

Bio-based polymers

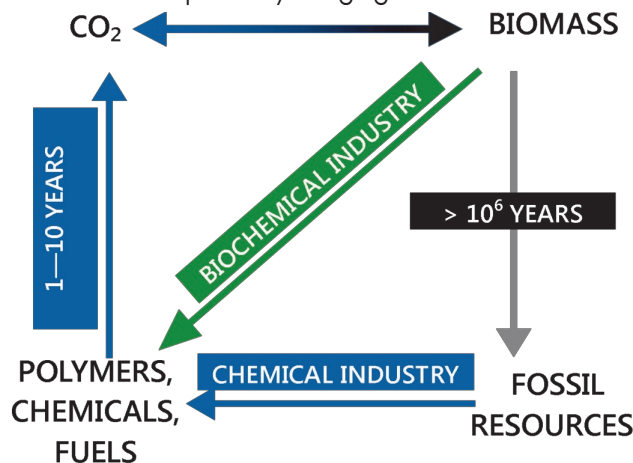
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Recently great attention is given to the concept of sustainable development. The most widely accepted definition of sustainable development is “development that meets the needs of the present without compromising the ability of future generations to meet their own needs” (World Commission on Environment and Development’s report “Our Common Future”, 1987). For a transition to a higher level of sustainability development it is necessary to make a number of technological and social changes, and one of these is to develop alternative resources of raw materials. This brochure presents the issue of renewable resources use for polymer and plastics production.

Carbon cycle and greenhouse effect

The intensive use of mineral resources (oil, coal, gas) results in their significant depletion but also brings a negative contribution to climate changes on the planet. Observable climate changes are directly related to the “greenhouse effect”. This effect is caused by an increase in the concentration so called green house gases (GHG) in the atmosphere that change the energy flows of our planet. The most abundant GHG is carbon dioxide resulting from emissions from fossil resource use. Transition to the use of renewable resources would allow to decrease the greenhouse effect and to reduce carbon dioxide emissions to the atmosphere by bringing into balance the “carbon cycle”.



The carbon cycle is the most important cycle of our ecosystem and it is balanced in the absence of influence of the results of human activity: the carbon dioxide produced by breathing of all living beings on the planet turns into organic compounds in the cells of plants by photosynthesis. Interference of man by introduction of mineral (fossil) resources into the carbon cycle leads to imbalance: transformation of organic substances of plant origin into mineral resources (e.g. prehistoric woods into oilfields) required millions of years while release of carbon dioxide from fossil-based products (fuels, chemicals, plastics, etc.) is done much faster (1-10 years). Thus “fossil sourced” carbon dioxide, that used to be in the form of immobilized mineral resources, enters the carbon cycle. The concentration of carbon dioxide



in the atmosphere increases since the overwhelming CO₂ emissions cannot be taken up by photosynthesis or other natural sinks. Hence it accumulates in the atmosphere, causing the "green house effect" leading to global climate changes.

Polymers and plastics are almost entirely based on fossil sources. A transition to the use of renewable resources (biomass) for the production of polymers would reduce the contribution to the greenhouse effect and would also allow us to preserve mineral resources for future generations.

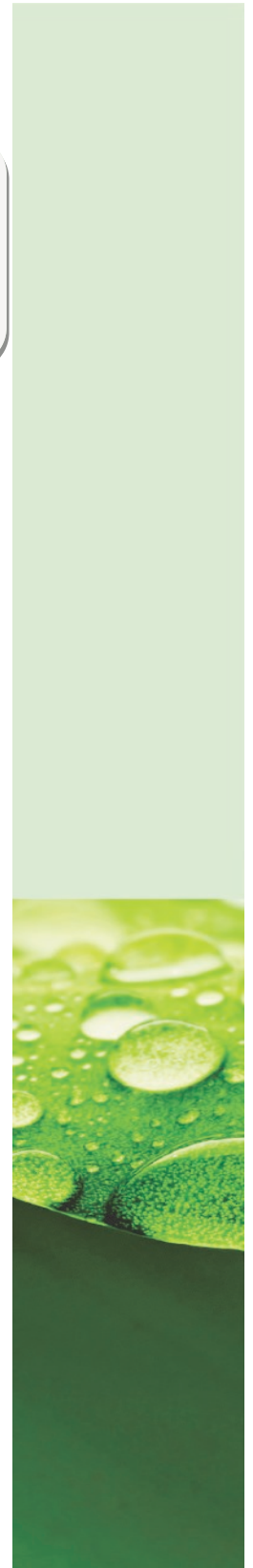
Renewable resources for polymer production

Polymers can be produced from various renewable resources. Currently resources most used for this purpose are products and byproducts from the agricultural sector that are rich in carbohydrates – especially saccharides, such as grain, sugar beet, sugar cane, etc. The use of food and feed resources for material production (so called 1st generation bioresources) is commonly presented as a weak point of this approach although all new studies show that there is no need to compromise life-sustaining production. (European Bioplastics study) Unsurprisingly all current research and development in the development of bio-based materials is focused on non food and feed renewable resources and waste resources such as lingo-cellulosic resources, agricultural waste, food waste, etc. (often referred to as 2nd generation bioresources).

Polymers from renewable resources

Use of natural polymers

Natural polymers are very common and widely spread, since they form the basis of all animals and plants for example as proteins and carbohydrates. Nature also provides numerous polymers and natural polymer composites that are very successfully used in many practical applications. Natural fibers such as cotton and hemp and wood as a composite are good examples. However **natural polymers in their native form are unsuitable to be used in the same way as plastics and need to be modified chemically, thermally or mechanically in order to gain technological usefulness.** Examples of modified natural polymers are cellulose acetate made by chemical modification of cellulose with acetic acid, vulcanized rubber produced by heating natural rubber under pressure in the presence of sulfur), thermoplastic starch produced from granular natural starch that is made amorphous through the application of heat, stress and plasticizers.



Among natural polymers **polyhydroxyalkanoates (PHAs)** are a very particular polymer class. Chemically they can be described as linear aliphatic polyesters and due to their thermoplastic behaviour (ability to be melted and shaped) they can in principle **be used directly as plastics without modification**. Polyhydroxybutyrate (PHB), the first discovered polymer from this group, occurs naturally in low amounts in the cells of some microorganisms and serves them as energy reserve material. In the 20th century scientists succeeded to obtain PHB in high yields in the cells of microorganisms through fermentation. It was also found out that by varying the type of carbon source, "digested" by microorganisms, different types of PHAs (with different chemical structures) can be synthesized. Production of PHAs consists of two steps:

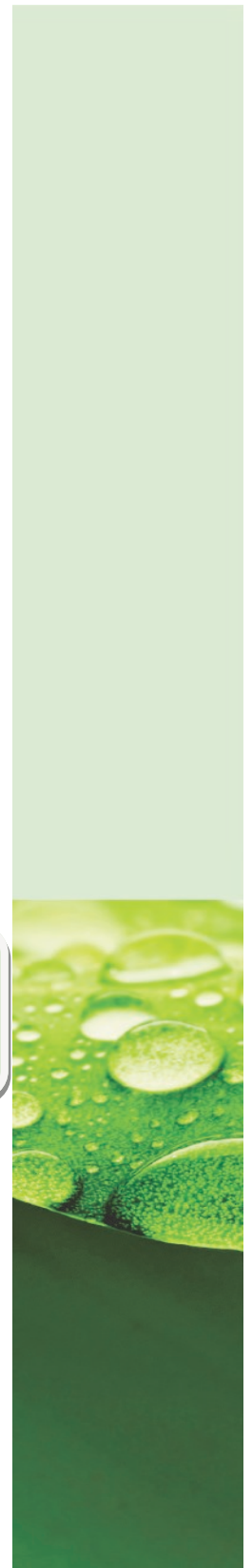
- 1) Fermentation, i.e. bio-chemical synthesis of PHAs in the cells of microorganisms using different carbon sources such as sugars, vegetable oils, fatty acids, etc) and
- 2) 2) extraction of the synthesized polymers from the cells. Several types of PHAs and their blends are available on the market.

They possess a variety of properties making them amenable for production of different types of final products: films, sheets, moulded articles, fibres, etc. PHAs are biodegradable. Because PHAs are biocompatible and bio-resorbable polymers they can be used in medicine, as well.

Building-blocks from renewable resources

By fermentation of renewable resources it is also possible to synthesize different building-blocks (intermediate substances), that can be further converted to polymers by reactions of polymerisation.

The production of the building-blocks can proceed through biochemical transformations (for example fermentation of sugars to lactic acid or succinic acid) or through chemical processes (for example hydrolysis of lipids to fatty acids and glycerol). The production of a polymer normally proceeds through classical chemical processes. In this way it is possible to synthesize newer bio-based polymers that are not made from fossil resources (for example polylactide) or bio-based variants of long known polymers that are normally made from fossil resources, such as bio-polyethylene or bio-polypropylene. The later bio-based "classical" polymers have exactly the same properties as petrochemical analogues and can replace them in all applications without additional modification. In addition it is possible to make partially bio-based polymers, normally co-polymers in which at least one building block (co-monomer) is bio-based. An example of this practice



is partially bio-based polyethylene terephthalate (bio-PET). Some examples of bio-based building blocks that have considerable potential are:

Lactic acid is an aliphatic hydroxy acids that can be used for the production of linear polyesters, in this case polylactic acid (PLA) also known as polylactide since lactide is. Production of PLA consists of 3 steps: 1) fermentation of sugars and starch for producing lactic acid and 2) production of lactide - a cyclic dimer of lactic acid that is in reality the monomer for the preparation of the polymer, and 3) the polymerization of lactide into PLA. PLA is a thermoplastic aliphatic polyester with properties comparable with those of classical thermoplastics (e.g. polystyrene) and can therefore find application in different areas, such as production of packaging materials (films, bottles), disposable dishes, sheets, fibres, etc. PLA biodegradable in industrial composting and since it is biocompatible and bio-resorbable polymer it finds also applications in medicine.

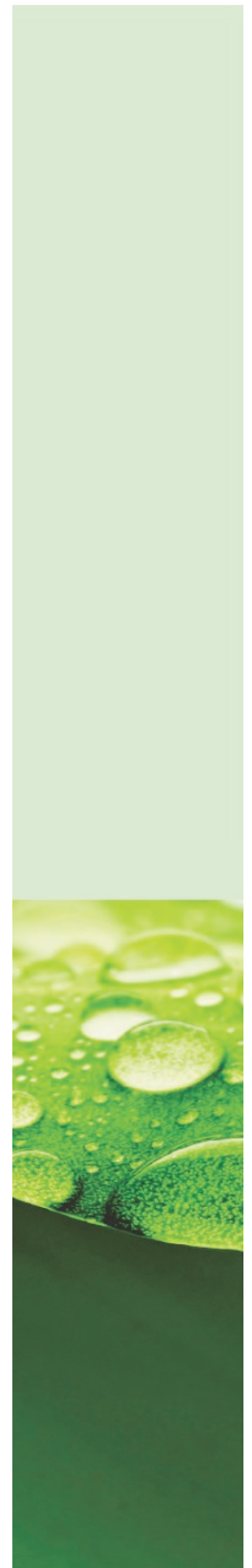
Ethanol produced by fermentation from renewable resources can be used as a bio-fuel but also as a raw material for polyethylene (PE) production.

Production of PE from renewable resources consists of several steps:

- 1) Synthesis of ethanol by fermentation process from sugars, extracted from natural materials e.g. sugarcane,
- 2) Chemical dehydration reaction transforming of ethanol into ethylene, and
- 3) “Classical” reaction of polymerisation of ethylene into polyethylene.

Bio-PE is chemically identical to fossil-based PE, has the same technical properties and is not biodegradable. PE in its different variants (LDPE, HDPE, LLDPE) is the plastic with the largest global production volume therefore the ability to efficiently produce bio-PE is of considerable importance. The same strategy can be used to achieve production of polypropylene (PP) another high-volume plastic of importance.

Ethylene glycol and terephthalic acid are monomers used in the synthesis of polyethylene terephthalate (PET) - a widely utilized **material** for beverage, food and other liquid containers as well as textiles, foils and fibers. Today partly bio-based PET is produced commercially by using bio-based ethylene glycol. Development of commercially viable routes for the production of bio-based terephthalic acid are in an advanced stage so 100 % bio-based PET is expected to be commercialized soon.



The number of building-blocks which can be used for production of polymers is constantly growing.

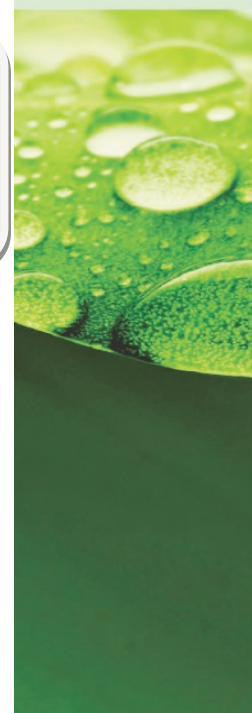
It is possible to use propylene derived from renewable resources for polypropylene production, bio-based succinic acid for production of partly bio-based polybutylenesuccinate (PBS), bio-butanediol for partly bio-based polybutylene terephthalate, etc. Commercially available are also some bio-based polyamides (for example, by using castor oil it is possible to produce bio-Nylon 11 and partly bio-based Nylon 6,10, some polyurethanes contain polyol components produced from soybean oil, castor oil etc.

Assessment of a fraction of "green" carbon in bio-based polymers

Synthetic polymers are macromolecules produced by polymerisation reactions of several types of monomers, which are small organic molecules that consist mainly of carbon atoms. So in case of use of monomers derived from different resources (renewable and oil) the final product, i.e. polymer, will contain in its structure only one part of carbon atoms having a "green" nature. The same situation will occur by using only one type of monomer but derived from different origin: for example, for production of polyethylene (PE) it is possible to use ethylene derived from oil as well as bio-ethylene, thus the percentage of "green" carbon in the final PE will depend on initial fractions of bio- and oil-based ethylene used.

Properties of polymers do not depend on the origin of used raw materials, that's why scientists have developed a special method for the identification of bio-based content in polymers. This method is based on the assessment of the content of a natural isotope of carbon ^{14}C in the polymer.

Atoms of carbon in nature can exist in the form of three isotopes: ^{12}C , ^{13}C and ^{14}C . Tissues of all living organisms contain a very low concentration of the isotope ^{14}C , and despite of its instability its concentration remains constant due to continual exchange with the environment. When the organism dies, the process of integrating ^{14}C atoms from the environment stops and its concentration in the material begins to decrease. The half-life of the isotope ^{14}C is 5.700 years meaning that after 50.000 years the content of isotope ^{14}C in the material decreases so that it cannot be detected anymore. Consequentially this means that the content of the isotope ^{14}C in the mineral resources is equal to zero, and accordingly the content of the isotope in all products produced from oil, natural gas, coal etc. is undetectable. At the same time the products made from renewable resources have



a measurable ^{14}C content. On this basis it is possible to distinguish between fossil based PE and bio-based PE, and to determine the bio-based content in for example PET.

The standard ASTM D6866 developed by the American Society of Testing and Materials (ASTM) is based on the principles described above. In Europe certification of products made from bio-based polymers are granted by two organizations: DIN CERTCO (Germany) and Vinçotte (Belgium). Depending on percentage of "green" carbon in the bio-based polymer, the end-product can receive different certification logo (please find more details on this matter in the Brochure "Certification of Bioplastics").

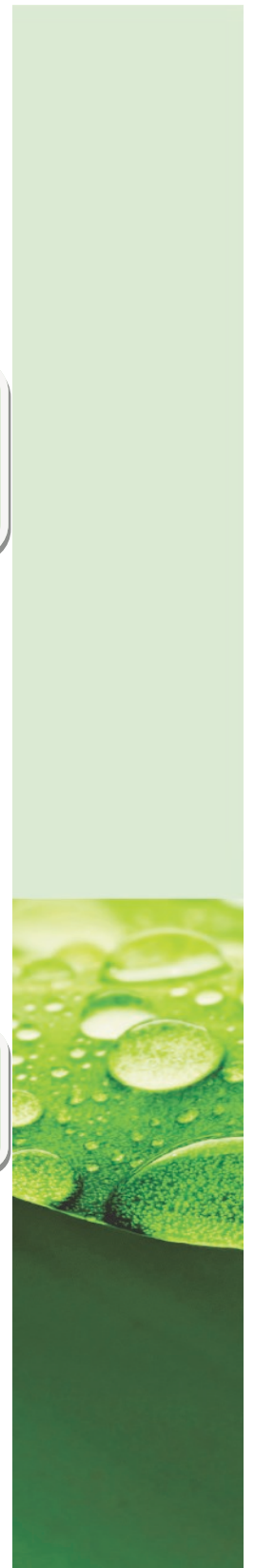
It is important to realize that the bio-based content expresses the percentage of carbon in the polymer that is bio-based and that the bio-based content can be anywhere in the range 0 - 100 %.

Are bio-based polymers biodegradable?

Using renewable resources it is possible to produce different types of polymers and each of these types will have its own particular properties and different susceptibility to biodegradation. Biodegradation is a process in which the substance (in our case polymer) decomposes under the action of microorganisms. A necessary key step in this process is that microorganisms consume the polymer or its degradation products as food. Apart from the environmental conditions where the process occurs a decisive role on biodegradation of polymers is played by their chemical structure.

The capacity of polymers to biodegrade is defined by their structure and does not depend on the raw material used to produce them.

Thus, products made of polyethylene will not biodegrade even if bio-based polyethylene is used, while many aliphatic polyesters, such as polyhydroxyalkanoates, polylactic acid etc. will biodegrade irrespective of resources used for their production.



This information leaflet is a part of the international project PLASTiCE.

Innovative value chain development for sustainable plastics in Central Europe drives the use of sustainable plastics, particularly biodegradable plastics and renewable resource-based plastics. The project is designed to promote the understanding of these materials within different communities. We contribute to creating an ordered regulatory environment and encourage collaboration and knowledge transfer between research and the industry.

The project is being implemented through the CENTRAL EUROPE programme (www.central2013.eu) co-financed by the ERDF (European Regional Development Fund).

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