thakur, and M.R. Kessler, eds., *Nanocomposites: Advanced Applciations*, Vol. 8 of *Handbook of Composites from Renewable Materials. Advanced Applications*, John Wiley & Sons, Inc., Hoboken, NJ; Scrivener Publishing LLC, Beverly, MA, 2017.
26. N. Shimpi, ed., *Biodegradable and Biocompatible Polymer Composites*, Elsevier Science, 2017.
27. S. Kurtz, ed., *PEEK Biomaterials Handbook*, William Andrew, Oxford, 2nd edition, 2019.
28. R. Tharanathan, *Trends in Food Science & Technology*, Vol. 14, p. 71, March 2003.
29. V. Siracusa, P. Rocculi, S. Romani, and M.D. Rosa, *Trends in Food Science & Technology*, Vol. 19, p. 634, December 2008.
30. B.M. Cherian, G.M. de Olyveira, L.M.M. Costa, A.L. Leão, M.R. de Morais Chaves, S.F. de Souza, and S. Narine, Bionanocomposites for natural food packing in P.M. Visakh, S. Thomas, L.B. Iturriaga, and P.D. Ribotta, eds., *Advances in Food Science and Technology*, chapter 9, pp. 265–299. Wiley-Scrivener, 2013.
31. R. Busquets, ed., *Emerging Nanotechnologies in Food Science*, Elsevier, Amsterdam, Netherlands, 2017.
32. D.R. Heldman, D.B. Lund, and C. Sabliov, eds., *Handbook of Food Engineering*, CRC press, Boca Raton, FL Cambridge, England, 3rd edition, 2019.
33. M.J.-L. Tschan, E. Brulé, P. Haquette, and C.M. Thomas, *Polymer Chemistry*, Vol. 3, p. 836, 2012.
34. K. Yao and C. Tang, *Macromolecules*, Vol. 46, p. 1689, March 2013.

35. S. Inoue, H. Koinuma, and T. Tsuruta, *Journal of Polymer Science Part B: Polymer Letters*, Vol. 7, p. 287, April 1969.
36. J.B. van Beilen and Y. Poirier, *The Plant Journal*, Vol. 54, p. 684, May 2008.
37. A. Gandini, *Macromolecules*, Vol. 41, p. 9491, December 2008.
38. P. Anastas, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998.
39. J.H. Clark and D.J. Macquarrie, *Handbook of Green Chemistry and Technology*, Blackwell Science, Oxford, England and Malden, MA, 2002.
40. M. Lancaster, *Green Chemistry: An Introductory Text*, Royal Society of Chemistry, Cambridge, 2010.
41. R. Luque, *Green Chemistry*, Nova Science Publishers, Hauppauge, NY, 2012.
42. J. Pohlman, *Green Chemistry*, Tap the power, knowledge is power, Wisconsin Legislative Reference Bureau, Madison, Wis., 2012.
43. J. Clark and F. Deswarte, eds., *Introduction to Chemicals from Biomass*, Wiley, Chichester, West Sussex, 2015.
44. S. Sharma, ed., *Green Chemistry for Dyes Removal from Wastewater: Research Trends and Applications*, Scrivener Publishing/Wiley, Hoboken, New Jersey, Salem, Massachusetts, 2015.
45. M. Lancaster, *Green Chemistry : An Introductory Text*, Royal Society of Chemistry, Cambridge, UK, 3rd edition, 2016.
46. G. Rothenberg, *Catalysis: Concepts and Green Applications*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2nd edition, 2017.
47. S. Muniyasamy, K. Mohanrasu, A. Gada, T.C. Mokhena, A. Mtibe, and T. Boobalan, *Integrating Green Chemistry and Sustainable Engineering*, John Wiley & Sons, Ltd., 2019.
48. J. Tao and R.J. Kazlauskas, *Biocatalysis for Green Chemistry and Chemical Process Development*, John Wiley & Sons, Hoboken, NJ, 2011.
49. R. Mathers and M.A.R. Meier, eds., *Green Polymerization Methods Renewable Starting Materials, Catalysis and Waste Reduction*, Wiley-VCH, Weinheim, Chichester, 2011.
50. P. Gallezot, *Catalysis Today*, Vol. 121, p. 76, March 2007.
51. M. Lancaster, Principles and concepts of green chemistry in *Green Chemistry: An Introductory Text*, chapter 1, pp. 1–20. Royal Society of Chemistry, Cambridge, 2010.
52. M. Poliakoff, J.M. Fitzpatrick, T.R. Farren, and P.T. Anastas, *Science*, Vol. 297, p. 807, August 2002.
53. P.T. Anastas and J.B. Zimmerman, *Environmental Science & Technology*, Vol. 37, p. 94A, March 2003.
54. W. McDonough, M. Braungart, P.T. Anastas, and J.B. Zimmerman, *Environmental Science & Technology*, Vol. 37, p. 434A, December 2003.

55. P.T. Anastas and N. Eghbali, *Chemical Society Reviews*, Vol. 39, p. 301, 2009.
56. F.J. Lozano, R. Lozano, P. Freire, C. Jiménez-Gonzalez, T. Sakao, M.G. Ortiz, A. Trianni, A. Carpenter, and T. Viveros, *Journal of Cleaner Production*, Vol. 172, p. 227, 2018.
57. R. Sheldon, *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, 2007.
58. C.K.S. Pillai, *Designed Monomers and Polymers*, Vol. 13, p. 87, 2010.
59. J.A. Rosewitz, H.A. Choshali, and N. Rahbar, *Cement and Concrete Composites*, Vol. 96, p. 252, 2019.
60. D. Ji and J. Kim, *ACS Nano*, Vol. 13, p. 2773, 2019.
61. D. Zhao, J.F. Kim, G. Ignacz, P. Pogany, Y.M. Lee, and G. Szekely, *ACS Nano*, Vol. 13, p. 125, 2019.
62. W. Xu, J. Liu, T. Chen, X. Jiang, X. Qian, Y. Zhang, Z. Jiang, and Y. Zhang, *Small*, Vol. in press, p. 1901582, 2019.
63. F. Börnke and I. Broer, *Current Opinion in Plant Biology*, Vol. 13, p. 353, June 2010.
64. J.B. van Beilen, *Biofuels, Bioproducts and Biorefining*, Vol. 2, p. 215, May 2008.
65. J. Du, L. Li, and S. Zhou, *Biotechnology Advances*, 2019.
66. A.V.E. Conradie and A.L. Botes, Methods, reagents and cells for biosynthesizing compounds, US Patent 9 896 702, assigned to Invista North America S.A.R.L. (Wilmington, DE), February 20, 2018.
67. Anonymous, Commercial outlook for biodegradable polymers, PERP Program PERP-94/95-S13, Nexant, Process Evaluation/Research Planning (PERP), White Plains, NY, USA, 1997.
68. L.S. Nair and C.T. Laurencin, *Progress in Polymer Science*, Vol. 32, p. 762, August 2007.
69. S. Joseph, M.J. John, L.A. Pothen, and S. Thomas, Raw and renewable polymers in P. Eyerer, M. Weller, and C. Hübner, eds., *Polymers - Opportunities and Risks*, Vol. 2 of *The Handbook of Environmental Chemistry*, pp. 55–80. Springer, Berlin Heidelberg, 2009.
70. T.L. Sporleder, P.D. Goldsmith, J. Cordier, and P. Godin, *International Food and Agribusiness Management Review*, Vol. 14, p. 35, 2011.
71. A. Iles and A.N. Martin, *Journal of Cleaner Production*, Vol. 45, p. 38, April 2013.
72. T.P. Haider, C. Völker, J. Kramm, K. Landfester, and F.R. Wurm, *Angewandte Chemie International Edition*, Vol. 58, p. 50, 2019.
73. G. Scott, *Polymers and the Environment*, Royal Society of Chemistry, Cambridge, 1999.
74. G. Scott, *Polymer Degradation and Stability*, Vol. 68, p. 1, April 2000.

75. C. Tolibas-Spurlock, B. Allred-Forsman, and D. Agnew-Von Moos, Compostable container for storing fluids, US Patent 8 245 848, assigned to Sacred Green, Inc. (Chehalis, WA), August 21, 2012.
76. J. Wróblewska-Krepsztul, T. Rydzkowski, G. Borowski, M. Szczypiński, T. Klepka, and V.K. Thakur, *International Journal of Polymer Analysis and Characterization*, Vol. 23, p. 383, 2018.
77. J.A. Bowden and C.C. Johnston, Biodegradable or compostable containers, US Patent 7 967 904, assigned to New Ice Limited (Isle of Man), June 28, 2011.
78. A.K. Mohanty, M. Misra, and L.T. Drzal, *Journal of Polymers and the Environment*, Vol. 10, p. 19, 2002.
79. E. Rudnik, *Compostable Polymer Materials*, Elsevier, Amsterdam London, 2008.
80. L.S. Dilkes-Hoffman, J.L. Lane, T. Grant, S. Pratt, P.A. Lant, and B. Laycock, *Journal of Cleaner Production*, Vol. 180, p. 325, 2018.
81. J.J. Blaker, K.-Y. Lee, and A. Bismarck, *Journal of Biobased Materials and Bioenergy*, Vol. 5, p. 1, March 2011.
82. Y. Long, *Biodegradable Polymer Blends and Composites from Renewable Resources*, Wiley, Hoboken, NJ, 2009.
83. A.K. Mohanty, M. Misra, and G. Hinrichsen, *Macromolecular Materials and Engineering*, Vol. 276-277, p. 1, 2000.
84. K. Khemani, P.J. Andersen, S.K. Hodson, and H. Schmidt, Biodegradable polymer films and sheets suitable for use as laminate coatings as well as wraps and other packaging materials, US Patent 6 573 340, assigned to Biotec Biologische Naturverpackungen GmbH & Co. KG (DE), June 3, 2003.
85. I. Takahashi and H. Iida, Biodegradable plastics composition, molded article of the composition, and method of controlling biodegradation rate, US Patent 7 816 424, assigned to Nisshinbo Industries, Inc. (Tokyo, JP), October 19, 2010.
86. Y. Imashiro and I. Takahashi, Process for producing polycarbodiimide resin, US Patent 5 373 080, assigned to Nisshinbo Industries, Inc. (Tokyo, JP), December 13, 1994.
87. A. Gandini and T.M. Lacerda, *Progress in Polymer Science*, Vol. 48, p. 1, 2015. Topical Volume on Polymer Chemistry.
88. N. Spassky, M. Wisniewski, C. Pluta, and A. Le Borgne, *Macromolecular Chemistry and Physics*, Vol. 197, p. 2627, September 1996.
89. H.C. Kolb, M.G. Finn, and K.B. Sharpless, *Angewandte Chemie International Edition*, Vol. 40, p. 2004, 2001.
90. J.E. Moses and A.D. Moorhouse, *Chemical Society Reviews*, Vol. 36, p. 1249, 2007.

91. V. Fokin, M.G. Finn, and K.B. Sharpless, Polymeric materials via click chemistry, US Patent 8 101 238, assigned to The Scripps Research Institute (La Jolla, CA), January 24, 2012.
92. G.L. Baker, M.R. Smith, III, X. Jiang, and E.B. Vogel, Functionalization of polyglycolides by "click" chemistry, US Patent Application 20 090 054 619, assigned to Board of Trustees of Michigan State University, East Lansing (MI), February 26, 2009.
93. O. Türünç, *Efficient Routes to Degradable and non-Degradable Renewable Polymers from Fatty Acids*. PhD thesis, Fakultät für Chemie und Biowissenschaften Karlsruher Institut für Technologie, University of Karlsruhe, Germany, 2012.
94. G.-L. Zhao, J. Hafrén, L. Deiana, and A. Córdova, *Macromolecular Rapid Communications*, Vol. 31, p. 740, April 2010.
95. S. Kobayashi and A. Makino, *Chemical Reviews*, Vol. 109, p. 5288, November 2009.
96. S. Kobayashi and H. Uyama, Enzymatic polymerization in *Encyclopedia of Polymer Science and Technology*. Wiley Blackwell (John Wiley & Sons), 2011.
97. A. Douka, S. Vouyiouka, L.-M. Papaspyridi, and C.D. Papaspyrides, *Progress in Polymer Science*, Vol. 79, p. 1, 2018.
98. J. Su, J. Noro, J. Fu, Q. Wang, C. Silva, and A. Cavaco-Paulo, *Journal of Cleaner Production*, Vol. 202, p. 792, 2018.
99. D. Maniar, K.F. Hohmann, Y. Jiang, A.J.J. Woortman, J. van Dijken, and K. Loos, *ACS Omega*, Vol. 3, p. 7077, 2018.
100. H. Zhao, L.O. Afriyie, N.E. Larm, and G.A. Baker, *RSC Advances*, Vol. 8, p. 36025, 2018.
101. S. Kobayashi, *Macromolecular Rapid Communications*, Vol. 30, p. 237, February 2009.
102. S. Okumura, M. Iwai, and Y. Tominaga, *Agricultural and biological chemistry*, Vol. 48, p. 2805, 1984.
103. A. Mahapatro, B. Kalra, A. Kumar, and R.A. Gross, *Biomacromolecules*, Vol. 4, p. 544, May 2003.
104. H. Uyama and S. Kobayashi, *Chemistry Letters, Japan*, Vol. 23, p. 1687, 1994.
105. U. Meyer, A.R.A. Palmans, T. Loontjens, and A. Heise, *Macromolecules*, Vol. 35, p. 2873, April 2002.
106. J.W. Peeters, A.R.A. Palmans, E.W. Meijer, C.E. Koning, and A. Heise, *Macromolecular Rapid Communications*, Vol. 26, p. 684, May 2005.
107. A. Harada, M. Osaki, Y. Takashima, and H. Yamaguchi, *Accounts of Chemical Research*, Vol. 41, p. 1143, September 2008.
108. R.J. Ellis, *Trends in Biochemical Sciences*, Vol. 31, p. 395, July 2006.
109. H. Zhang, J. Shen, Z. Liu, A. Hao, Y. Bai, and W. An, *Supramolecular Chemistry*, Vol. 22, p. 297, May 2010.
110. Y. Kaneko and J.-I. Kadokawa, *The Chemical Record*, Vol. 5, p. 36, 2005.

111. Y. Kaneko, K. Beppu, and J.-I. Kadokawa, *Biomacromolecules*, Vol. 8, p. 2983, October 2007.
112. Y. Kaneko, K. Beppu, and J.-I. Kadokawa, *Macromolecular Chemistry and Physics*, Vol. 209, p. 1037, May 2008.
113. Y. Kaneko, K. Beppu, T. Kyutoku, and J.-I. Kadokawa, *Polymer Journal*, Vol. 41, p. 279, 2009.
114. Y. Kaneko, K. Beppu, and J.-I. Kadokawa, *Polymer Journal*, Vol. 41, p. 792, 2009.
115. J.-I. Kadokawa, S. Orio, and K. Yamamoto, *RSC Advances*, Vol. 9, p. 16176, 2019.
116. J.-I. Kadokawa, K. Yano, S. Orio, and K. Yamamoto, *ACS Omega*, Vol. 4, p. 6331, 2019.
117. M.P. Coughlan and L.G. Ljungdahl, Comparative biochemistry of fungal and bacterial cellulolytic enzyme systems, in J. Millet, ed., *Biochemistry and Genetics of Cellulose Degradation*, number 43 in FEMS Symposia, pp. 11–30, Delft, the Netherlands, 1988. Federation of European Microbiological Societies, Academic Press, Inc.
118. G.-Q. Chen, *Plastics from Bacteria: Natural Functions and Applications*, Springer, Heidelberg; New York, 2010.
119. F. Acevedo, P. Villegas, V. Urtuvia, J. Hermosilla, R. Navia, and M. Seeger, *International Journal of Biological Macromolecules*, Vol. 106, p. 692 , 2018.
120. CEN, Biobased products - overview of standards, Review of Standards CEN/TR 16208, European Committee for Standardization (CEN), Brussels, Belgium, 2011.
121. P. Kamath, Biobased products, Review of Standards EN 16575, European Committee for Standardization (CEN), Brussels, Belgium, 2014.
122. European Commission, A European Strategy for Plastics in a Circular Economy, Technical report, European Union, 2018.
123. A. Krzan, S. Hemjinda, S. Miertus, A. Corti, and E. Chiellini, *Polymer Degradation and Stability*, Vol. 91, p. 2819, December 2006.
124. Plastics – Methods for the preparation of samples for biodegradation testing of plastic materials, ISO Standard 10210:2012, International Organization for Standardization, Geneva, Switzerland, 2012.
125. Plastics – Determination of the ultimate anaerobic biodegradation of plastic materials in controlled slurry digestion systems – Method by measurement of biogas production, ISO Standard 13975, International Organization for Standardization, Geneva, Switzerland, 2019.
126. Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium – Method by measuring the oxygen demand in a closed respirometer, ISO Standard 14851, International Organization for Standardization, Geneva, Switzerland, 2019.

127. Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium – Method by analysis of evolved carbon dioxide, ISO Standard 14852, International Organization for Standardization, Geneva, Switzerland, 2018.
128. Plastics – Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test, ISO Standard 16929:2018-04, International Organization for Standardization, Geneva, Switzerland, 2018.
129. Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions – Method by analysis of evolved carbon dioxide – Part 1: General method, ISO Standard 14855-1-2012, International Organization for Standardization, Geneva, Switzerland, 2005.
130. Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions – Method by analysis of evolved carbon dioxide – Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test, ISO Standard 14855-2, International Organization for Standardization, Geneva, Switzerland, 2018.
131. Plastics – Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved, ISO Standard 17556, International Organization for Standardization, Geneva, Switzerland, 2019.
132. Specifications for compostable plastics, ISO Standard 17088:2012-06, International Organization for Standardization, Geneva, Switzerland, 2012.
133. Plastics – Biodegradable mulch films for use in agriculture and horticulture – Requirements and test methods, ISO/AWI Standard 23517, International Organization for Standardization, Geneva, Switzerland, 2019.
134. Plastics – Determination of the ultimate anaerobic biodegradation under high-solids anaerobic-digestion conditions – Method by analysis of released biogas, ISO Standard 15985, International Organization for Standardization, Geneva, Switzerland, 2014.
135. Plastics – Determination of aerobic biodegradation of non-floating plastic materials in a seawater/sandy sediment interface – Method by measuring the oxygen demand in closed respirometer, ISO Standard 18830, International Organization for Standardization, Geneva, Switzerland, 2016.
136. Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium - Method by analysis of evolved carbon dioxide, ISO Standard 2018, International Organization for Standardization, Geneva, Switzerland, 2018.

137. Subcommittee: D20.96, Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions, incorporating thermophilic temperatures, ASTM Standard D5338-15, ASTM International, West Conshohocken, PA, 2015. http://www.astm.org/Standards/D5338.htm.
138. Standard test method for determining anaerobic biodegradation of plastic materials under high-solids anaerobic-digestion conditions, ASTM Standard D5511, ASTM International, West Conshohocken, PA, 2018.
139. Standard test method for determining anaerobic biodegradation of plastic materials under accelerated landfill conditions, ASTM Standard D5526, ASTM International, West Conshohocken, PA, 2018.
140. Standard test method for determining biodegradability of materials exposed to source-separated organic municipal solid waste mesophilic composting conditions by respirometry, ASTM Standard D5929-18, ASTM International, West Conshohocken, PA, 2018. https://www.astm.org/Standards/D5929.htm.
141. Standard test method for determining aerobic biodegradation of plastic materials in soil, ASTM Standard D5988-18, ASTM International, West Conshohocken, PA, 2018.
142. Standard specification for compostable plastics, ASTM Standard D6400-04, ASTM International, West Conshohocken, PA, 2004.
143. Standard test method for determining aerobic biodegradation of plastic materials in the marine environment by a defined microbial consortium or natural sea water inoculum, ASTM Standard D6691-17, ASTM International, West Conshohocken, PA, 2009.
144. Standard test method for determining the aerobic degradation and anaerobic biodegradation of plastic materials under accelerated bioreactor landfill conditions, ASTM Standard D7475, ASTM International, West Conshohocken, PA, 2011.
145. Plastics – Guidelines for the recovery and recycling of plastics waste, ISO Standard 15270:2008, International Organization for Standardization, Geneva, Switzerland, 2008.
146. Plastics – Determination of the ultimate anaerobic biodegradation of plastic materials in controlled slurry digestion systems – Method by measurement of biogas production, ISO Standard 13975:2012, International Organization for Standardization, Geneva, Switzerland, 2012.
147. Plastics – Determination of the ultimate anaerobic biodegradation and disintegration under high-solids anaerobic-digestion conditions – Method by analysis of released biogas, ISO Standard 15985:2004, International Organization for Standardization, Geneva, Switzerland, 2004.

148. Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium – Method by measuring the oxygen demand in a closed respirometer, ISO Standard 14851:1999, International Organization for Standardization, Geneva, Switzerland, 1999.
149. Plastics – Determination of aerobic biodegradation of non-floating plastic materials in a seawater/sediment interface – Method by analysis of evolved carbon dioxide, ISO Standard 19679, International Organization for Standardization, Geneva, Switzerland, 2016.
150. Subcommittee: D20.96, Standard test method for determining aerobic biodegradation of plastic materials in soil, ASTM Standard D5988-12, ASTM International, West Conshohocken, PA, 2012.
151. Plastics – Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved, ISO Standard 17556:2012, International Organization for Standardization, Geneva, Switzerland, 2012.
152. Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation, ASTM Standard D6954-18, ASTM International, West Conshohocken, PA, 2018. http://www.astm.org/Standards/D6954.htm.
153. Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium – Method by analysis of evolved carbon dioxide, ISO Standard 14852:1999, International Organization for Standardization, Geneva, Switzerland, 1999.
154. Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions – Method by analysis of evolved carbon dioxide, ISO Standard 14855, International Organization for Standardization, Geneva, Switzerland, 2005.
155. Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions – Method by analysis of evolved carbon dioxide – Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test, ISO Standard 14855-2-2018, International Organization for Standardization, Geneva, Switzerland, 2018.
156. Plastics – Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system – Method by measurement of biogas production, ISO Standard 14853:2005, International Organization for Standardization, Geneva, Switzerland, 2005.
157. OECD, Biodegradability in seawater, OECD Guidelines for the Testing of Chemicals 306, OECD Publishing, Paris, France, 1992.

158. Standard specification for non-floating biodegradable plastics in the marine environment, ASTM Standard D7081-05, ASTM International, West Conshohocken, PA, 2005.
159. R.M. Gohil, N.M. Hasty, R.A. Hayes, J.V. Kurian, Y. Liang, E.J. Stancik, M. Strukelj, and S.Y.-T. Tseng, Aliphatic-aromatic polyesters, and articles made therefrom, US Patent 7 888 405, assigned to E. I. du Pont de Nemours and Company (Wilmington, DE), February 15, 2011.
160. A.A. Rosen and M. Rubin, *Water Pollution Control Federation*, Vol. 37, p. 1302, September 1965.
161. L.A. Currie, Source apportionment of atmospheric particles in J. Buffle and H.P. van Leeuwen, eds., *Environmental Particles*, Vol. 1 of *IUPAC Environmental Analytical Chemistry Series*, pp. 3–74. Lewis Publishers, Inc., Chelsea, MI, 1992.
162. Y.-P. Hsieh, *Soil Science Society of America Journal*, Vol. 56, p. 460, March 1992.
163. J.A. Bassham, A.A. Benson, and M. Calvin, *J. Biol. Chem.*, Vol. 185, p. 781, August 1950.
164. C.R. Slack and M.D. Hatch, *The Biochemical Journal*, Vol. 103, p. 660, March 1967.
165. M.D. Hatch, *Photosynthesis Research*, Vol. 73, p. 251, 2002.
166. H.-L. Schmidt, *Naturwissenschaften*, Vol. 90, p. 537, December 2003.
167. G. Fronza, C. Fuganti, P. Grasselli, F. Reniero, C. Guillou, O. Breas, E. Sada, A. Rossmann, and A. Hermann, *Journal of Agricultural and Food Chemistry*, Vol. 46, p. 477, February 1998.
168. B. Byrne, K.J. Wengenroth, and D.A. Kruger, *Journal of Agricultural and Food Chemistry*, Vol. 34, p. 736, July 1986.