plastice

Innovative value chain development for sustainable plastics in Central Europe

CENTRAL EUROPE
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EUROPEAN UNION
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# BIOPOLYMERS AND BIOPLASTICS

## PLASTICS ALIGNED WITH NATURE

INFORMATIONAL - EDUCATIONAL MATERIAL FOR TEACHERS AND LABORATORY ASSISTANTS OF CHEMISTRY AT PRIMARY AND SECONDARY SCHOOLS

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# CONTENT:









# INTRODUCTION

In 2010, 265 million tons of plastics were produced worldwide, of that 57 million in Europe [1]. The production and consumption of polymeric materials is expected to grow at least as long as ‘developing countries’ do not reach such an average consumption as in developed countries.

Currently, about 80 % of all polymeric materials are produced by the petrochemical industry, i.e. they are produced from fossil (non-renewable) resources. Along with the increased use of plastics the burden on the environment is also increasing. In addition to the environmental impacts caused by the mere production of polymers and plastics, there is a growing burden of waste, generated when users discard products that are no longer needed. Waste has been a pressing problem for many years; with the increasing mass consumption of products with a short life span, the amount of waste is also increasing rapidly. Dumping grounds have numerous potential negative environmental impacts (seepage of leachate into the groundwater, odours, destruction of the local flora and fauna, local changes in the environment, soil pollution, ...) and they also require a lot of space. Waste plastics that one way or another find their way into the natural environment, of course represents an even greater danger. The re-use and recycling of products are two of the options to reduce the amount of landfilled waste and related environmental burdens. Polymers which are bio-degradable or made from renewable resources also represent an alternative possibility. These are newer and less well-known materials that promise a greater sustainability of plastics in the future. These materials are the subject of the present publication.

# OBJECTIVE

The first plastics, which were claimed to be biodegradable, appeared on the market more than twenty years ago. Their appearance on the market did not bring immediate success, primarily due to poor evidence of their actual biodegradability, i.e. the characteristics that were presented as their greatest advantage [2].
Scientific and technological development in the field of bio-degradation and biopolymers has since then progressed significantly and today we can buy verified biodegradable plastic products in most of the larger shops. Regarding this, Central Europe can pride itself especially on its strong scientific base in the field of biopolymers and bioplastics, only, it should be made better use of, also industrially.
The international project: PLASTiCE - Innovative value chain development for sustainable plastics in Central Europe; is intended for the promotion of new, more environmentally friendly and sustainable types of plastics. The emphasis of the project is the identification and elimination of restrictions, which in Central Europe prevent the faster and more widespread use of sustainable types of plastics, especially biodegradable plastics and plastics from renewable resources (together bioplastics).

**The specific objectives are:**
- Greater awareness of target groups about bioplastics.
- Improvement of mechanisms for technology transfer and the exchange of knowledge about biodegradable plastics with industrial users.
- Improvement of access to scientific discoveries, the use of existing knowledge and its adaptation to the requirements of manufacturers of biodegradable polymers and plastics.
- The strengthening of cooperation between research institutions and business.

More about the project and the latest news can be found at: www.plastice.org, on Facebook: www.facebook.com/PlasticeSlovenia, and on the YouTube channel of the project - www.youtube.com/user/plasticeproject - you will find videos of our lectures.

The present work is intended for chemistry teachers and laboratory assistants at primary and secondary schools. On the whole, it covers impartial and science-based information from the field of biodegradable plastics and plastics based on renewable resources, which are suitable to pass on to pupils/students. Thus, we want to raise awareness among a wider audience and to acquaint them with the possibility of the choice that they have. The success of the bioplastics’ breakthrough on the markets, and the development of biopolymers are inseparable from the conscious, discerning and critical consumers who realise that they have the possibility of choice and that with their choice they can co-create a future that is rightfully theirs and their successors’.

# OUTLINE

The content of the present material is divided into four chapters. The first chapter explains, step by step, how polymers and plastics are derived from monomers. It clarifies the difference between the so called conventional plastics made on the basis of fossil fuels, and bioplastics; a greater emphasis is on biopolymers and bioplastics themselves - what they are, how they are acquired, and how biodegradation occurs. It also describes why bioplastics represent an important alternative to conventional plastics.

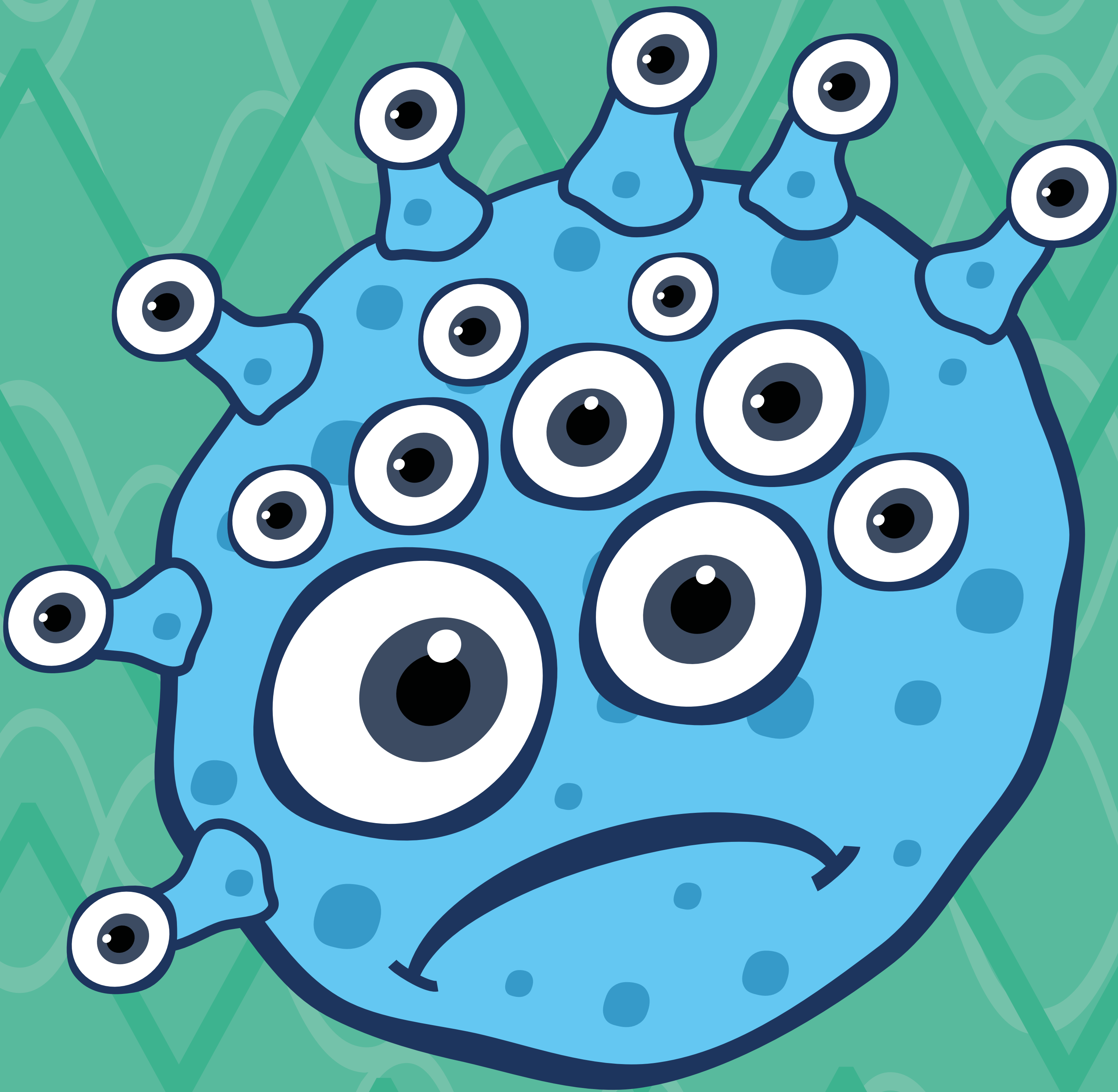
The second chapter focuses on plastics derived from renewable resources. This group of plastics can, especially in the future, significantly contribute to reducing the use of fossil fuels and the consequences that their use entails. The chapter also explains why not necessarily all plastics based on renewable resources are also biodegradable.

The third part is dedicated to bioplastics that consumers can come across and use at work or at home. It explains everything that can be produced from bioplastics, and how to handle bioplastic products when we no longer need them. It also describes certification marks that are the only guarantee of the actual nature of the material.

Key messages, which at the same time represent a brief summary of each of the parts, are highlighted at the end of each chapter.

In the fourth chapter, you will find a description of one short (appropriate to perform in the classroom during a lesson) and two longer (suitable for laboratory practice) experiments, which you can perform with the students, so they will find it easier to imagine what bioplastics are, how they can easily make them themselves, and what the differences and similarities with conventional plastics are. Also described is an attempt of composting, which can take place over a longer period of time and thus gives students a very practical understanding of biodegradation and composting.

At the end of this publication, you will find a glossary of terms used in the literature.

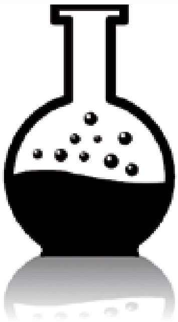


# BIOPLASTICS: ORIGIN, FORMATION AND DECOMPOSITION

# 1

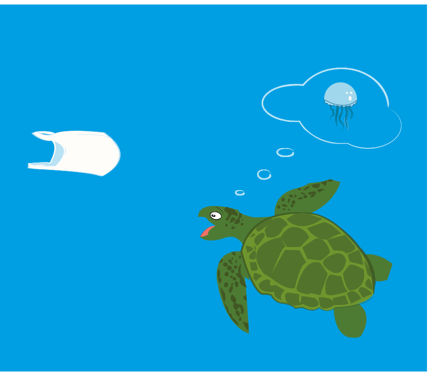
*The mind is the driving force of human development, and since ancient times, man, when looking for optimal ways to meet his needs and quench the thirst of his curiosity with research, discovered and invented everything from stone tools and fire, to nanomaterials.*
*Somewhere between the fire and nanomaterials, plastics were discovered. People had the need for a material as durable as possible. The beginnings of plastics reach back to 1869, when John Wesley Hyatt invented nitrocellulose, a composite material that was initially used for billiard balls. Nitrocellulose (later known under the trade name celluloid) was the first industrial plastics. Less than a century and a half later, ironically, we are faced with the problem of lasting endurance and alarming quantities of plastic waste in the environment. Let's look at how the originally desired feature that provoked the development of the first plastics, has become the core of the problem, and what ways out of the current quandary bioplastics offers us.*

## SYNTHETIC POLYMERS AND THE PROBLEM THEY POSE



**Plastic materials (plastics) contain as the key component synthetic polymers, which are characterised by high molecular mass.** Due to simple processing and the many options for making cost-effective products that elevate living standard and the quality and comfort of life, polymeric materials successfully penetrated the global market. Each one of us meets a wide range of plastic materials and products made from them daily, because polymeric materials, due to their amazing diversity, cover an unbelievably wide range of characteristics and applications. The food we buy in shops is wrapped in different types of plastics, as well as personal hygiene products, sports equipment made from plastics, children's toys, stationery, kitchen utensils, etc.

Due to the exceptional growth of the production and the use of polymers, consideration about the consequences of plastic products use, and the waste management of these products when they become waste, is a current and pressing issue. Concerns focus **on the potential impact of artificial substances on human health and the damage they cause to the environment.** Almost all plastics today are synthesised from raw materials which we derive from fossil fuels via the petrochemical industry. **Global warming** is linked to the exploitation of **fossil fuels - at the same time we are spending precious non-renewable resource of the materials.** In addition, part of the **plastics** finds its way **into the natural environment**, where they represent a **permanent foreign body**, as they consist of artificially synthesised polymers which do not usually occur in nature. As such, they can represent a source of organic pollutant release into the environment, and the entering of the former into the food chain. Since we have been using plastics in such large quantities »only« in the last few decades, all these impacts and potential dangers are not even known yet. It is indisputable, however, that an overwhelming amount of materials and substances are entering our environment, that have simply never been there before, and to which nature over the course of evolution has not been adjusted. Not only are plastics (like all other) waste a blight on the view of the landscape, but also organisms can accidentally ingest them, entangle themselves in them, or choke on them.



It is no longer a new discovery that in the Pacific Ocean there is a large floating mass of plastic waste, which covers an area equal to twice the size of the continental parts of the U.S. In 2006, the United Nations Environment Programme estimated that **every square mile of ocean contains 46,000 units of floating plastics.** Since plastics decays slowly in the natural environment, mainly due to the effects of non-living factors, it mostly accumulates there, and we cannot avoid the problem of its presence. New research shows that this problem is present in all the world's seas and oceans. In 2010, there were 265 million tons of plastics produced in the world, 57 million of that in Europe [Plastics Europe, 2010]. In the same year, a total of 724,500 tons of bioplastics were produced in the world, which is, in comparison with the millions of tons of conventional plastics produced that year, a very small proportion. [3] It is predicted that polymer production will reach one million tons of annual production in a few years time.

If durability was initially regarded as one of the advantages of plastics, facing the problem of huge amounts of waste plastics means that that is today no longer its (positive) attribute, but a property you want to bypass, and if at all possible, not at the expense of the loss of its other appealing attributes.

While recycling and incineration represent alternatives to landfill disposal of plastic products, they understandably also have their own weaknesses. With the recycling of plastics theirs quality deteriorates, as well as the collection costs can be high. Recycling, of course, improves the utilisation of the material (since we exploit the same material more times), but recycling cannot run indefinitely, which means that we must sooner or later face the waste, which needs »final« treatment. Incinerators are a sensible energy use of the material after we've taken advantage of the other options, but in cases where they are not technologically advanced enough or are incorrectly operated (e.g. combustion at too low temperatures), they can release toxic substances into the environment.

According to the experts, biodegradable polymers represent a major alternative when dealing with the above-mentioned problems. The principle of most of these approaches is - modeling on natural processes with the objective of ever deeper integration of synthetic polymers and plastics with natural materials and energy circuits. On the basis of the modern understanding of correlations between the structure and properties of polymers, and knowledge of the workings of natural processes, materials have been developed that combine the expected properties of plastics, enable efficient processing and usability of products, and are at the same time biodegradable.

# (BIODEGRADABLE) POLYMERS AND PLASTICS

**Polymers** (Greek: poly-many, meros-particle) are compounds **with high molecular mass**, constructed of interlinking, **perennial basic building blocks**, called **monomers**. Simplified they can be compared to a pearl necklace - each pearl represents one monomer unit; a few tens of pearls are strung on the necklace, and so the necklace is a polymer. Also, a paper clip can also represent a monomer, and a polymer is represented by a chain of these clips, obtained when we attach them to one another.

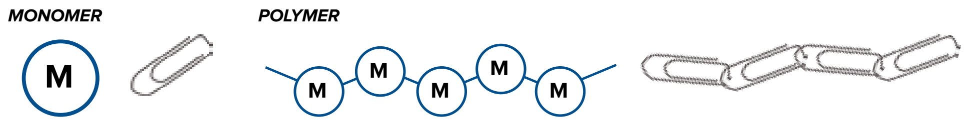
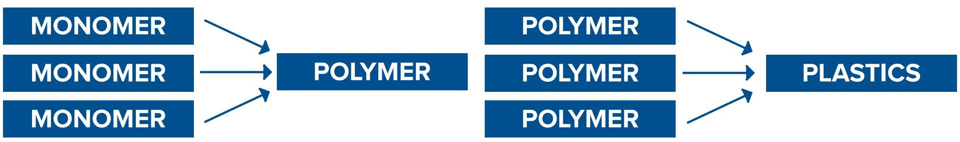


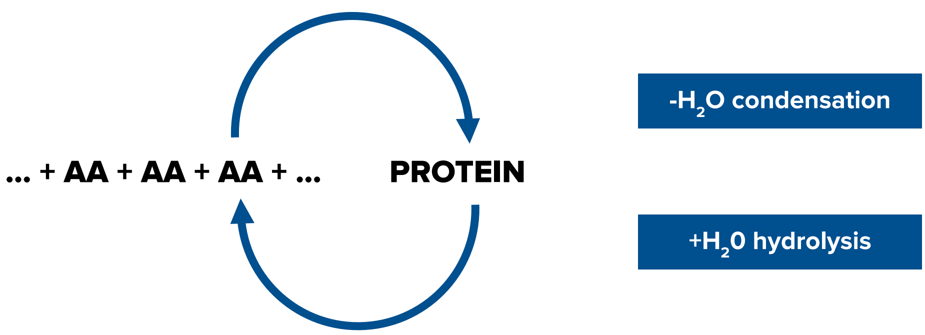

*Figure 1: Simple explanation of the connection of the monomer and the polymer*

Many examples of polymers are extremely important to our lives: e.g. DNA - of which the monomeric unit is a nucleotide, proteins that produce enzymes and our muscles are composed of amino acids. Polymers are also: cellulose - an essential component of wood, and starch – an energy reserve of plants that can be found for example in potatoes and corn; their monomeric unit is glucose.

**Plastics are a material** formulated and prepared for use. **The main components of plastics are the polymers with additives as fillers (inorganic or organic), pigments, lubricants, inhibitors of oxidation, etc.** There are many different **types of plastic materials**. The choice of polymers on which they are based is the key. PET (polyethylene terephthalate), from which almost all the bottles for water and other beverages are made, is well known to all; also often encountered is polypropylene (PP), from which automobile parts, the casing for household appliances and pipes for hot water are made; and polystyrene (PS), which is used for packaging in the cosmetic and pharmaceutical industries and for cutlery; polyethylene (PE) - bags, toys, cables, lids/caps, ... The aforementioned types of plastics are the most widespread, representing about 75 % of all produced plastics. We can see that all of the names include the poly-prefix, which indicates that it is a polymeric material, consisting of monomeric units.




Let's look in more detail at the **chemical reactions** which are necessary for the formation of polymers. By combining several amino-acids (AA), a protein (polymer) is formed. It is condensation, whereby water is separated during the reaction. The reaction is also carried out in the opposite direction; with the hydrolysis (binding with water) of a protein, amino acids are obtained.




Polyethene (polyethylene) is also formed by polymerisation, namely by chain growth polymerisation, wherein the monomers are connected by coupling.

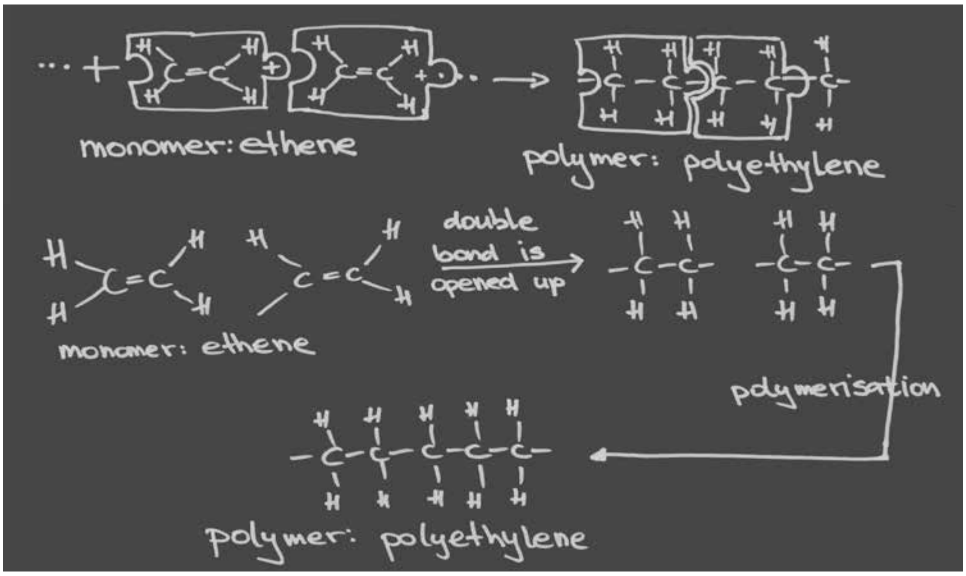



*Figure 2: Polymerisation of ethene – formation of polyethylene*

Let's take a look at how one of the most well-known polyesters, poly(ethylene terephthalate), known under the label PET, is formed. First we will explain the formation of esters.

**Esters** are compounds with the ester functional group -COO, which is on both sides of the group bound to the random organic group (R-COO-$R_1$). Esters are formed during **esterification**. This is a reaction between carboxylic acid and alcohol. The reaction usually happens at the presence of a strong acid (such as $H_2SO_4$) as a catalyst.

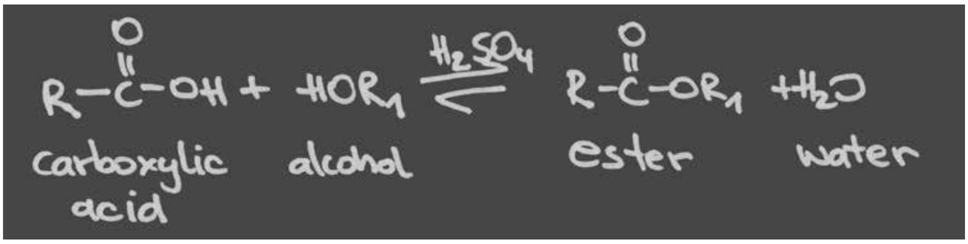
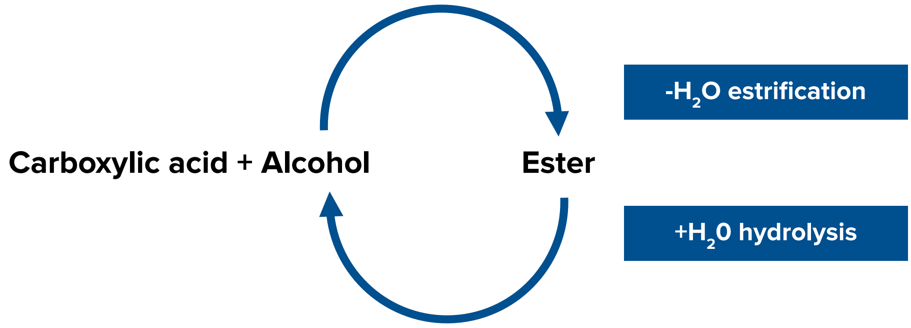



*Figure 3: Formation of esters*

The hydrolysis of esters is a reaction of ester with water, wherein the molecule is split, and carboxylic acid and alcohol are formed, that is, the units that form ester (it is an analogous process of protein hydrolysis - proteins are 'chemically-wise' polyamides, linked to the amide group).




Polyesters are the product of a poly-condensation reaction. They are derived from monomers, wherein water is normally separated. A key feature of a monomer from which we can make a polymer, is having at least two functional groups that can form at least two bonds. Only in such a way can we form a (polymer) chain.

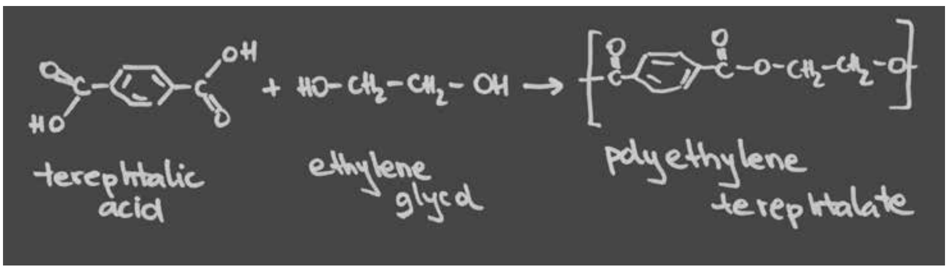



*Figure 4. Estrification: Formation of polyethylene terephthalate - PET*

**Living organisms in metabolic processes, themselves, synthesise different polymers**, which they need to perform various functions, the carriers of genetic information (DNA), material to provide rigidity in cell walls (cellulose), substances for energy storage (in some microorganisms, polyester) etc. In addition to natural polymers there are also numerous synthetic polymers which are, in principle, more or less similar to the natural ones, but are produced artificially by man, and in nature as such they do not exist. This group accounts for almost all the plastics that we use.

**Division of polymers according to their origin is, therefore, as follows:**

1) NATURAL POLYMERS

2) ARTIFICIAL/SYNTHETIC POLYMERS

## POLYMERS OF NATURAL ORIGIN

Most of the living world is based on polymers. They can be found in animals (hydrocarbons, proteins, fats, nucleic acids, etc.), plants (e.g. cellulose, oils, starches, even polyesters) as well as in lower organisms. Natural polymers are produced in the growth cycles of cells of living organisms. Their synthesis includes enzyme-catalysed polymerisation reactions of activated monomers, which occur within cells as products of complex metabolic processes. For materials created by nature it applies that they can also be degraded by nature. All the natural polymers represent stored energy and matter, which is in decomposition (metabolism) released and made available for reuse. Therefore in nature, for natural polymers, there are enzymatic systems for their degradation. This concept also includes our food consumption, which largely consists of biopolymers. Of course, the process runs also internally: during the time of abundance the organism synthesises polymers, at the time of a lack it consumes them. Such is, for example, the purpose of excess fat in our bodies.

Invisible, generally present and almost always active disintegrants of natural organic materials - are microorganisms (bacteria, fungi, algae). Microorganisms have through evolution adapted to natural polymers, as well as to other (low molecular) natural substances, and have developed methods for metabolism. They can again degrade polymers to their basic building blocks. Some of the natural polymers are: cellulose, lignin, starch, chitin, pectin, agar,....

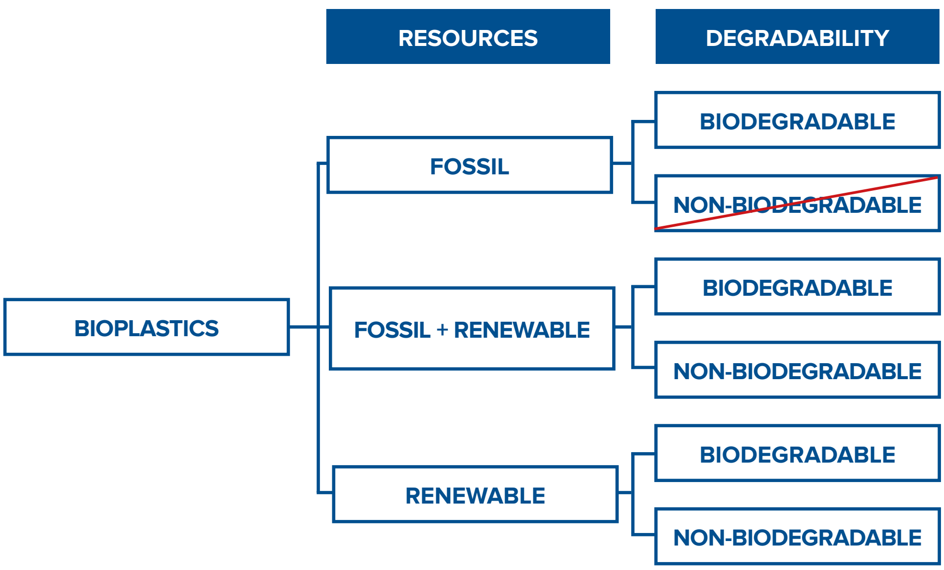
## POLYMERS OF ARTIFICIAL ORIGIN

With biosynthesis polymers are produced in a manner identical to the natural. Many microorganisms in nature, for example, synthesise polyester as a substance for energy storage. On an industrial scale this is a fermentation of sugar (glucose) under the influence of microorganisms and under the optimal conditions, so as to ensure the effective formation of large quantities of polyester. It is therefore a natural polymer but its production is closely controlled, therefore we consider its source artificial.

Chemo-synthetic polymers are usually derived from oil. These are polymers which do not occur in nature as such, and therefore, when they end up in the natural environment, they there represent a durable foreign object, since they cannot be incorporated into the natural cycle. It is estimated that the discarded plastic bottle remains in the natural environment for 450 years. Among these polymers, degradability is otherwise achieved with the integration of hydrolytically unstable bonds into the polymer (e.g. ester-, amide groups, ...).

**According to the source, bioplastics are divided into:**
- bioplastics from renewable resources,
- bioplastics from fossil resources and
- bioplastics from a mixture of renewable and fossil resources,

and by **the ability of degradation** on **biodegradable** plastics, including also compostable plastics, and plastics which are NOT **biodegradable**. With the combination of these two criteria, source of the material and degradability, we have 6 options, which are shown in the figure below.




*If we consider the definition of bioplastics, we quickly realise that we have an intruder in this diagram. Of the six possible types of plastics there is only one that does not belong to bioplastics. This is plastics which is made from fossil resources and is non-biodegradable. Although this type of plastics represents only one of the six possible combinations, it by far exceeds bioplastics in terms of use and distribution in the marketplace.*

*Figure 5: Distribution of bioplastics according to the source and the susceptibility to biodegradation*

The definition, which is recognised today, and is practically the most used, denotes bioplastics as biodegradable plastics and/or plastics from renewable resources [3]. This definition is in use in the industry, and indicates that it is not necessary that bioplastics are also biodegradable. According to this definition, bioplastics also include plastics which are not biodegradable, but are made from renewable resources. For a better idea, please refer to the following coordinate system.

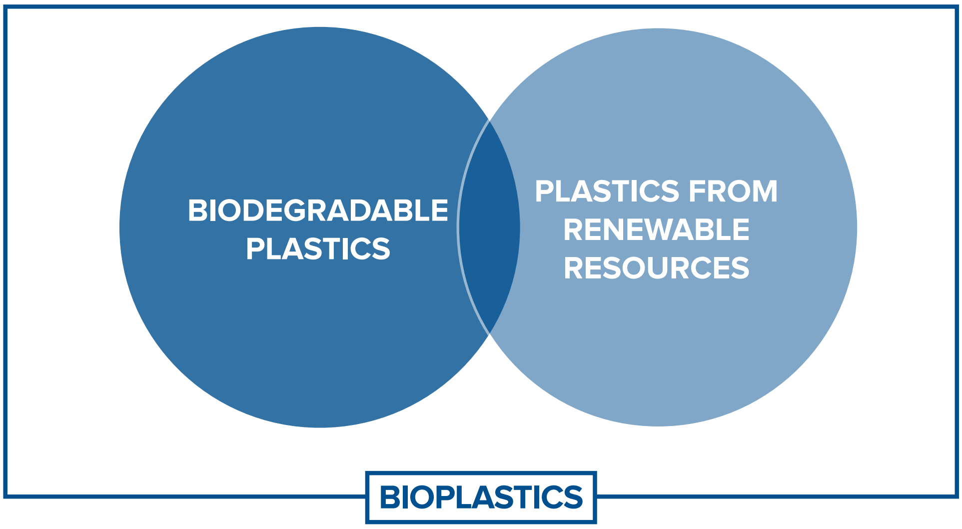



*Figure 6: European Bioplastics definition of bioplastics*

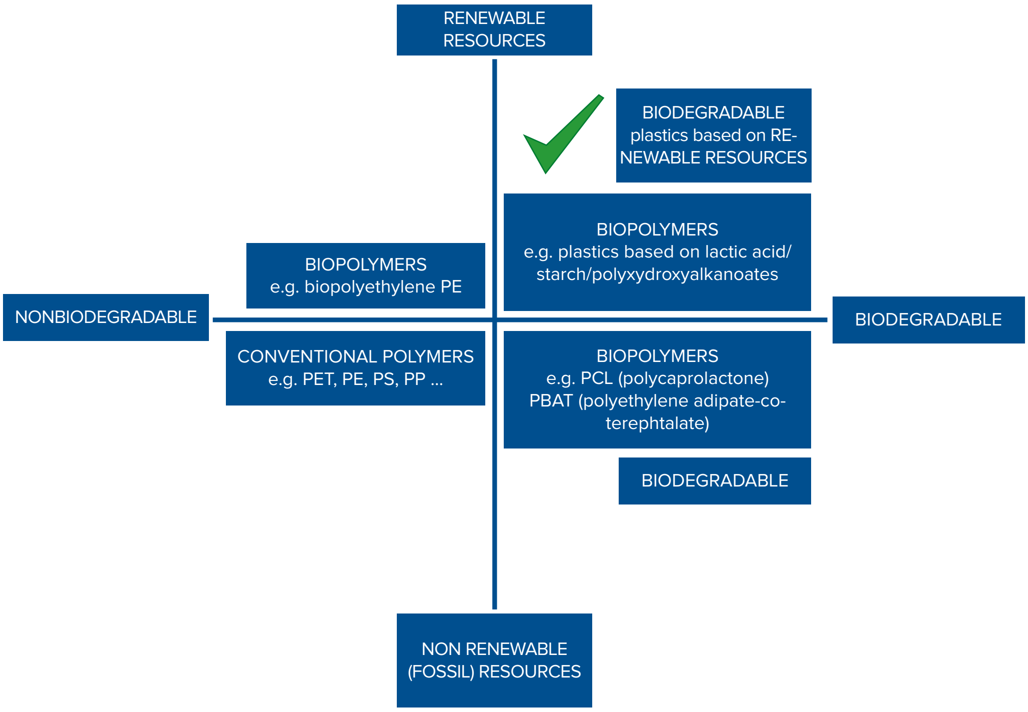



*Figure 7: Plastics "Coordinate system"*

In the pursuit of objectives of **sustainable development** and the **reduction of environmental impacts, biodegradable plastics from renewable resources** logically represent the best possibility, but we must do everything in our power to optimise the use of non-biodegradable plastics from non-renewable resources.

At this point we will explain the concept of (non)renewable resources. Among renewable resources are those which are of natural origin, but their quantity is not decreasing due to human use, as they are fairly quickly restored through natural processes. These include wind-, solar-, geothermal-, wave- and tidal energy, biomass, ... Even fossil fuels are in essence a natural resource - created from dead organisms. The problem is that fossil resources are generated over millions of years, while human beings consume them at the level of centuries. From the perspective of human life, oil and natural gas are therefore non-renewable resources; while we can not claim this if we look at the situation through the prism of the geological age of the Earth. Due to the speed of the human exploitation of fossil fuels it has come to a discrepancy in the timeline - carbon, which has been forming over millions of years, is released in accelerated fashion (over decades and centuries) back into the cycle, not to be bound again for a long time. Thus, **there is no possibility that during the time of one human's life, as much fossil resources are created as are consumed**. We as mankind have gotten involved in the natural cycle, but we are not abiding its natural properties. With our high reliance on fossil fuels we are taking from the Earth's reserves, but we are not replacing them. So we are preventing future generations from having the same possibilities to use this resource as we do. Thus, fossil fuels are considered non-renewable. Nobody knows exactly for how many years we can still rely on the reserves of fossil fuels, though mostly experts agree that at some point they will simply run out, i.e. that mankind will completely use up this natural resource. In addition to the fact that we can not infinitely exploit fossil fuels, the burning of them emits large quantities of carbon dioxide into the environment. This is one of the main greenhouse gases, blamed for warming of the Earth's atmosphere and the associated climate change.

**Expedience of the use of bioplastics is simplistically presented in the following diagram:**

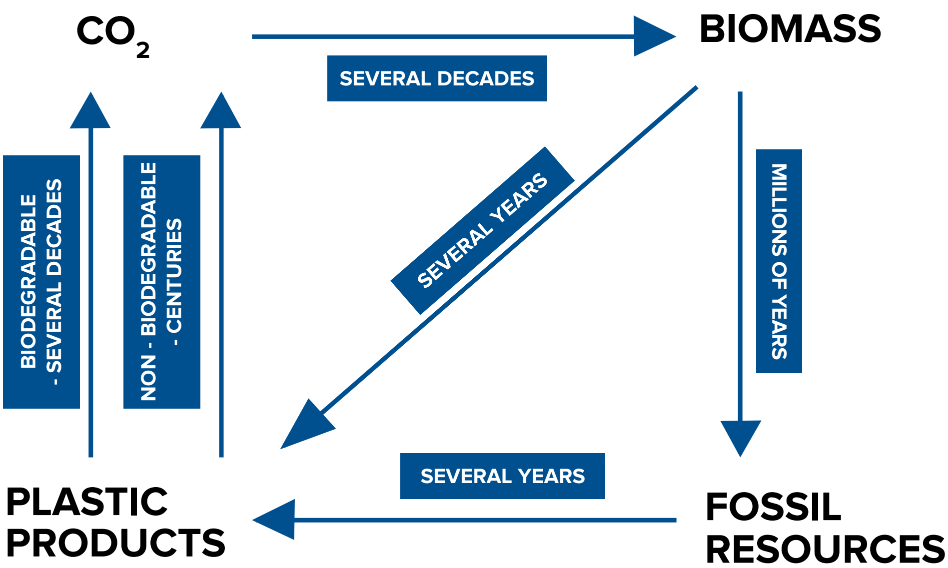



*Figure 8: Rational use of bioplastics*

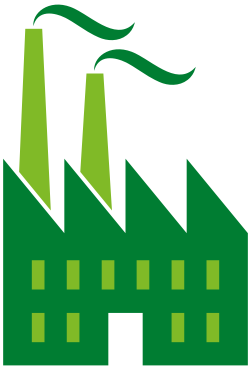
By avoiding the use of fossil fuels we only circulate within the triangle: BIOMASS-PLASTIC PRODUCTS-$CO_2$; and remain within the timescales that are rightfully ours.

## BIOLOGICAL DECOMPOSITION

**Biodegradability** is a specific feature of some plastic materials or polymers that plastic materials are composed of; **biological degradation** or, shortened, biodegradation, denotes the process of **degradation of the polymer material under the influence of biotic (living) factors.** The process of biodegradation is based on the fact that organisms, mainly microorganisms (bacteria, fungi, and algae) identify the polymer as a source of organic building blocks (e.g. simple saccharides, amino acids, etc...) and source of energy they need for life. Simply put, **biodegradable polymers represent food to the microorganisms**. The polymer chemically reacts under the influence of either cellular or extra-cellular enzymes, wherein the polymer chain is split. The process can take place under the influence of a variety of enzymes, and gradually leads to smaller molecules. The latter enter the metabolic processes that take place inside the cells (e.g. Krebs cycle) and alongside the emission of energy are converted into water, carbon dioxide, biomass and other basic products of the biological conversion. A characteristic of products of degradation is that they are not toxic and are quite commonly present in the natural environment as well as in living organisms. Artificial material (e.g. plastics) is in this way converted into elements, which are normally present in nature. **The process of conversion of organic carbon** (in our case, the polymer), into inorganic carbon – e.g. carbon dioxide, is called mineralisation.

## BIODEGRADABILITY

Despite the fact that we want to make as much biodegradable plastics as possible from renewable resources, it is a fact that the **susceptibility of polymers or plastics to biodegradation is solely dependent on the chemical structure** of the polymer. For biodegradability itself, it does not matter whether the polymer is made on the basis of renewable resources (biomass) or on the basis of non-renewable (fossil fuel) resources, but only what its final structure is. **Biodegradable polymers** can thus be made based on either **renewable or non-renewable** resources. **It is very often wrongly assumed that all biodegradable polymers are made from renewable resources.**



## THE PRODUCTION PATH AND TYPES OF BIOPLASTICS

The way of plastics production also does **not influence biodegradability** at all. Procedures can be **synthethical** (chemical) or **biotechnological** (under the influence of enzymes or microorganisms), and the most common are:

- preparation of plastics on the basis of a natural polymer, which is mechanically or chemically treated (for example, plastics based on destructured starch);
- chemical synthesis of a monomer-based polymer, obtained by biotechnological conversion of renewable resources (e.g. the use of lactic acid from the fermentation of sugars for the production of polylactic acid (polylactide, PLA)). In this case, the polymer is made chemically on the basis of renewable energy sources;
- a polymer, resulting from a biotechnological procedure based on renewable resources (for example, fermentation of sugars, in which the natural microorganisms synthesise thermoplastic aliphatic polyesters e.g. polyhydroxybutyrate);
- chemical synthesis of a polymer based on building blocks, obtained by a (petro)chemical process from non-renewable resources.

Today, commercial biodegradable plastics on the open market are offered by an increasing number of manufacturers. Although there are many different materials available, they mostly fall into one of the following groups:

- plastics based on starch (starch based plastics);
- plastics based on polylactic acid (polylactide, polylactic acid, PLA);
- plastics based on polyhydroxyalkanoates (PHA's: PHB, PHBV, etc..)
- plastics based on aliphatic-aromatic polyesters;
- plastics based on cellulose (cellophane, etc..)
- plastics based on lignin.

**Plastics**, in addition to polymers, **contain** other materials and substances or **additives**, which jointly determine the possibility of processing and final characteristics of the product. These can be **additives to stabilise the materials, lubricants, pigments** (colourants), **various fillers**, and more. Although these additions represent a small percentage of all materials in plastics, it is extremely important for biodegradable plastics that also all added components are biodegradable. According to the standards for compostable plastics, it is necessary to test every additive, as well as other substances that are present in the end product (e.g. dye for printing). For components whose share is less than 1 %, it is not essential that they are compostable, but all these components must not amount to more than 5 %. Materials may not exceed the permitted levels for heavy metal content and also **may not adversely affect the quality of the compost.**

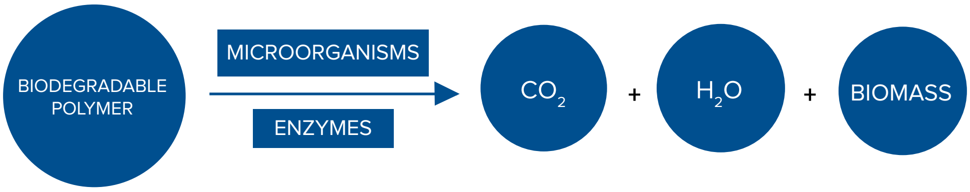
## BIOCOMPOSITES

Various **composites** containing **natural components** (often called biocomposites) are also available. **The composite is a mixture of base polymer** or plastics, **and fillers**, which improve the chemical or mechanical properties of the material, or makes it less expensive. In biocomposites, various natural **fibres** (e.g. hemp) or **fillers** such as wood flour are most commonly found. Non-modified natural fillers are, by definition, biodegradable, as needs to be the base polymer (e.g. polylactide filled with natural fibres) for us to say that the biocomposite is biodegradable. It is wrong to think that because of containing natural fillers (e.g. starch or wood flour), the non-biodegradable material will become biodegradable. Inorganic fillers are, of course, not biodegradable and therefore the biodegradability condition does not apply to them.

# BIODEGRADATION

**What happens when a biodegradable product is no longer required and is properly disposed in the biological waste stream?**

**Biodegradable polymers represent food to microorganisms. Biological degradation** thus takes place **under the influence** of various microorganisms, **which due to enzymes** they have, can decompose polymers. During the metabolic processes, biodegradable polymers in the final stage, under **aerobic conditions** are converted into **water, carbon dioxide and biomass**; under anaerobic conditions into **methane, water and biomass.** The characteristic of those final products of degradation is that they are non-toxic, and thus normally present in nature, as well as in living organisms.




In the process of degradation the first to occur is fragmentation, during which the material, under the influence of both **living and non-living factors, mechanically disintegrates**, these disintegrated products then **mineralise** in the **next phase**, under the **influence of microorganisms**. The **second phase is that essential step** that must occur, **for us to** be able to **talk about biodegradation**, because only here the **metabolism of partially degraded polymer fragments into the final products occures.**

## FRAGMENTATION + MINERALISATION = BIODEGRADATION

Due to a combination of many different structures of polymers, a large number of enzymes produced by microorganisms, and a variety of reaction conditions, the **process of biodegradation can not be unambiguously described.** In principle, the reactions can be divided into those in which the **oxidation occurs** (oxidation is a chemical reaction - burning as well as corroding are processes of oxidation; the substance, which is being oxidised, emits electrons; in this process it may, for example, merge with oxygen or emit hydrogen), and those in which **hydrolysis** occurs (a chemical reaction in which the compound reacts with water molecules and is broken down into small parts). **The reactions can be carried out simultaneously or in succession.**

At the macroscopic level, decomposition shows itself as the changing and deteriorating of the key properties of the material. These changes are mainly a consequence of the shortening of the polymer chains which define the characteristics of the polymer or plastics. Shortening of the polymer chains is manifested on the outside in the loss of mechanical properties such as e.g. tensile strength, tenacity and flexural strength. For users, the effect of decomposition in the loss of mechanical properties is easily noticeable by the reduction of bearing strength and fast or simple disintegration of the material. This process may take place under the influence of abiotic (e.g. ultraviolet light, heat, water) as well as biotic agents (enzymatic processes).

Monitoring the final step of biodegradation is based on determining the degree of mineralisation. Since, in the course of aerobic metabolism, organic carbon is converted to carbon dioxide, the most prevalent method of tracking this phase is measuring the amount of carbon dioxide, produced in a closed system. In order to work properly, it is necessary to maintain, in a closed system, a living culture of microorganisms and appropriate conditions (humidity, temperature, pH, absence of toxic substances) for their existence. In the process, from the known mass of the added polymer whose composition we are aware of – we find out the proportion or amount of carbon which it contains, and then, with a thorough measurement, we figure out how much of this carbon was, in the process of biodegradation, converted into carbon dioxide. Basically, the process is the same as that of a person who ingests food, out of which he/she acquires energy, and exhales carbon dioxide. As this method is the generally accepted basis of determining biodegradability, automated devices (respirometers) are now available that help us determine with great accuracy, the final aerobic biodegradability, and decomposition of polymeric materials under controlled composting conditions.

There are many microorganisms, which are capable of biologically degrading polymers. There are great differences between them, since they are active under very different conditions (moisture, pH, temperature), and are more or less specialised in the degradation of various substrates (the substance which microorganisms will degrade, through the functioning of the enzyme or mixture of enzymes - » food« for microorganisms). The latter is also associated with the kind of enzyme systems used, since that determines what they are able to decompose. An example of this type of specialisation includes white-rot fungi, which in nature, among other things, break down lignin, in so doing using oxidases-enzymes that catalyse the oxidation.

When testing, as a rule, we use microorganisms found in nature or in certain places where microbiological activity is increased (e.g. compost, sewage systems, wastewater treatment plants), or places where there is a presence of material which we want to decompose (e.g. production plant). It is to be expected that in these locations there are microorganisms, which are adapted to the new substrate, and thus it comes down to natural selection. Work with carefully selected microorganisms has been limited only to laboratory research, since, for practical applications (e.g. composting) the activity of natural and stable groups is intended.

# THE DURATION OF THE BIODEGRADATION AND THE RISK OF PLASTICS ENTRY INTO NATURE

If the main advantage of biodegradable plastics is their lesser durability in the environment, it is logical that the important question arises: how long does biodegradation take? In principle, it can be presumed that any organic material under the combined influence of the environment and microorganisms will in some time decompose both mechanically and chemically. In terms of the potential spread of degradation products in the environment, and in terms of the usability of plastic products which need to provide features such as load capacity, water resistance etc. - it is important to know in what amount of time they will decompose and mineralise. Knowing the biodegradation rate also affects the way the material is treated when it becomes waste.

Proper waste management of biodegradable plastics is constituted by **aerobic or anaerobic decomposition**. In the process of aerobic degradation (with the presence of air), the organic substance - with the help of aerobic microorganisms - is converted into **$CO_2$, water and cell biomass** (compost); in the process of anaerobic degradation (in the absence of air), the organic substance – with the help of anaerobic microorganisms - is converted into **$CH_4$ and $CO_2$ (biogas), traces of $H_2$ and $H_2S$, and cell biomass.**

The rate of biodegradation is therefore very important for plastics that are suitable for composting (compostable plastics). It should be noted that **only some biodegradable plastics are suitable for composting on a domestic compost heap** (along with food scraps and other household waste of organic origin). Such plastics are specially marked with a certification logo, which undoubtedly indicates that the product is suitable for home composting, which takes place at much lower temperatures than industrial composting.

OK compost VINÇOTTE

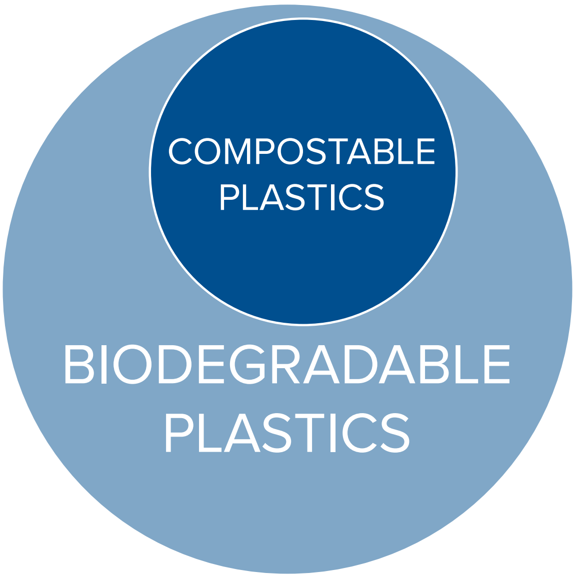
*Figure 9: Certification label attesting plastics suitable for home composting awarded by Vinçotte*

Mostly biodegradable plastics decompose during the process of industrial composting. **Compostable plastics do not introduce toxic substances into compost.**

Industrial composting is a process during which a conversion of biodegradable waste into stable, hygienised products that are further used in agriculture [3], takes place. Industrial composting is performed at higher temperatures than those in domestic composting; the temperature of the compost heap needs to be higher than 60 °C for at least one week, in order to remove pathogens [3]. In accordance with the **standard EN 13432**, more than 90 % of the material/product must be mineralised in **less than 6 months**. Compostable plastics will, during industrial composting, fragment and mineralise; and consequently the use of compost in agriculture will not lead to the leakage of plastic particles into the environment. It is important that the time required for the degradation of bioplastics is consistent with the composting cycle.

Biodegradable plastics will therefore be, in the process of industrial composting, mineralized in maximum 180 days, while conventional plastics as waste burdens the environment and does not fall apart for centuries.

It is important to be aware that **biodegradability refers to the degradation of the material under the influence of microorganisms; conditions** for decomposition and **how long decomposition will last are not defined. From a practical point of view, a more appropriate word is 'compostability', referring to biodegradability under specified conditions and within a limited timeframe.**
All compostable plastics are therefore biodegradable; but not all biodegradable plastics are also compostable, since biodegradation can take longer than the composting cycle (does not meet standard requirements for compostability). Compostable plastics are therefore a subgroup of biodegradable plastics.




## KEY MESSAGES

- *Due to the huge amount of plastic polymers, which consumers discard, a need for alternatives to artificial plastics has emerged. One of the alternatives are bioplastics.*
- *Biodegradation is a specific feature of certain plastic materials. It indicates the process of degradation of polymeric material under the influence of biotic (living) factors.*
- *In view of the origin, polymers can be divided into natural and artificial.*
- *Plastics can be biodegradable or non-biodegradable.*
- *The source for plastic material can be renewable or non-renewable.*
- *Bioplastics are biodegradable and/or maxe from renewable resources. [3]*
- *The chemical structure of a polymer determines its (un)susceptibility to biodegradation.*
- *Procedures for the production of bioplastics can be synthethical (chemical) or biotechnological (under the influence of enzymes or microorganisms).*
- *Biodegradable plastics decompose under the combined influence of abiotic (e.g. UV light, water, heat) and biotic (bacteria, fungi, algae) factors. In the first stage, the material loses physical strength and physically degrades - fragments, and in the second step, the organisms metabolise the resulting particles, and mineralisation occurs (the process of converting organic matter into inorganic forms). The end products of biodegradation are biomass, $CO_2$ and water.*
- *The product is compostable, if all its components are compostable.*
- *Fragmentation + Mineralisation = Biodegradation*
- *Biodegradable polymers are food to microorganisms.*
- *Compostable plastics are always biodegradable. Biodegradable plastics are not always compostable.*

# 2

# PLASTICS FROM RENEWABLE RESOURCES

*As already mentioned, bioplastics are plastics which are biodegradable and/or made from biomass. The combination of biodegradability using a renewable resource for the production of biodegradable plastics brings the revolutionary possibility that the complete life cycle of plastics is in line with the natural circulation of materials: plastics come from natural renewable resources, to which they are also returned. This can not be achieved with any other plastics, and is currently the best approximation to the behaviour of natural material, e.g. a leaf, which in autumn falls from the tree, and the next spring is already the base from which the new shoot grows.*

The best examples of plastics from renewable resources are: plastics from **cellulose, polylactides, plastics based on starch and plastics from soya. Polymers synthesised by microorganisms - polyhydroxyalkanoates (PHA)** – also deserve attention. Bioplastics from renewable resources represent a new generation of plastics that reduces the impact on the environment, both in terms of energy consumption and the amount of greenhouse gas emissions. Natural polymers (biopolymers) are a key component of living organisms. The most common natural polymers are polysaccharides (cellulose, starch, glycogen) and proteins (gluten, collagen, enzymes), among other forms of natural polymers are lignin, polyesters, etc...

The use of polymers from renewable resources can reduce dependence on fossil fuels. Their higher price represents an important limit to the spread of their use. The development of plastics from renewable resources is currently at its peak, but before its completely successful launched on the large markets, some limitations regarding use and processing will need to be overcome; the introduction of plastics from renewable resources in industrial production is also a problem. The question is whether it is possible to produce all currently known polymers from renewable resources on an industrial scale.

**FUNDAMENTALLY, POLYMERS BASED ON RENEWABLE RESOURCES ARE DIVIDED INTO THREE CATEGORIES:**

1. Polymers directly extracted/removed from biomass: polysaccharides, for example starch and cellulose; proteins, for example casein and gluten.
2. Polymers made by classical chemical synthesis using monomers from renewable resources. A good example for this category is polylactide, bio-polyester formed by polymerisation of monomers, i.e. lactic acid.
3. Polymers obtained with the help of microorganisms or genetically modified bacteria. The main representatives of this group are polyhydroxyalkanoates (PHA), but research in the field of bacterially synthesised cellulose is also booming.

Plastics from renewable resources are not necessarily also biodegradable (e.g. polyethylene from sugar cane).

The history of plastics from renewable resources is much longer than the history of plastics from fossil resources. The first artificial thermoplastic - celluloid, was discovered in the second half of the 19$^{th}$ Century. Since then, many compounds from renewable resources have been discovered, but the discoveries of many of them have remained commercially unexplored due to the very low prices of synthetic polymers obtained via the petrochemical industry. The rebirth of bioplastics has been happening in the last few decades. Many polymers based on renewable resources have been developed. The most commonly used polymers are starch and PLA, which in 2003 were also the only industrially produced polymers from renewable resources. Now, the production of bio-polyethylene (from ethylene) and epoxy resins from renewable resources (from epichlorohydrin) are also slowly developing.

Ideally, plastics would be 100 % derived from renewable resources. An example of that is biopolyethylene (Bio-PE) wherein the petrochemical plastics are replaced with chemically identical plastics from renewable resources. In cases where only one of the raw materials is substituted the percentage of substitution is smaller.

## RENEWABLE RESOURCES SUITABLE FOR MAKING PLASTICS

**To make plastics from renewable resources any renewable polymer** that can be chemically or biochemically transformed into a polymer which can then be converted into plastics - is suitable. In doing so, there is a possibility that **only a part** (e.g. one monomer which forms a copolymer) or only **part of the components** that form plastics come from a renewable resource. In this way we get materials that are **partially from renewable resources**. Even partial substitution of fossil resources with renewable resources (along with efficient use!) is useful, as it contributes to the conservation of fossil resources and reduces the carbon footprint (because the renewable part of the material is neutral or nearly neutral in terms of greenhouse gas emissions).

From the above-described strategies for making plastics from renewable resources the most commonly used approach is that in which a biopolymer (a natural polymer) is converted into plastics. The most known example is the use of starch or cellulose. In the case that a polymer in use is also suitable for food, we encounter an ethical dilemma: is it appropriate to use food for the production of materials? In addition to the use of polymers, the use of sugars or other natural substances which can be fermented and thus converted into biopolymers (e.g. PHA), or useful monomers (for example, lactic acid for PLA), also falls into this category. In the given situation, when the production of materials from renewable resources is relatively low, such use is not critical, but if predictions about future growth in the production of plastics (and other materials) from renewables come true - today's approach is unacceptable.

Renewable resources that we use today are called first-generation technologies, but in the future we will increasingly use the second generation technologies - "waste renewable resources", and the third generation technologies, which will be based on new industrial purposive transformations that will not interfere with the sources of food or classic waste. The third generation of renewable energy sources requires significant development some also classify specially adapted organisms (genetic engineering) in this group, which raises further questions.

The current situation is not alarming because biomass, on the whole, is relatively poorly exploited and we have a lot of room for improvement and better exploitation without additional production, agricultural burdens or eating away at basic raw materials for food. Especially great potential lies in "waste renewable resources". With these we can often combine safe handling/use of relatively burdensome waste, and production of technologically useful materials. An example is for instance the use of whey from cheese production to produce biopolymers and bioplastics. We can use proteins and sugars (for the fermentation of e.g. PHA) from whey. A similar example is the use of waste animal products (bone meal, waste from slaughterhouses and meat processing), which is in development. The quantities of such waste are considerable and today actually represent a problem and cost for safe disposal. In the future we may therefore expect the production of materials from renewable resources to become even better integrated into the emerging process of renewable resource use. Through this we will achieve greater efficiency and a lower environmental burden.

## ADVANTAGES OF PLASTICS FROM RENEWABLE RESOURCES

Plastics from renewable resources have several important advantages. They reduce the consumption of fossil fuels and carbon footprint (lower $CO_2$ emissions). If they are biodegradable, they further reduce the amount of waste that must be disposed of at landfills or burned in incinerators, by which the burden on the environment is further reduced. They are cost competitive and have the same range of characteristics and applications as plastics derived from fossil fuels.

## DETERMINING THE SHARE OF RENEWABLES IN PLASTICS

Currently there is no law demanding that manufacturers disclose the contents of renewable energy sources in a product. The proportion of renewable energy sources in plastic materials can vary from 1 to 100 %. It is determined by the isotopic analysis of carbon, through which we determine the proportion of carbon isotope $^{14}C$ present/measure its activity.

Materials, both those based on fossil fuels and those based on renewable resources, are mainly composed of carbon, which is present in the environment in three forms (isotopes): $^{12}C$, $^{13}C$ and $^{14}C$. The $^{14}C$ isotope is unstable, decays slowly and is naturally present in all living organisms. The activity of $^{14}C$ is very stable, since it is related to the concentration of the isotope in the environment, which is almost constant. When an organism dies out, it does not absorb more carbon $^{14}C$ from the environment, only decay takes place. The concentration of $^{14}C$ is halved every 5700 years. This does not affect the human life cycle; but in 50,000 years the $^{14}C$ content drops to undetectable levels. This means that the concentration of $^{14}C$ in fossil fuels is negligible.

| | | |
|---|---|---|
| Activity of $^{14}C$ 100 % | ⟷ | 100 % C from a renewable resource |
| Activity of $^{14}C$ 30 % | ⟷ | 30 % C from a renewable resource |
| Activity of $^{14}C$ 0 % | ⟷ | all C from a fossil resource |

## STARCH

Starchy foods have always been an important part of the human diet. Therefore it is not surprising that, early in human history, other applications of this natural material that is present in abundance, developed. Among other things, there is evidence that in 4000BC they were already using starch as a coating for papyrus.

Starch is a carbohydrate, a plant reserve polysaccharide; most higher plants produce it and use it as a form of storage (stock) energy. They store it inside the cells, in the form of spherical granules, the so-called starch granules. A glycosidic bond links monomer glucose units which build amylose and amylopectin - two different molecules of starch. There is more amylopectin in starch grains than amylose, between 70 and 90 %, and 10 and 30 %, respectively. Amylose is not branched, while amylopectin is branched at every 12-30 glucose residues. The presence of starch is proven with iodine solution; iodine binds itself into a helix, which results in blue colouration. Most commercially available starch is derived from corn (79 %), potato (9 %), wheat (7 %), rice, and barley. These plants contain large amounts of starch, usually between 60 and 90 % of the dry weight.

Starch in the process of composting rapidly biodegrades in many different environments. The toughness and water resistance of starch, however, are worse than in most petroleum-derived polymers, so numerous ways to overcome this are being searched. Better characteristics are achieved if the starch is blended with more waterproof polymers or if it is chemically modified.

The main component of starch plastics is starch, the structure of which is slightly modified (destructured starch). Starch can be destructured with energy and heat, and so the crystal structure is completely disrupted. Only destructured starch behaves as a thermoplastic (thermoplastics are linear and/or slightly branched polymers, capable of (multiple) softening and transformation at elevated temperatures) and can be treated as a traditional plastics; if it is used in its natural form it is too sensitive to moisture.

Thermoplastic starch-based polymers represent one of the classes of biodegradable materials that have the best short-term potential, and enable the development of fully biodegradable products for specific conditions of use. Thermoplastic starch composites can achieve a starch content of up to 50 %.

Starch-based films, which can be found on the market, are mainly made of starch, blended with thermoplastic polyesters, with the intention of obtaining a biodegradable and compostable product. When these films are used to manufacture bags for recycling organic waste, packaging and packaging materials, hygiene products and agriculture; the properties of these films are similar to those of LDPE. Destructured starch, combined with other synthetic polymers, can meet quite broad market needs. Currently, quite a lot of starch-based products are commercially available.

### PRODUCTS BASED ON STARCH:

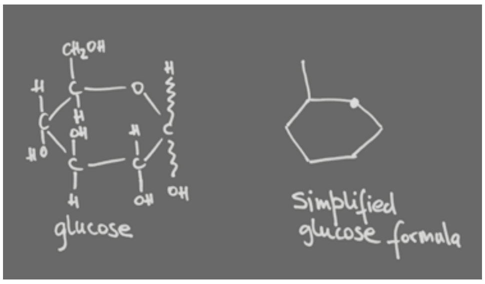
- Water-soluble chips as spacers to protect the contents of packages and other expanded materials as a replacement for polystyrene (styrofoam);
- Shopping bags;
- Bags for the bio-waste storage;
- Food packaging and packaging (e.g. bags for fruit, vegetables, bread - their important advantage over other materials is ventilation, which improves the storage conditions of these foods);
- Hygiene products and cosmetics products (nappies, sanitary napkins, toothpicks, cotton swabs,...).

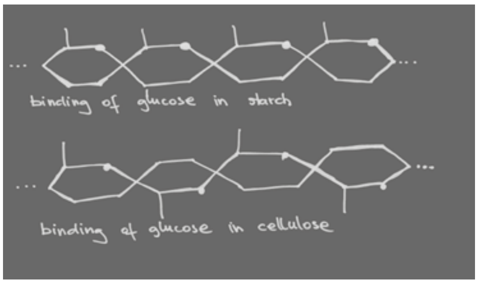
## CELLULOSE

Cellulose, as starch, is a carbohydrate. It is a structural polysaccharide, while starch is one of the storage polysaccharides. In terms of quantity, cellulose is the most represented polymer on Earth and is the main support for trees and other plants (cotton, flax, jute, sugarcane, cereals,...).

In addition to higher plants, acetic acid bacteria also synthesise cellulose. Bacterially synthesised cellulose has great potential within the packaging industry, but it is still more or less unexplored. Certain (acetic acid) bacteria can synthesise almost pure cellulose with the same chemical and physical properties as those which cellulose from plants have.

Cellulose consists of linear chains of mutually interlinked - from a few hundred to over ten thousand - glucose units, which are, as with starch, interconnected with a glycosidic bond. Although starch and cellulose have the same monomer unit, their polymeric chains differ in the orientation of glucose units.




The main sources of cellulose for industrial processes are wood and cotton. Cellulose is the main component of paper, cardboard and textiles made of cotton, flax or other plant fibres. It is also used for the production of fibres, films and cellulose derivatives. In fact, the first industrial polymers (celluloid, cellophane) were based on cellulose, though today the field of cellulose-based materials is still not fully explored. By incorporating cellulose fibres into polymeric materials, biocomposite products are obtained, which have significant additional opportunities for their handling once they become waste (composting as an alternative to landfilling). Cellulose fibres are used as a matrix for biodegradable polymer composites, in order to improve mechanical properties and hydrophobicity. Cellulose fibres are also mixed with starch, so as to achieve improved mechanical properties, gas permeability and water resistance.

### CELLULOSE, CELLULOSE FIBRE AND CELLULOSE DERIVATIVES ARE USED FOR:

- Toys,
- sports equipment,
- medical applications,
- decor,
- car interiors,
- furniture,
- construction, ...

## SOYA/SOYA PROTEIN

A lot of research on soya-based plastics was done in the 1940s. That's when soya protein was mostly used as s filler, which reduced the price of plastics based on oil. Today it is still used, this time with the purpose of increased biodegradability of plastics. In comparison to plastics from casein, zein and glycine, soya protein is also economically competitive.


The soya bean is rich in oil and proteins, usually the dry mass contains about 40 % of the protein and 20 % of the oil. Soya protein is globular, reactive and often water-soluble. Approximately 98 % of the proteins in soya beans are stored in the cell organelle, i.e."protein corpuscle".
The processing of soya protein usually takes a change of physical state, and sometimes also a chemical reaction occurs. In the case of processing polymers, there are many processes included, for example extraction, injection moulding, casting, designing,...

Research results show that soya protein itself, or mixed with starch, is suitable for the production of plastic products such as packaging, toys, sports equipment, containers,... Injection moulded plastics shows the appropriate mechanical and water resistance properties. After use these products are collected and recycled, thus lessening the burden on the environment.

Films made of soya proteins show good characteristics as barriers to oxygen, as well as to UV-radiation. Thus, they are useful for packaging materials. They are also useful for foils in agriculture, which, after they are no longer needed, need not be removed from agricultural land, as they biodegrade. As far as they are correctly processed, soya proteins may be processed into foam products of different densities; as they may also be processed into insulation materials with different thermal properties.

The biodegradability, non-flammability and non-electrostaticity of plastics from soya proteins represent unique and attractive attributes. Along with the economic competitiveness of plastics from soya sources, it represents an environmentally friendly and promising alternative to conventional plastics.

## POLYLACTIC ACID (PLA)

Polylactic acid (polylactide) is the most widely used biodegradable aliphatic polyester. The monomer, lactic acid, is found in blood and muscle tissue as a metabolic product of the metabolism of glucose. The co-polymer is formed in the process of the chemical polymerisation of lactic acid. Lactic acid is produced via the fermentation of glucose, which can be obtained from various sources of sugar (cane sugar, potatoes and tapioca). Polylactic acid is water-resistant and unstable in the halogenated hydrocarbons. It is developed primarily for degradable packaging materials and in the industrial composting process it decomposes within three weeks. Industrial production of polylactic acid started in 2002. Polylactide became the first polymer from renewable resources to be produced on an industrial scale.

PLA is currently used for packaging (cups, bowls, foils and food storage containers), textiles (t-shirts and furniture textiles), hygiene products (nappies), foils for agriculture and cutlery. Foamed polylactide is used as an insulator and is an alternative to foamed polystyrene (styrofoam). Polylactates have good mechanical properties, similar to PET and PP. Danone's yogurt pots are thermoformed pots made from polylactic acid.

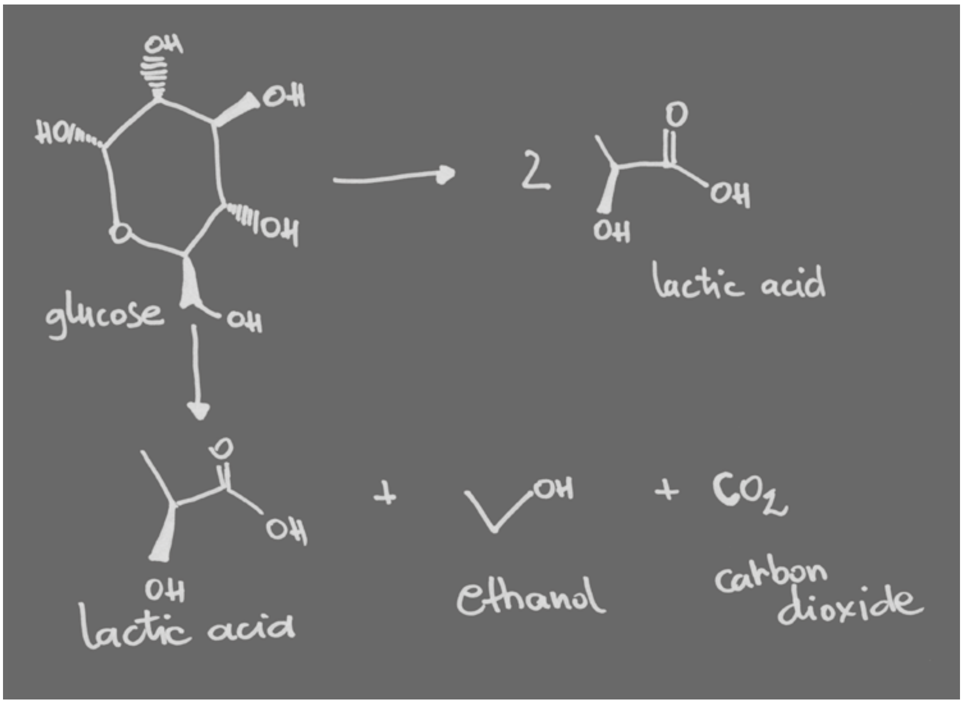



*Figure 10: two types of bacterial production of lactic acid*

## POLYHYDROXYALKANOATES (PHA)

Polyhydroxyalkanoates are natural aliphatic polyesters, synthesised through the fermentation of sugar and lipids (glucose, sucrose, vegetable oils, even glycerine from the production of biodiesel) by a wide variety of bacteria, as an intercellular carbon and energy reserve, when the cells grow in stressful conditions. They can combine more than 150 monomers, thus obtaining materials with various characteristics. Polyhydroxyalkanoates are biodegradable, and biodegradation usually takes place with enzymes. They can change mechanical and biological compatibility by mixing, altering the surface or combining polyhydroxyalkanoates with other polymers, enzymes or inorganic materials, which allows them a wider range of uses.

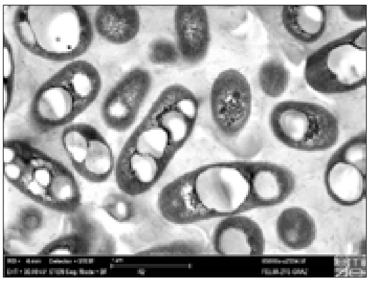


*Figure 11: Polymer granules inside the bacteria (Source: M. Koller, TU Graz)*

For production, bacteria are grown in a suitable medium and are supplied with a sufficient amount of nourishment so that they grow fast. When a bacterial population reaches the desired size, the composition of nutrients is changed, thus encouraging bacteria to synthesise PHA. The quantity of PHA in the intercellular spaces may represent up to 80 % of the dry weight of the organism. Bio-synthesis of PHA is usually encouraged in conditions of shortage (shortage of certain micro-elements: phosphorus, nitrogen, elements in traces or lack of oxygen) and excess amounts of carbon. Synthesis with the help of a microorganism in the soil can be profitable: the lack of nitrogen or phosphorus stimulates the bacteria to produce one kilogram of the polymer out of 3 kilograms of sugar. Depending on the culture of bacteria, homo- or co-polyesters are produced. Polyesters are stored in the body in the form of granules.

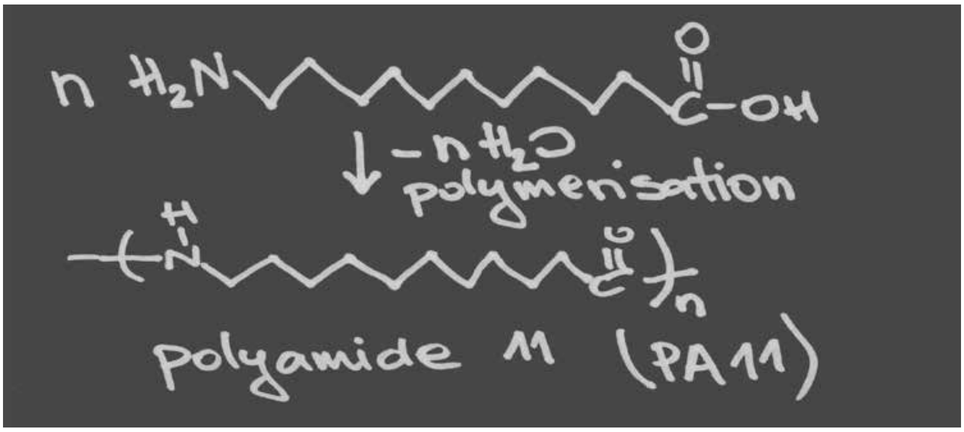
PHA polymers are thermoplastics and can be cultivated/treated with equipment for processing conventional plastics. They are used as hardeners in cosmetic products, for hygiene products, packaging products and golf tees. Contrary to other types of bioplastics (e.g. PLA), PHA plastics are UV stable, they whitstand temperatures up to 180°C and hardly leak water. Polyhydroxybutyrate is a barrier for moisture and odours, and is in terms of its characteristics similar to polypropylene.

## POLYAMIDE 11

If a polymer is obtained from a renewable resource it does not necessarily imply that it is also biodegradable. Such an example is polyamide 11 (nylon 11). It is obtained from castor oil, is highly water-resistant and also has other desired thermic, physical, chemical and mechanical characteristics. It is resistant to chemical and thermic influences and is thus versatilely useful. At the same time it is affordable and it is used for electrical cables, in the automotive industry and for pneumatic and hydraulic pipes. It is used in areas where safety, durability and versatility are key, and is often a cheaper alternative than metals and rubber in high-tech applications.

The development of polyamide 11 started in 1938 with the production of undecanoic acid by cracking castor oil. Cracking is a high-temperature and/or catalysed procedure of splitting large hydrocarbon molecules into smaller ones. Pilot production started in 1944, and industrial production 11 years later in France.

From the seeds of the plant Ricinus communis first the oil is extracted and then converted into polyamide 11. The seeds are ground, and the process of the separating oil from the seeds is carried out in two possible ways: by crushing and/or by extraction with solvents. Castor seeds contain almost 50 % oil.




## BIO-POLYETHYLENE

Just as polyamide 11, bio-polyethylene is also obtained from renewable resources (sugar cane), it is not biodegradable and its characteristics are the same as those of polyethylene obtained from oil. Bio-polyethylene is mostly used for packaging.

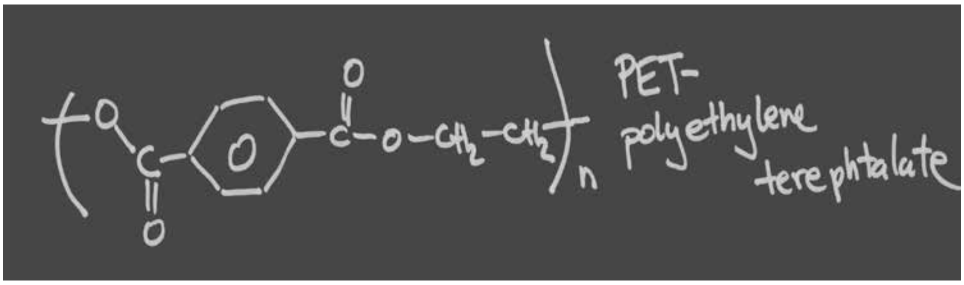
Polyethylene from renewable resources is obtained by polymerisation of ethylene, obtained from renewable resources. Many plants produce ethylene during the gestation of their fruit. Industrial production of ethylene is based on the dehydration of ethanol. The emergence of polyethylene on the basis of renewable resources is not new, since it first emerged about 40 years ago in India, where ethanol was processed into ethylene and then into PE, PVC and styrene. In Brazil in the 1980s, ethanol was used for processing PE and PVC. Later, the production of bio-polyethylene decreased due to low oil/petrol prices, but today – due to global warming awareness and limited amounts of non-renewable resources (which also reflects on the rising prices of oil) – bio-polyethylene is becoming attractive again.

The production of bio-polyethylene is based on the use of sugar cane as the source of ethanol. The sugar cane is cleaned and crushed in a sugar grinder. Thus the main product, sugar-cane juice, is obtained, as well as so called 'bagasse', a by-product. In Brazil, the by-product is usually used to produce energy to power the mill. The rest of the energy is usually sold to the electricity grid. The sugar cane juice is then fermented to ethanol in anaerobic conditions. The obtained ethanol is distilled in order to create 98.5 % ethanol that is then dehydrated at temperatures between 300 and 600 °C.

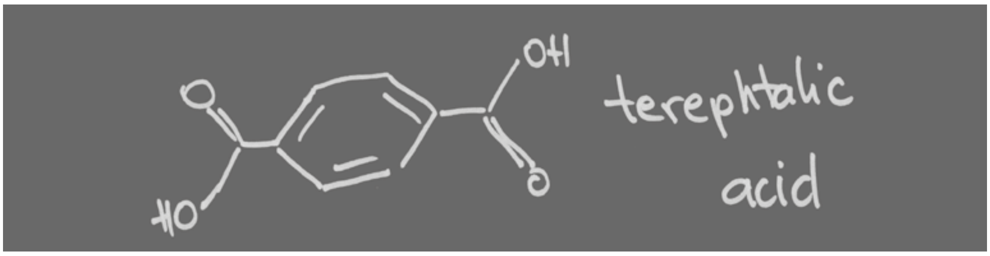
**Sugar cane** —*fermentation / distillation*→ **Ethanol** —*dehydration*→ **Ethylene** —*polymerisation*→ **Bio-polyethylene**

Polyethylene from renewable resources is an important chemical in the chemical industry. It is by far the most important product obtained from ethylene, and also an important intermediate (by-product) for producing PVC, PET, PS and polyols for polyurethanes (PUR). PE and PVC from renewable resources are slowly coming into mass production, and in the future it is possible to expect more polymers based on ethylene from renewable resources. PE from renewable resources can be used for the same products as PE from fossil fuels.

## BIO-POLYETHYLENE TEREPHTHALATE (BIO-PET)



Polyethylene terephthalate (PET) is plastics made of ethylene glycol (e.g. one of the main ingredients of antifreeze – a liquid against freezing) and terephthalic acid (TPA), and is mainly used as a material for the production of plastic bottles. Recently PET containing 30 % material (by weight) from renewable resources was developed and came in use. That 30 % is represented by ethylene glycol (EG), obtained from sugar cane. The problem in obtaining 100 % biobased PET is the production of terephthalic acid from renewable resources. Terephthalic acid is a colourless liquid, mostly used as a precursor for production of PET. The main resource for the production of terephthalic acid is para-xylene, obtained from toluene in the presence of a catalyst. In November, 2001, Japan announced that it had synthesised the first PET based merely on renewable resources. They obtained terephthalic acid from para-xylene, which was obtained from biomass via isobutanol as the intermediate product.




**Production of ethylene glycol from renewable resources:**
The most recognised is the way of synthesis from plant fibres (cellulose being the source material) which are converted into EG using a catalyst. For a long time, platinum was used as a catalyst, which was reflected in high costs. In 2008, platinum was replaced by tungsten carbide and hydrogen as the catalyst, which reduced production costs. A key step is the decomposition of cellulose fibres. Cellulose consists of hydroxyl groups and oxygen atoms, among which hydrogen bonds are formed that make cellulose almost unpenetrable. Cellulose is thus inert to many reagents, though under certain conditions (P=60 bars and a hydrogen atmosphere) hydrogen gas can penetrate through the structure of cellulose and split the cellulose into small molecular fragments. The catalyst can further reduce the molecules.
According to the large amounts of antifreeze and PET used every year, the annual consumption of ethylene glycol is very high (20 million tons).

**Other ways are also possible, for example:**

- Oxidation of ethylene to ethylene oxide, followed by hydrolysis to ethylene glycol. The source of ethylene can be methionine (enzyme use) or dehydrated ethanol.
- The reaction of methanol (source: fermentation) and formaldehyde (source: lower alkyl alcohols) in the presence of a catalyst (organic peroxide).

## KEY MESSAGES

- *Biodegradable plastics can be produced from renewable resources.*
- *Plastics from renewable resources may be either biodegradable or non-biodegradable.*
- *Biodegradability is not a characteristic linked to the origin of the substance, but only linked to the chemical structure and the environment in which degradation takes place.*
- *Pursuing sustainable development objectives and reducing environmental burdens, we strive to increase the use of biodegradable plastics from renewable resources.*
- *The share of renewable resources in plastic materials is determined by isotopic analysis of carbon.*
- *With the increased use of renewable resources to produce plastics, the use of fossil resources and $CO_2$ emissions are reduced.*
- *The potential of renewable resources for processing into plastic products is not fully exploited.*
- *For processing into bioplastics, a wide range of natural polymers is available. Most commonly used are starch, polylactides, polyamide 11 and epoxy resins based on renewable resources.*

# 3

# BIODEGRADABLE PLASTICS IN EVERYDAY LIFE

*Despite living in an era where we are constantly in touch with new information, many people have never encountered the concept of biodegradable plastics. That is why they could not have thought, an alternative product to that they normally buy, exists. Informing and raising consumers' awareness about their choice is crucial for the successful launch of new niche products on the market. As long as people are not aware they have a choice, changes will not occur. But it always starts slowly, and at the beginning ...*

## PLASTICS AT EVERY STEP

Each of us uses and discards many plastic products daily. The vast majority of food is packaged in one of the plastic polymers (PET, PP, LDPE, HDPE, PS,...), we use plastic bags to transfer things, electronic equipment casings are made of plastics, as well as toys and our sports equipment. Even the car interiors are made of plastics.

According to the development of the technologies, we could – in principle – produce most of the products that are currently made out of artificial plastics and are not biodegradable, out of biodegradable plastics. Realistically, that is not to be expected. The range of biodegradable materials and product production is smaller and hence more expensive. Biodegradable materials are slowly creating smaller markets and are not yet competitive with the big ones that are dominated by artificial (plastic) mass which have been produced effectively and on a massive scale for decades already.

## POSSIBILITY OF CHOICE

In such a case, the consumer has a lot of power. The markets are based on the principle of supply and demand. With increasing demands, the supply also grows, followed by growing production and fall in prices. The more people wanting to buy products made of bioplastics, the greater the need for their production, therefore their prices will eventually fall. Unfortunately this does not happen overnight, so it is necessary to inform consumers about their choices, teach them about the aspects of new possibilities and remind them of other people that will live on Earth after them and also – as them – needing drinking water, clear air and unpolluted soil for food production.

## HOW TO RECOGNISE BIODEGRADABLE PRODUCTS?

Since biodegradable plastics normally do not seem different from the more common, non-biodegradable plastics, we need to rely on marks and labels on products to identify biodegradable products, which indicate whether the product is biodegradable or suitable for composting. That is clearly stated by a certification mark that needs to contain also the certificate number. Labels such as "100 % degradable" or "environmentally friendly", at the absence of a certification mark, do not assure actual biodegradability and may mislead consumers.

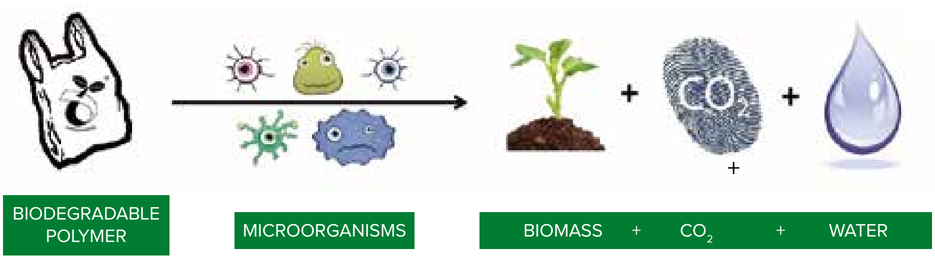



*Figure 12: The fate of biodegradable bag*

When deciding about buying a product made of biodegradable materials in a shop, you should be careful that it does bear a certification mark and certificate number. You may come across one of the following:

| COUNTRY – CERTIFICATION BODY | LOGO |
|---|---|
| USA – Biodegradable Products Institute | Source: Biodegradable Products Institute |
| EU – DIN CERTCO and Australia – Australasian Bioplastics Association (for industrial composting) | Source: European Bioplastics |
| EU – Vincotte (for industrial composting) | Source: AIB Vincotte; Source: European Bioplastics |
| EU – Vincotte (for home composting) | Source: AIB Vincotte |
| EU – Vincotte (degradability in the soil) | Source: AIB Vincotte |
| EU – Vincotte (degradability in water) | Source: AIB Vincotte |

## QUALITY OF PRODUCTS

Every consumer's worry, that a product made of biodegradable plastics are of lower quality than those of artificial plastic mass, is superfluous. Biodegradable plastic bag has the same characteristics as a non-biodegradable one; its degradation will occur after a longer period of time and under the right conditions (especially under industrial composting conditions), and not before the product would have served its purpose.

## WHAT TO DO WITH BIODEGRADABLE PLASTICS WHEN THEY BECOME WASTE?

By no means do we dispose of biodegradable plastics in the natural environment; and likewise we do not dispose of compostable plastics there. It is true that both biodegradable plastics and compostable plastics will decompose in nature, but quite some time is needed for that. In the meantime, they represent a pollutant in nature, which just like all the other waste, poses a danger to animals and spoils the environment. One of the key factors of industrial composting is high temperature, therefore degradation in the natural environment (land or water) takes much longer time.

After the use of biodegradable plastic product, place it among organic waste (brown containers ).

Proper waste management of biodegradable plastics is either aerobic (composting) or anaerobic (biogas) decomposition. We should not place biodegradable plastics into the normal waste bins for packaging (yellow container ), since due to its different processing characteristics it can create problems when recycling all the other, non-biodegradable types of plastics.

Biodegradable plastics decomposition optimally takes place under conditions of industrial processing of organic waste. This process is slower in nature which is why we do not dispose of biodegradable (as well as non-biodegradable) plastics into the natural environment.

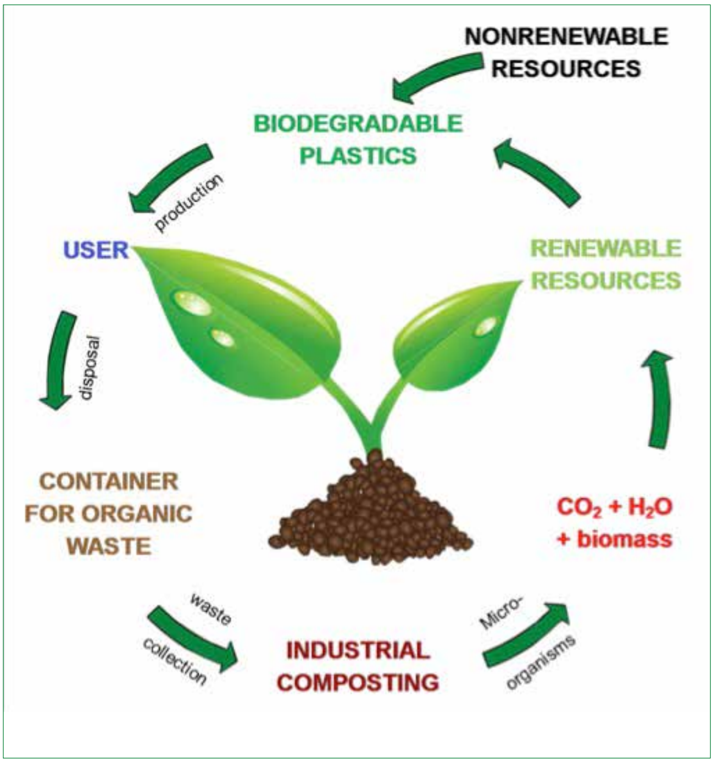
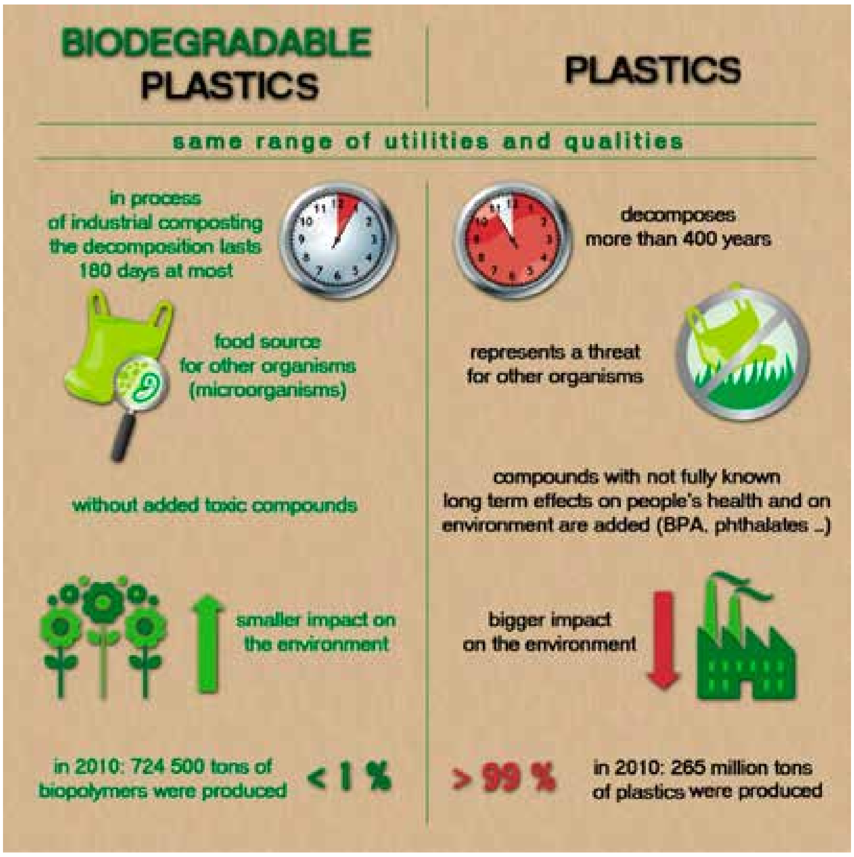
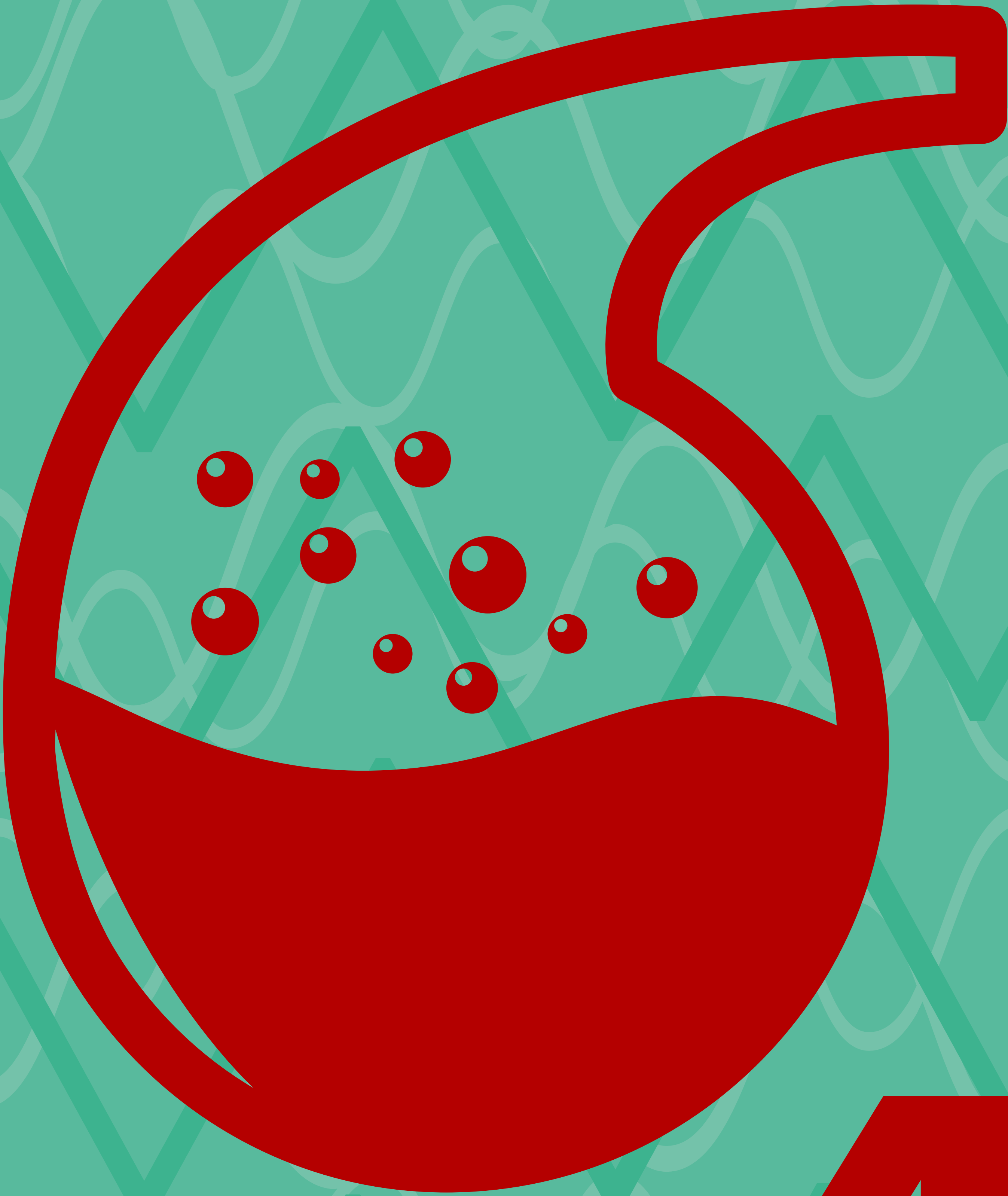



*Figure 13:The life-cycle of biodegradable plastics*

## KEY MESSAGES

- *Life without the use of plastic products is practically unimaginable.*
- *Every consumer has the power to accelerate the launch of biodegradable plastics on the markets.*
- *The range of biodegradable plastic products and their use is persistently growing.*
- *The certification mark undoubtedly confirms a product's biodegradability.*
- *The characteristics and quality of products from biodegradable plastics are equal to those from usual, non-biodegradable plastics.*
- *We do not dispose of biodegradable plastics in the natural environment. Biodegradable plastic waste should be placed into the organic waste bin.*
- *By buying a biodegradable plastic product we reduce the burden on the environment, include plastics in natural circulation and follow objectives of sustainable development.*





# 4

# SUGGESTIONS FOR EXPERIMENTS

*In addition to biodegradable bags, foil wrapping for grocery vegetables, plastic granules from polylactic acid and other products made of biodegradable plastics that you can show your students - there are three practical experiments that you can perform together with the students, described below. The first one is very short and suitable to include into your lesson, since you do not need more than a few minutes, a cup and some water. The second and the third experiment are suitable for laboratory practice.*

## 1. A QUICK ILLUSTRATION OF THE DIFFERENCE BETWEEN STARCH PACKAGING PEANUTS AND POLYSTYRENE PACKAGING PEANUTS

Place a piece of polystyrene, which is comparable in size with a piece made of thermoplastic starch, into a cup of water. Stir and shortly (within minutes) you can notice that the starch peanut dissolves in water, while the polystyrene remains unaffected.
The experiment illustrates how a starch peanut is susceptible to dissolution in water and would therefore rapidly disintegrate in the natural environment, while polystyrene remains in unchanged form for a longer time.

## 2. PLASTICS FROM POTATOES

In the laboratory we can easily make plastics out of renewable resources – potato. Follow the steps below, and for better illustration take a look at this short video (http://www.youtube.com/watch?v=VUkyW1Pir9g&feature=related).

### MATERIALS:

*Potato*
*Water*
*Mortar and pestle*
*Grater*
*Measuring cylinder*
*Cups x3*
*Glass stick*
*Oven*
*Laboratory scales*
*0.1 M HCl*
*0.1 M NaOH*
*Glycerol (2 mL)*
*A little glass saucer to cover the cup*
*Burner*
*Tripod*
*Universal indicator*
*Petri dish*
*Food colouring*
*Protective equipment*

### PROCEDURE:

1. *peel one large potato and grate it into the mortar*
2. *add 100 mL of water*
3. *in the mortar, crush the potato, covered with water, with the pestle*
4. *pour the new formed liquid, gathered in the mortar, through a strainer into the cup*
5. *again pour water over potato in the mortar and pour the liquid through the strainer into the same cup*
6. *after about 7 minutes, a sediment of starch gathers on the bottom of the cup*
7. *the fluid above starch sediment simply pour into another cup, so only the starch sediment remains in the first cup*
8. *pour 100 mL of water over the starch sediment and stir it with the glass stick*
9. *wait for the starch to sediment again (about 7 minutes) and simply pour the water into the second cup, so that only pure, wet starch remains in the first cup*
10. *dry the starch from the first cup in the oven (about 10 minutues at 80 °C), what remains is white starch dust*
11. *add 25 mL of water and 3 mL 0.1 M HCL to the 2.5 grams of dry starch dust, that we have in the cup, and stir with the glass stick in order to get a hazy white solution*
12. *add 2 mL of glycerol to the cup and stir with the glass stick*
13. *cover the cup with the glass saucer and place on the tripod, under which we have placed the burner – warm it above the flame for 15 minutes*
14. *after 15 minutes turn the burner off, carefully remove the hot cup and wait for it to cool*
15. *with the glass stick, apply some substance from the cup onto the universal indicator – it turns red, which means the substance is acidic*
16. *add a little 0.1 M NaOH and stir with the glass stick*
17. *again apply the substance to the universal indicator – it turns green which means the substance now has a neutral pH*
18. *pour the substance from the cup, using a glass stick, into the petri dish and spread out evenly*
19. *if you wish, add some food colouring and stir with the glass stick, so that your plastics will be coloured*
20. *dry in the oven [for how long + at which T – data not available in the video] and you have yourself plastics from potato!*

This is how you can easily and quickly create plastics out of potatoes yourself. Learners can compare this plastics (in appearance, touch, solidity, flexibility) to the plastics derived from fossil fuels.

## 3. PLASTICS FROM CORN STARCH

### MATERIALS:

*Burner*
*Pot*
*A spatula for stirring*
*Teaspoon*
*Tablespoon*
*Water*
*Corn starch*
*Glycerol*
*Acetic acid - glacial*
*Plastics grounding, onto which we spread the plastics at the end of the experiment*

This is a simple and quick technique for making plastics out of corn starch. The experiment is similar to the previous one, except it is faster to make, since you can use already prepared starch to make plastics, whereas in the previous attempt you make the starch on your own from potato. For better illustration watch the short video: http://www.youtube.com/watch?v=5M_eDLyfzp8

### PROCEDURE:

1. *Measure out 1 tablespoon of corn starch, 4 tablespoons of water, 1 teaspoon of glycerol and 1 teaspoon of acetic acid, into the pot. Stir well.*
2. *When it is all well mixed, turn on the stove and continue stirring. At first, there will be a milky white liquid in the pot, that will soon start to thicken.*
3. *Continue stirring, while the liquid is thickening. When it becomes sticky and almost transparent, turn the stove off and smear the substance as thick as we wish onto the pre-prepared base, and let it cool.*

## 4. COMPOSTING

### MATERIALS:

*Soil/compost*
*Scales*
*Glass cup/planting pot*
*Mosquito net*
*Water*

*Different materials (apple slice, banana peel, fabric, freezer bag (PE), coin or nail, paper, biological waste bag made of compostable plastics – pay attention to the certificatory mark)*

This experiment can last the whole year. At the beginning of the school year place samples into compost/soil, then check every month what is happening with the material. Composting teaches the learners an important lesson – recycling and re-use of materials. It includes soil, digging and water.

### PROCEDURE:

1. *Fill half the cup/planting pot with soil/compost.*
2. *Fasten the composting materials into the mosquito net and weigh perhaps even photograph the prepared sample. Attach the sample to some fishing line or metallic string, place into the cup/pot, bury it in the soil and top it up with some water.*
3. *Once a month dig the samples out, wash, dry and weigh them, then re-bury them.*

Thus we monitor the decomposition of different materials over a long period of time and can particularly compare the decomposition of a usual polyethylene bag with decomposition of a compostable biological waste bag.

Since the composting temperatures will not be the same as those during industrial composting, it is likely the degradation of compostable bag will take longer than 6 months.

# GLOSSARY OF TERMS

***Aerobic degradation*** *- biological decomposition in the presence of oxygen or air, where carbon is converted into carbon dioxide and biomass*

***Anaerobic degradation*** *– biological decomposition in the absence of oxygen or air, where carbon is converted into methane and biomass*

***Biological degradation (bio degradation)*** *– degradation under the influence of biological systems*

***Biomass (renewable resources)*** *– substances of biological origin, with the exception of those in geological formations and fossilised organic substances*

***Bioplastics*** *– plastics, that are biodegradable and/or based on biomass. In medicine also use which means biocompatibility – compatibility of plastics with human or animal tissues is possible*

***Biopolymer*** *– is a polymer, obtained from either renewable resources and/or is biodegradable*

***Biodegradable plastics*** *– plastics, that are, in relation to conditions of the process, aerobic or anaerobic, entirely degradable into carbon dioxide, methane, water, biomass and inorganic materials*

***Certificate*** *– A written statement, issued by an authorised organisation, which confirms that the material or product conforms to the standard. The certificate includes permission to use the certification mark (logo), which informs the users about the adequacy standard.*

***Fragmentation*** *– physical (mechanical) degradation of substances/material into smaller parts*

***Hydrolysis*** *– a chemical reaction, in which compounds react with water molecules and split into smaller parts*

***HDPE (High Density Polyethylene)*** *– high density polyethylene*

***Composting*** *– the process of organic waste treatment, in which aerobic microorganisms biologically decompose organic material*

***Compostable plastics*** *(plastics suitable for composting) - plastics, that are (under composting conditions) biodegradable at a rate, comparable to the compost cycle, and that meets the requirements of the corresponding standards*

***LDPE (Low-density polyethylene)*** *– low-density polyethylene*

***Mineralisation*** *– the process of conversion of organic carbon into inorganic forms ($CO_2$), that occurs under the influence of metabolism of microorganisms*

***Oxidation*** *– a chemical reaction (e.g. burning, corrosion); a substance that becomes oxidised, emits electrons; in this process it can, e.g. merge with oxygen or it emits hydrogen*

***PE (Polyethylene)*** *– a plastic polymer with a wide range of applications*

***Persistent organic pollutants (POPs)*** *- organic compounds that are resistant to decomposition in the environment through chemical, biological, photolytic processes; e.g. pesticides*

***Plastics*** *– material, whose main components are polymers*

***Plastics based on renewable resources*** *– plastics that are produced from renewable resources (e.g. cellulose, lignin, starch,….), and not from fossil fuels*

***Polymer*** *– a substance with a high molecular mass, made of perennial basic elements*

***PP (Polypropylene)*** *– plastics with a wide range of applications*

***PS (Polystyrene)*** *– one of the most commonly used plastic types*

***Thermoplastics*** *– linear and/or slightly branched polymers, capable of (multiple) softening and transformation at elevated temperature (HDPE, LDPE, PP, PS, PVC, PET,…)*

***Sustainable development*** *– development that meets current needs, without jeopardizing the chances of future generations to meet their own needs*

## SOURCES AND LITERATURE: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