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Biodegradable polymers and plastics

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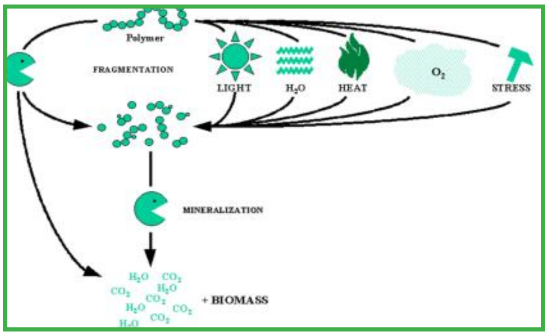
Plastics are typically composed of artificial synthetic polymers. Their structure is not naturally occurring, so plastics are not biodegradable. Based on the advancements in the understanding of the correlation between the polymer structure and properties and the natural processes, new materials were developed that have the properties and the usability of plastics but are biodegradable. This publication presents the core principles of biodegradable plastics relating to their properties, manufacturing, classification, standardization aspects and environmental impacts.

Polymer – substance of high molar mass that is composed of repeating structural units.

Plastic – material composed mainly of polymers.

Biodegradable plastics – plastics that will fully decompose to carbon dioxide, methane, water, biomass and inorganic compounds under aerobic or anaerobic conditions and the action of living organisms.

Biodegradation



Biodegradation or biotic degradation is a specific property of certain plastic materials - that is, of the polymers these materials are made of. It is a process by which a polymer material decomposes under the influence of biotic components (living organisms). Microorganisms (bacteria, fungi, algae) recognize polymers as a source of organic compounds (e.g. simple monosaccharides, amino acids, etc.) and energy that sustain them. In other words, biodegradable polymers are their food. Under the influence of intracellular and extracellular enzymes (endo- and exoenzymes) the polymer undergoes chemical reactions and the polymer degrades by the process of scission of the polymer chain, oxidation, etc. The result of this process that can be affected by a great number of different enzymes are increasingly smaller molecules, which enter into cellular metabolic processes (such as the Krebs cycle), generating energy and turning into water, carbon dioxide, biomass and other basic products of biotic decomposition. These products are non -toxic and occur normally in nature and in living organisms. This process turns artificial materials, such as plastics, into natural components. A process, in which an organic substance, such as a polymer, is converted to an inorganic substance, such as carbon dioxide, is called **mineralization**.

There are many factors involved in the process of biodegradation – different combinations of polymer structures, numerous enzymes produced by microorganisms, and variable reaction conditions – which make it difficult to define biodegradation in general terms. At their

core, chemical reactions that take place during biodegradation can be classified into two groups: those based on **oxidation** and those based on **hydrolysis**. These reactions can occur either simultaneously or successively. The decomposition of condensation polymers (e.g. polyesters and polyamides) takes place through hydrolysis, while decomposition of polymers in which the main chain contains only carbon atoms (e.g. polyvinyl alcohol, lignin) includes oxidation which can be followed by hydrolysis of the products of oxidation.

Microorganisms recognize biodegradable polymers as food

At the macroscopic level, the degradation is revealed through changes and deterioration of key material properties (e. g. cranking, breakage, fragmentation,...). These changes are primarily the result of the shortening of polymer chains that most define the properties of the polymer and the plastic material. Analytically, the changes can be seen at the molecular level by measuring the concentration of functional groups produced during degradation. Most commonly, infrared spectroscopy is used to determine the amount of the carbonyl groups (-(C=O)-) that are the result of the oxidation process.

However, even though their occurrence and concentration is a clear indication of the unfolding of the process and the irreversible chemical changes of the polymer that is now becoming increasingly more susceptible to chain scission, the occurrence of carbonyl groups does not imply polymer chain scission, which substantially affects the mechanical properties of the material. Chain scission is analyzed directly by measuring the distribution of molar masses of the polymer. Molar masses can be determined either by measuring the melt or solution viscosity or by using size-exclusion chromatography or, in case of lower molar masses, mass spectrometry. This provides us with information on the statistical distribution of the molar masses, or the average molar mass (average length of the polymer chain) and the width of the distribution indicating the range of the chain lengths. The shortening of the polymer chains results in the loss of the mechanical properties, such as tensile strength, toughness and flexural strength. Users can observe the effects of degradation of mechanical properties as lessened bearing capacity and quick or simple decomposition of the material. This process can be affected by non-living (e.g. ultraviolet light, heat, water) or living factors (enzymes, organisms).

Decomposition generally begins with **fragmentation**, i.e. the material that is exposed to living or non-living factors undergoes a chemical decomposition of the polymer and therefore decomposes mechanically (fragments). In the next phase, the products of this decomposition are mineralized by microorganisms. This second phase is a necessary step that characterizes this process as biodegradation, because the partially degraded polymers (fragments) are hereby metabolized into end products. There are other cases (oxo-degradable materials) where the material undergoes a quick fragmentation under the influence of heat and UV light but the mineralization stage is very slow, which means that the relatively inert micro particles of the plastic material remain that have a poor susceptibility to biodegradation.

FRAGMENTATION
+
MINERALIZATION
=
BIODEGRADATION

The **final stage of biodegradation** is determined by the mineralization level. Because organic carbon is converted to carbon dioxide in the process of aerobic metabolism, the most widely used method of monitoring this stage is by measuring the amount of carbon dioxide formed in a closed system. To ensure proper results, adequate conditions must be maintained in the closed system (humidity, temperature, pH, absence of toxic substances) for the existence of the microorganism culture.

The method consists of determining the share or amount of carbon in a polymer with a known structure and known mass. This is followed by precise measurements to establish the amount of carbon that was converted to carbon dioxide during biodegradation. At its core, this process is similar to human metabolism, where food is converted to energy and exhaled as carbon dioxide. Alternatively, biodegradation can also be monitored based on measuring the oxygen consumption (which is converted to carbon dioxide) within the closed system. The most widely used method of determining the final biodegradability is measuring the amount of released carbon dioxide. Because this is a generally accepted basis for determining biodegradability, automated devices are now available that measure with great accuracy the biological transformation of the polymer. However, many of the parameters must nevertheless be monitored and a vital microorganism culture, e.g. such as found in mature compost, must be used.

During the aerobic process, the carbon from the polymer is converted to carbon dioxide.

There are many microorganisms capable of biologically degrading polymers. They differ strongly from one another in that they are active under very different conditions (humidity, pH, temperature, salinity, etc.) and therefore more or less specialized for decomposing different substrates depending on what enzymatic systems they are using. These conditions largely define what they are able to decompose. An example of such specialization by a microorganism can be find in the fungus Phanerochaete chyrsosporium and other white-rot fungi, that decompose lignin in natural environments by using oxidases that catalyze oxidation. For testing purposes, we use microorganisms that can be found in natural environments or places with increased microbiological activity (e.g. compost, sewage, water treatment plants) or locations that contain the material we want to decompose (e.g. manufacturing sites). The premise is that these places contain microorganisms that have adapted to the new substrate and are the result of natural selection. The work with carefully selected microorganisms is limited to laboratory research as practical usage (e.g. composting) presupposes natural and stable systems.

This raises an important question: **what is the time frame in which biodegradation should occur in order to be of practical value?** Generally, it can be predicted that any organic material, including ordinary plastics, will degrade mechanically and chemically under the influence of the environment and microorganisms. This however may take a very long time. It is extremely important to know the exact rates of degradation and mineralization. This is important not only in terms of use – certain properties of plastic materials, such as bearing strength and water tightness, must be guaranteed

– but also in terms of the environmental impact of the decomposition products (e.g. fragments).

An example where the rate of biodegradation is important and highly limited is **compostable plastics**. Ordinary plastics remain unchanged during a composting cycle lasting a few weeks and unless removed from the compost, they will remain in the natural environment. If plastics fragment and the resulting particles cannot be mineralized, the compost will include microscopic particles of artificial substances whose long-term impact on the natural living and nonliving environments is unknown. This represents a certain risk because the particles, once dispersed in nature, cannot be gathered easily and will remain in nature for a long period of time. Compostable plastics, on the other hand, will fragment during the composting cycle and the mineralization process will begin within the period, required for the degradation of bio-waste (e.g. grass, household waste). Only with compostable plastics can we be certain that no artificial substances with unknown environmental impact were introduced to the natural environment.

The difference between both cases is in the rates of decomposition and mineralization. The general rule is that the biodegradation rate must be known, as it affects the usage and the proper handling of the material once it becomes waste.

Biodegradable or compostable?
Compostable plastics are a subgroup of biodegradable plastics and are biologically decomposed under composting conditions and within the relatively short period of a composting cycle.

◊ **Compostable always means biodegradable.**
◊ **Biodegradable does not necessarily mean compostable.**

The most widely used criterion for the biodegradation of plastics is that their fragmentation rate must keep up with the composting cycle; however, mineralization can also take longer. There are methods in place that help determine longer biodegradation rates and are applied in cases such as when using biodegradable plastics in agriculture. The rule is that compostable plastics are biodegradable, while biodegradable plastics are not necessarily compostable (because biodegradation may take longer than required in composting). Therefore, compostable plastics are a subgroup of biodegradable plastics.

Materials

Biodegradable plastics may be manufactured from renewable or non-renewable resources

The susceptibility of a polymer or a plastic material to biodegradation depends exclusively on the chemical structure of the polymer. For this reason, whether the polymer is made of renewable resources (biomass) or non-renewable (fossil) resources is irrelevant to biodegradability. What matters is the final structure. Biodegradable polymers can be therefore be made of renewable or non-renewable resources.

A common misunderstanding is that all biodegradable polymers are made from renewable resources.

The **manufacturing of biodegradable polymers** can include different procedures without affecting material biodegradability. They can be synthetic (chemical) or bio-technological (effected by microorganisms or enzymes). The most common procedures are:

- Manufacturing plastics from a natural polymer that has been processed mechanically or chemically (e.g. plastics based on destructured starch).
- Chemical synthesis of a polymer from a monomer produced by bio-technological conversion of a renewable resource (e.g. use of lactic acid produced from the fermentation of sugars for the production of polyactic acid – PLA). In this case, the polymer is produced chemically based on a renewable resource.
- Production of a polymer by a bio-technological procedure based on a renewable resource (e.g. fermentation of sugars where natural microorganisms synthesize thermoplastic aliphatic polyesters, such as polyhydroxybutyrate - PHB).
- Chemical synthesis of a polymer based on the components obtained by petro chemical processes from non-renewable resources.

Today, commercial biodegradable plastics are offered on the market by an increasing number of manufacturers. Those most common materials can be classified into the following groups:

- Starch-based plastics
- Polylactide-based plastics (PLA)
- Polyhydroxyalkanoate-based plastics (PHB, PHBV, etc.)
- Aliphatic-aromatic-polyester-based plastics
- Cellulose-based plastics (cellophane, etc.)
- Lignin-based plastics

All components of the material must be biodegradable

Apart from the polymers, plastics contain other materials or additives and this combination determines their processing options and the product's final properties. These other materials include stabilization additives, lubricants, pigments, different fillers, and others. For biodegradable plastics it is very important that all additional components are biodegradable as well. The standards for compostable plastics require the testing of all additives (and other substances used in the production of the final product, e.g. inks and colors) to ensure they do not have a negative effect on the compost.

Different **composites** containing natural components (biocomposites) are also available. A composite is a mixture of a polymer or plastic and the filler that is added to improve the chemical or mechanical properties of the material or to lower the cost of the material. Biocomposites most often consist of various natural fibers (e.g. hemp) or fillers such as wood flour. Chemically unaltered natural fillers are biodegradable by default, but the polymer must also be biodegradable (e.g. polylactide filled with natural fibers) for a composite to be biodegradable. It is a commonly mistaken belief that including a natural filler (e.g. starch or wood flour) into a material that is not biodegradable will make it biodegradable. Naturally, inorganic fillers are not biodegradable and biodegradability does not apply to them.

Effect of biodegradable plastics

There are two main aspects based on which the consumer decides whether or not they will use a plastic material: the **economic/commercial** aspect and the **environmental** aspect. Even though they cannot be entirely separated – using environmentally less harmful materials can have commercial and marketing benefits and can help achieve higher prices – they can be treated separately.

The main advantage of biodegradable plastics applies to environmental properties, primarily when it comes to the handling of **waste plastics** and the effects of their decomposition on the environment. When biodegradable plastics decompose biologically, the resulting natural components do not affect the environment in any harmful way. Even though the ordinary, non-biodegradable plastics do not release harmful substances into the environment, they are relatively durable and dangerous, mostly to animals, and may cause inconveniences, such as blockage of sewage systems. With biodegradable plastics, which decompose more quickly, these negative effects are not altogether removed, which means that biodegradable plastics must not be dumped in the natural environment. However, if they do make their way there by error, they will cause less damage than non-biodegradable plastics.

Biodegradable plastics are not designed to be disposed of in nature!

The advantage of biodegradable plastics is that they decompose into natural substances and do not require separate collection, sorting, recycling or any other final waste solution (disposal at landfills or burning) as is the case with non-biodegradable plastics. While these measures reduce the environmental impact of waste they cannot eliminate it or establish the state of natural processes as can be done with biodegradable plastics. Their wholly natural degradation allows artificial materials-bioplastics to enter the natural cycle.

Biodegradable plastics are not foreign to the natural environment like ordinary plastics, whose influence can only be diminished but not eliminated. But despite these advantages, they need to be collected, usually together with biological waste, and processed aerobically or anaerobically. The more common method is the aerobic process of composting. Compostable plastics are customized for industrial composting that differs from the domestic composting in temperature; the temperature of industrial composting is higher which means that degradation happens more quickly. If biodegradable plastics are not collected together with organic waste and are processed with mixed waste, it is harder to take advantage of their biodegradability. In fact they can have a negative effect on the recycling process. The mechanical and biological processing of mixed municipal waste, depending on the succession of the operations, it is most likely that biodegradable plastics will be part of the fraction that is directly or indirectly intended for burning. In this case, biodegradable plastics have no biodegradability advantage over non-biodegradable plastics. If they are disposed of in a landfill, they will decompose, as any other organic material, to carbon dioxide (or methane when the environment runs out of oxygen). Because modern landfills are isolated from the natural environment, the remaining biomass will not enter the natural material cycle. In this case, the utilization of biodegradable plastics is suboptimal.

The advantages of biodegradable plastics over other types of plastics are of value only if proper handling of biodegradable plastics is applied; that is, if after they have been used, the plastics are disposed of under such conditions that enable their biological decomposition and the entering of the products into natural cycles. A **combination of biodegradability and the use of renewable resources** to produce biodegradable plastics provides a unique possibility of aligning the entire life cycle of plastics with the natural cycles: **plastics are produced from and return to the natural renewable resource**. This cannot be achieved with any other type of plastics and is currently the best imitation of a natural material; like a leaf that falls off a tree in the fall and provides food for the budding plant in the following spring. Plastics still require human intervention but the gap between this and the natural ideal is getting smaller every day.

Glossary of terms

Aerobic decomposition – biological decomposition in the presence of oxygen or air, where carbon is converted to carbon dioxide and biomass.

Anaerobic decomposition – biological decomposition in the absence of oxygen or air, where carbon is converted to methane and biomass.

Biological decomposition (= biodegradation) – decomposition under the influence of biological systems.

Biomass (= renewable resource) – substance of biological origin, with the exception of geological formations and fossilized biological matter.

Bioplastics – plastics that are biodegradable and/or biomass-based. In medicine the term can signify biocompatibility – the compatibility of plastics with human or animal tissues.

Biodegradable plastics – plastics that will fully decompose to carbon dioxide, methane, water, biomass and inorganic compounds under aerobic or anaerobic conditions.

Certificate – written statement issued by an authorized organization confirming that the material or product complies with a standard. The certificate includes permission to use labels and logos that indicate compliance with the standard.

Composting – processing of organic waste where aerobic microorganisms biologically decompose organic material.

Compostable plastics – plastics that biologically decompose under the composting conditions with a degradation rate that is comparable to the duration of the composting cycle and complies with applicable requirements.

Plastic – material composed mainly of polymers.

Polymer – substance of high molecular weight that is composed of repeating structural units

Additional information on sustainability aspects of plastics is available at **www.plastice.org.**

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